Secondary Bonding. Part 2.[1] Crystal and Molecular Structures of Diethyltin Dichloride, Dibromide, and Di-iodide

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The crystal and molecular structures of the diethyltin dihalides, R_2SnX_2 [(1) X = Cl, (2) X = Br, (3) X = I], have been determined from diffractometer data. Crystal parameters are: (1), monoclinic, space group $P2_1/c$, a = 9.677(3), b = 9.835(2), c = 9.243(3) Å, β = 102.73(2)°, Z = 4, 811 observed reflections, R 0.047; (2), orthorhombic, space group $C222_1$, a = 9.786(2), b = 10.006(3), c = 9.494(2) Å, Z = 4, 289 observed reflections, R 0.058; (3), orthorhombic, space group $Pbcn$, a = 13.469(4), b = 5.385(2), c = 13.733(4) Å, Z = 4, 342 observed reflections, R 0.049. In (2) and (3), the individual molecules have crystallographic symmetry 2. All three compounds form chains of interacting molecules with each tin atom forming four primary and two secondary bonds such that the geometry may be described as intermediate between tetrahedral and octahedral. The lengths of the secondary bonds in (1) and (2) are 3.461(4) and 3.777(4) Å, 0.39 and 0.17 Å less than the sum of the respective van der Waals radii, with C–Sn–C angles opened to 134.0(6) and 135.9(10)°. For (3) the secondary bond distance is 4.284(5) Å, longer than the sum of the van der Waals radii, although the C–Sn–C angle [130.2(11)°] shows that the interaction is still stereochemically important. The packing in (3) also differs from that in (1) and (2).

The lengths of these secondary bonds are compared with other known examples in organotin(IV) chemistry, and factors influencing the strength of the interactions are discussed.

THERE have been a wealth of physical measurements made on organotin(IV) compounds since Sn is readily adaptable to many physical techniques. In particular, their crystal chemistry has been extensively investigated,[2] and there has been much discussion of molecular association.

This discussion concerns the significance of certain inter- and intra-molecular contact distances in the crystal, which are less than the sum of the relevant van der Waals radii. Furthermore, these interactions appear to be stereochemically important in affecting the primary geometry at the tin atom and the packing in the crystal. The name 'secondary bonds'[3] has been suggested by us for these interactions, although other terms have been used.

These long bonds have been discussed in terms of electrostatic interactions between the atoms, but a more satisfactory description is in terms of three-centre four-electron (3*c*-4*e*) molecular orbitals.[3] In a system of the type Y–A · · · X, the secondary bond A · · · X is formed by donation from a lone pair on X into the σ* orbital of the Y–A primary bond. Alternatively (and equivalently), the interaction of the three σ-symmetry atomic orbitals (on Y, A, and X) gives a filled bonding molecular orbital concentrated between A and Y, a filled non-bonding or weakly bonding orbital concentrated between A and X, and an empty antibonding orbital. The overall scheme is identical to the MO description of the hydrogen bond.

This paper forms part of a systematic investigation of secondary bonding. Here the effect of the halogen and organo-groups on the degree of association in the diorganotin dihalides are studied.

Previous Results.—Of the four diorganotin(IV) dihalides whose crystal structures are known, Me_2SnF_2 has the Sn atoms octahedrally co-ordinated by forming two *trans*-bonds to methyl groups and four equal Sn–F bonds (2.14 Å), giving a regular two-dimensional layer lattice.[4] In both Me_2SnCl_2 (ref. 5) and $(CH_2Cl)_2SnCl_2$ (ref. 6) the tin atoms can be regarded as being four-co-ordinate, but it is also possible to distinguish infinite chains in the crystal held together by weak intermolecular interactions. The tin atoms are strongly distorted from the expected tetrahedrally co-ordinated arrangement by further secondary bonds to chlorine atoms of other molecules. In the crystal structure of Ph_2SnCl_2, the original authors described the structure in terms of isolated molecules without any intermolecular tin–chlorine bridging.[7] This has been criticised by Bokii *et al.*[6] who point out that the Sn–Cl bond lengths are different, and that the chlorine atoms involved in the longer of the Sn–Cl bonds are also involved in short intermolecular interactions of 3.77—3.78 Å with the tin atoms of neighbouring molecules. These interactions produce linear groups of four molecules, the two terminal tin atoms remaining four-co-ordinate while the central tin atoms can be viewed as six-co-ordinate.

As well as the diorganotin(IV) dihalides, the crystal structures are known of several nominally four-co-ordinate dialkyltin(IV) compounds containing pseudohalides[8] and many trialkyl- and triaryl-tin(IV) halides

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[1] Part I, N. W. Alcock and R. M. C. Countryman, *J.C.S. Dalton*, 1977, 217.

[2] For reviews see R. Okawara and M. Wada, *Adv. Organometallic Chem.*, 1967, **5**, 137; N. G. Bokii and Yu. T. Struchkov, *J. Struct. Chem.*, 1968, **9**, 663; B. Y. K. Ho and J. J. Zuckerman, *J. Organometallic Chem.*, 1973, **49**, 1; P. J. Smith, 'A Bibliography of Organotin *X*-ray Crystal Structures,' No. 484, London, TRI, 1975.

[3] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

[4] E. O. Schlemper and D. Britton, *Inorg. Chem.*, 1966, **5**, 995.

[5] (*a*) J. D. Graybeal and D. A. Berta, U.S. Nat. Bur. Stand., Spec. Publ. No. 301, 1967, p. 393 (This structural analysis was based upon an incorrect space group); A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc.* (*A*), 1970, 2862.

[6] N. G. Bokii, Yu. T. Struchkov, and A. K. Prokofiev, *J. Struct. Chem.*, 1972, **13**, 619.

[7] P. T. Greene and R. F. Bryan, *J. Chem.Soc.* (*A*), 1971, 2549.

[8] Y. M. Chow, *Inorg. Chem.*, 1970, **9**, 794; 1971, **10**, 673; R. A. Forder and G. M. Sheldrick, *J. Organometallic Chem.*, 1970, **22**, 611; J. Konnert, D. Britton, and Y. M. Chow, *Acta Cryst.*, 1972, **B28**, 180.

and pseudohalides.[9] Three review articles [10] have discussed the intermolecular bonding in the organometallic pseudohalides of several heavy atoms including tin in terms of donor–acceptor bonding. Most of these compounds are also associated in the crystal, and the secondary bonds to the O, S, and N ligands appear to be much stronger than those to chlorine. It also appears that some compounds which are not associated by secondary bonding at room temperature may be associated at lower temperatures. This is seen in triphenyltin(IV) chloride whose room-temperature crystal structure shows discrete molecules with the valence angles about the tin being very close to normal tetrahedral values.[11] The authors suggested that the significant difference in the ^{35}Cl n.q.r. spectra at 303 and 77 K (ref. 12) was due to the appearance of a polymeric structure with trigonal-bipyramidal tin and a weak secondary bond $Sn \cdots Cl$ (as has been suggested [13] for Me_3SnCl) at the lower temperature. However, a recent series of Mössbauer measurements over a range of temperatures has failed to discover any gross structural changes in Ph_3SnCl, whilst the association in Me_2SnCl_2 becomes stronger at lower temperatures.[14]

EXPERIMENTAL

The title compounds were recrystallised from dry isopentane, and to prevent air-moisture hydrolysis were sealed under nitrogen in Lindemann capillary tubes which had been baked *in vacuo* for several hours.

Crystal Data.—Unit-cell and space-group data are listed in Table 1. Unit-cell constants and their standard deviations were obtained from least-squares refinement of the diffracting positions of 15 reflections on a Syntex $P2_1$ diffractometer, by use of Mo-K_α radiation ($\lambda = 0.710\,69$ Å). D_m measurements were not made because of the moisture sensitivity of the crystals and their solubility in most organic solvents, although D_c values are in reasonable agreement with the values quoted for Me_2SnCl_2 and Ph_2SnCl_2. All reflection data were collected on a Syntex $P2_1$ diffractometer under the following conditions, by use of graphite-monochromated Mo radiation.

TABLE 1

Unit-cell data for the diethyltin(IV) dihalides

Compound	System	Space group	a/Å	b/Å	c/Å	β/°	U/Å^3	Z	D_c	μ(Mo-K_α)/cm^{-1}
Et_2SnCl_2	Monoclinic	$P2_1/c$	9.677 (3)	9.835 (2)	9.243 (3)	102.73(2)	858.1(4)	4	1.92	35.35
Et_2SnBr_2	Orthorhombic	$C222_1$	9.786 (2)	10.006 (3)	9.494 (2)		929.7(4)	4	2.40	117.70
Et_2SnI_2	Orthorhombic	$Pbcn$	13.469 (4)	5.385 (2)	13.733 (4)		996.0(6)	4	2.87	87.61

(*a*) Et_2SnCl_2, *Compound* (1). Data were collected from a needle-shaped crystal of dimensions 0.052 × 0.052 × 0.48 mm bounded by the faces {001}, {010}, {100}. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$, indicate space group $P2_1/c$. Reflections were measured using a θ—2θ scan and scan range ($K_{\alpha_1} - 0.95$) to ($K_{\alpha_2} + 0.95$), to 2θ$_{\text{max.}}$ of 50°. A variable scan-rate of 1.3—29.5° min^{-1} was used, depending on the intensity of a preliminary 2-s count. Background counts were recorded at each end of the scan. The intensities of 3 standard reflections monitored every 80 reflections showed a steady loss of intensity and the collected data were rescaled according to the equation $F = F_0(1 + 0.000\,65t)(1 + 0.002\,54\sin\theta/\lambda\,.\,t)$. The maximum rescale factor was 1.1458. 1 709 Data were collected, of which 811 were considered observed having $I/\sigma(I) \geqslant 3.0$.

(*b*) Et_2SnBr_2, *Compound* (2). Data were collected from a crystal of dimensions 0.211 × 0.260 × 0.343 mm bound by the faces {110} and {001}. Systematic absences hkl, $h + k \neq 2n$; $00l$, $l \neq 2n$, indicate space group $C222_1$, with the Sn on special positions, symmetry 2. Reflections were measured as in (*a*), scan range ($K_{\alpha_1} - 0.9$) to ($K_{\alpha_2} +$ 0.9), and variable scan rate of 1.5—29.3° min^{-1} to 2θ$_{\text{max.}}$ of 55°. The intensities of 4 standard reflections recorded after every 50 reflections again showed a steady loss in intensity, and collected data were rescaled according to the equation $F = F_0(1 + 0.000\,420\,4t)(1 + 0.001\,272\,4\sin\theta/\lambda\,.\,t)$; maximum rescale factor 1.0524. Of 1 263 data measured, including systematic absences due to the centering condition, 289 were considered observed.

(*c*) Et_2SnI_2, *Compound* (3). Data were collected from a needle-shaped crystal, needle axis *a* (dimensions unknown). Systematic absences $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h + k \neq 2n$, indicate space group $Pbcn$ with the Sn on special positions, symmetry 2. Reflections were measured as before, scan range ($K_{\alpha_1} - 0.9$) to ($K_{\alpha_2} + 0.9$), variable scan rate of 3—29.3° min^{-1} to 2θ$_{\text{max.}}$ of 52°. The intensities of 3 standard reflections recorded after every 60 reflections showed a steady drop in intensity, and collected data were rescaled in two sections according to the equations: $F = F_0(1 + 0.007\,655t)(1 - 0.004\,628\sin\theta/\lambda\,.\,t)$ for $t \leqslant 15.18$, and $F = F_0(1 + 0.002\,832\,3t)(1 - 0.000\,960\,8\sin\theta/\lambda\,.\,t)$ for $t > 15.18$; maximum rescale factor 1.0682. Of 1 187 data measured, 342 were considered observed.

For compounds (1) and (2) Lorentz, polarisation, and absorption corrections were applied, the last with the program ABSCOR.[15] For (3) Lorentz and polarisation corrections were made, but crystal decomposition prevented

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[9] R. A. Forder and G. M. Sheldrick, *J.C.S. Dalton*, 1969, 1125; *J. Organometallic Chem.*, 1970, **21**, 115; R. Hulme, *J. Chem. Soc.*, 1963, 1524; N. Kasai, K. Yasuda, and R. Okawara, *J. Organometallic Chem.*, 1965, **3**, 172; E. O. Schlemper and D. Britton, *Inorg. Chem.*, 1966, **5**, 507; Y. M. Chow and D. Britton, *Acta Cryst.*, 1971, **B27**, 856; H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332; J. B. Hall and D. Britton, *Acta Cryst.*, 1972, **B28**, 2133; A. M. Domingos and G. M. Sheldrick, *J. Organometallic Chem.*, 1974, **67**, 257.

[10] J. S. Thayer and R. West, *Adv. Organometallic Chem.*, 1967, **15**, 169; M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 133; D. Britton, *Perspectives in Structural Chem.*, 1967, **1**, 109.

[11] N. G. Bokii, G. N. Zahkarova, and Yu. T. Struchkov, *Zhur. strukt. Khim.*, 1970, **11**, 895.

[12] P. Green and J. Graybeal, *J. Amer. Chem. Soc.*, 1967, **89**, 4305; T. Srivastava, *J. Organometallic Chem.*, 1967, **10**, 373.

[13] H. A. Stöckler, personal communication, quoted in *J. Amer. Chem. Soc.*, 1968, **90**, 3234; A. G. Davies, H. J. Milledge, and D. C. Puxley, unpublished work, quoted in M.T.P. Internat. Rev. Sci., 1972, **4**, 280.

[14] G. M. Bancroft, K. D. Bulter, and T. K. Sham, *J. Chem. Soc.* (*A*), 1975, 1483.

[15] N. W. Alcock, 'The Analytical Method for Absorption Correction,' in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970.

any measurement of the dimensions of the crystal for absorption correction.

In all three cases, structure solution was attempted successfully, using three-dimensional Patterson maps to locate the heavy atoms and Fourier maps to locate the other non-hydrogen atoms. Block-diagonal least-squares refinement with anisotropic temperature factors for all atoms, with correction for the effects of anomalous dispersion, produced final R factors of 0.047 (1), 0.058 (2), and 0.049 (3). The weights used were based on counting statistics. Scattering factors for neutral non-hydrogen atoms were taken from ref. 16. Computing was on an ICL 4130 computer with the programs of Dr. D. Russell. Final co-ordinates are listed in Table 2, significant bond lengths and angles in Table 3. Structure factors and anisotropic thermal parameters for the three compounds are listed in Supplementary Publication No. SUP 21983 (14 pp., 1 microfiche).* Views of the compounds are in Figures 1—3.

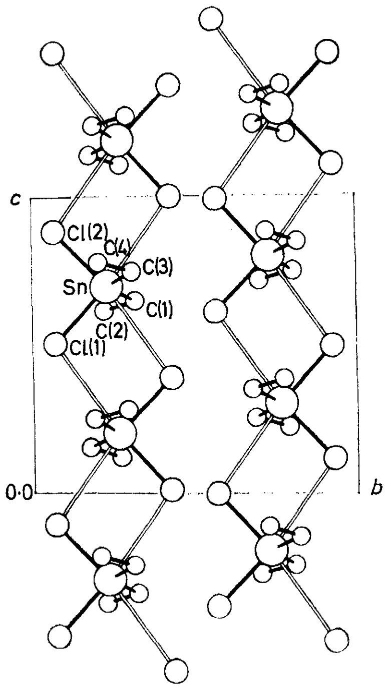

FIGURE 1 Et_2SnCl_2 projected down a; primary bonds are shown closed; secondary bonds open

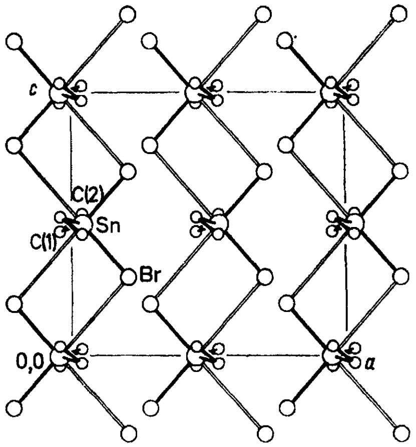

FIGURE 2 Et_2SnBr_2 projected down b

TABLE 2

Atomic co-ordinates ($\times$ 10^4) with standard deviations in parentheses

Atom	X	Y	Z
(1) Et_2SnCl_2			
Sn	2 788(1)	2 312(1)	7 006(1)
Cl(1)	2 774(5)	705(4)	5 071(4)
Cl(2)	2 738(4)	672(4)	8 898(4)
C(1)	751(14)	3 238(15)	6 542(16)
C(2)	−413(20)	2 217(25)	6 152(34)
C(3)	4 912(16)	3 100(15)	7 494(16)
C(4)	6 028(16)	2 021(18)	7 800(20)
(2) Et_2SnBr_2			
Sn	431(3)	0(0)	5 000(0)
Br	2 100(3)	48(21)	3 002(3)
C(1)	−420(26)	1 956(25)	4 745(31)
C(2)	393(28)	3 001(31)	5 366(61)
(3) Et_2SnI_2			
I	1 245(1)	965(5)	1 531(1)
Sn	0(0)	4 080(6)	2 500(0)
C(1)	904(19)	5 829(54)	3 644(15)
C(2)	1 501(21)	3 739(77)	4 220(17)

DISCUSSION

In all three compounds, the individual molecules interact to form chains. Probably as a result, there are significant angular distortions from tetrahedral values in the individual molecules. The values of the angles C–Sn–C and X–Sn–X are respectively 134.0(6) and 96.0(1) for (1), 135.9(10) and 98.5(1) for (2), and 130.2(11) and 104.0(2)° for (3).

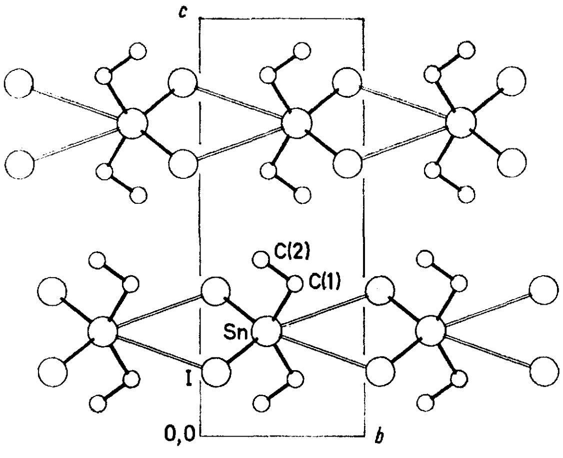

FIGURE 3 Et_2SnI_2 projected down a

Although there are few other Sn–C(Et) bond distances available for comparison, there should be little difference between Sn–C(Me) and Sn–C(Et). The Sn–C(Et) bond in dichloro(ethyl)hydroxotin [17] is 2.20(3) Å and a large number of Sn–C(Me) distances in the solid state for a

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[16] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[17] P. C. Lecomte, J. Protas, and M. Devaud, *Acta Cryst.*, 1976, **B32**, 923.

variety of distorted geometries at tin give Sn–C from 2.07 to 2.22 Å.[18] The Sn–C distance in $SnMe_4$ has been determined most recently by gas-phase electron diffraction as 2.144(3) Å.[19] The present values are quite close to those quoted, but they do seem to show a slight systematic increase from (1) to (3). For Sn–Cl bonds, electron diffraction has shown a regular contraction in the bond length with increasing halogen substitution in the series $Me_{4-n}SnCl_n$ (n = 1—4). The Sn–Cl distances are 2.351(7) (Me_3SnCl), 2.327(3) (Me_2SnCl_2), 2.304(3) ($MeSnCl_3$), and 2.281(4) Å ($SnCl_4$). The Sn–C distances are essentially constant (2.104—2.108 Å).[20] The Sn–Cl distance in (chloromethyl)trichlorostannane is 2.340 Å, intermediate between those for Me_3SnCl and Me_2SnCl_2, presumably owing to the inductive effect of the chloromethyl group.[21]

TABLE 3

Bond distances (Å) and bond angles (°) with standard deviations in parentheses

(*a*) Distances

Compound	Sn–X	Sn–C	C–C	Sn ··· X	Δ [a]	Sn ··· X [b]	X ··· X
Me_2SnCl_2 [c]	2.40(4)	2.21(8)		3.54(5)	1.14	3.85	
$(CH_2Cl)_2SnCl_2$ [d]	2.37(2)	2.18(7)		3.71 (3.21) [e]	1.34(0.84)		
Et_2SnCl_2 [f]	2.385(3)	2.132(13)	1.452(25)	3.483(4)			
	2.384(4)	2.167(15)	1.471(22)	3.440(4)	1.08		3.544(6)
Et_2SnBr_2 [f]	2.505(4)	2.162(26)	1.456(46)	3.777(4)	1.27	3.95	3.795(4)
Et_2SnI_2 [f]	2.719(4)	2.178(27)	1.573(49)	4.284(5)	1.565	4.08	
Ph_2SnCl_2 (1) [g]	2.353(2)	2.119(5)		3.78	1.44		4.284(3)
	2.336(2)	2.105(5)				3.85	
(2)	2.357(2)	2.118(5)		3.77	1.44		
	2.336(2)	2 112(5)					

(*b*) Angles

Compound	X–Sn–X	C–Sn–C	C–Sn–X		Sn–C–C	X ··· Sn–X	Sn ··· X–Sn
Me_2SnCl_2	93.0(20)	123.5(45)	109.0(45)				
$(CH_2Cl)_2SnCl_2$	97.0(20)	135.0(60)	105.0(20)				
Et_2SnCl_2	96.0(1)	134.0(6)	106.3(4)		112.1(12)	173.0(1)	104.0(1)
			105.4(4)		113.6(10)	172.0(1)	102.8(1)
Et_2SnBr_2	98.5(1)	135.9(10)	97.5(9)		114.0(20)	179.5(5)	98.2(1)
Et_2SnI_2	104.0(2)	130.2(11)	105.6(8)		110.0(21)	158.0(1)	98.0(1)
Ph_2SnCl_2 (1)	101.7(1)	123.9(2)	106.0(2)	108.8(2)			
			106.5(2)	107.8(2)			
(2)	97.8(1)	127.0(2)	110.1(2)	105.0(2)			
			107.1(2)	105.9(2)			

[a] Δ = (Sn ··· X) minus (Sn–X). [b] van der Waals distance, from A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441. [c] Ref. 5. [d] Ref. 6. [e] Value in parenthesis is Sn–Cl intramolecular distance. [f] This work. [g] Ref. 7.

Crystallographic determinations of the Sn–Cl bond length have generally fallen in the range from 2.318 to 2.584 Å,[22] with the length of the Sn–Cl bond increasing as the co-ordination of the tin changes from tetrahedral to octahedral. The longest recorded Sn–Cl distance is 2.696(3) Å in $[Me_3SnCl_2]^-$,[23] although bridging Sn ··· Cl distances of 2.805, 2.96, and 2.78 Å occur in the transition-metal complexes $[(bipy)Mo(CO)_3(SnMeCl_2)Cl]$, $[(dth)W(CO)_3(SnMeCl_2)Cl]$, and $[(dth)Mo(CO)_3(SnCl_3)Cl]$ [24] (bipy = αα′-bipyridyl, dth = 2,5-dithiahexane). The present mean Sn–Cl bond length 2.384 Å does not differ significantly from those for the other two dialkyltin dichlorides listed in Table 3 although it is *ca.* 0.04 Å longer than that in Ph_2SnCl_2. It is clearly considerably longer than that in Me_2SnCl_2 in the gas phase.[20]

Examples of Sn–Br and Sn–I bond distances are less numerous. The observed values [Sn–Br 2.505(4) and Sn–I 2.719(4) Å] are again longer than the gas-phase bond lengths in $SnBr_4$ and SnI_4 [2.44(2) and 2.64(4) Å],[25a] while in crystalline $SnBr_4$ and SnI_4 the respective values are 2.41 and 2.69(2) Å.[25b] Electron-diffraction measurements on Me_nSnX_{4-n} (X = Br and I) are probably not very accurate as the molecules were assumed to be tetrahedral and no allowance was made for scattering phase shift; in Me_2SnX_2 Sn–Br was 2.45(2) and Sn–I 2.69(3) Å, and for this series a contraction was reported with increasing halogen substitution,[26] although the values quoted above for SnX_4 seem not to bear this out.

Considering solid-state values, the observed Sn–Br value is in good agreement with that [2.504(5) Å] in (4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-buta-1,3-dienyl)dimethyltin bromide which is also distorted from tetrahedral geometry by secondary-bond interactions.[27] In the two isomers of bis[1,2-bis(ethoxycarbonyl)ethyl]tin dibromide, Sn–Br distances of 2.516(6), 2.588(6), and

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[22] P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S Dalton*, 1974, 1723.

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[24] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1268, 1273; R. A. Anderson and F. W. B. Einstein, *Acta Cryst.*, 1976, **B32**, 966.

[25] (*a*) M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393; (*b*) P. Brand and H. Sackmann, *Acta Cryst.*, 1963, **16**, 446; F. Mellow and I. Fankuchen, *Acta Cryst.*, 1955, **8**, 343.

[26] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.

[27] F. P. Boer, J. J. Flynn, jun., H. H. Freedman, S. V. McKinley, and V. R. Sandel, *J. Amer. Chem. Soc.*, 1967, **89**, 5068; F. P. Boer, G. A. Doorakian, H. H. Freedman, and S. V. McKinley, *ibid.*, 1970, **92**, 1225.

2.504(5) Å were found in distorted octahedral structures.[28] The only other examples of solid-state Sn–Br distances are for organotin–transition-metal compounds, where more complex bonding and packing effects occur, *e.g.* $[(Br_3Sn)Fe(CO)_2(\eta\text{-}C_5H_5)]$ mean 2.501(2), $[(Br_2Sn)\{Mn(CO)_5\}_2]$ 2.548(2), and $[(BrSn)\{Co(CO)_4\}_3]$ 2.520(5) Å.[29] The mean value for $[(Br_3Sn)Mo(\eta\text{-}C_5H_5)Br]$ is 2.506(8) Å, but this compound also possesses a long bridging Sn–Br distance of 3.411 Å (*cf.* ref. 24) which results in trigonal-bipyramidal geometry at the tin atom.[29d]

The observed Sn–I for (3) also agrees with that [2.729(3) Å] in 1,4-bis(iododiphenyl)-1,4-distannabutane which contains a tetrahedral tin atom.[30]

Intermolecular Interactions.—The strength of the intermolecular interactions can be deduced from the length of the secondary bonds and the angles around tin (especially C–Sn–C). In Et_2SnCl_2 and Et_2SnBr_2 the lengths of the secondary bonds (see Table 3) are 0.39 and 0.17 Å less than the sum of their appropriate van der Waals radii. The weakest interaction occurs in Et_2SnI_2, where the $Sn \cdots I$ secondary-bond distance [4.284(5) Å] is greater than the sum of the tin and iodine van der Waals radii. However, it can be argued that the interaction is still present since the value of the C–Sn–C angle of 130.2(11)° is much larger than the tetrahedral value. Taking into account only the difference between the secondary-bond distance and the sum of the van der Waals radii, it would appear that the strength of the secondary bonding is in the order $Cl > Br > I$. However, if the apparent difference in the C–Sn–C angle is genuine, then the order may be $Cl \approx Br > I$. It has also been suggested, from n.q.r. measurements, that bromine bridging is stronger than chlorine bridging.[31] Zahrobsky,[32] by use of a simple stereochemical model which optimises the van der Waals forces between the bonded and neighbouring atoms (regarded as spheres), has predicted intermolecular distances of 3.81 and 4.11 Å for Me_2SnBr_2 and Me_2SnI_2. The distances quoted are reasonable although the steric requirements of the larger ethyl group might affect these results. However, this model only calculates the C–Sn–C angles as being 125 and 124° respectively.

The mode of bridging in the Et_2SnCl_2 and Et_2SnBr_2 chains is also different from that in Et_2SnI_2 where both bridging secondary bonds $Sn \cdots I$ involve the halogen atoms on the same neighbouring molecule (Figure 3). In Et_2SnCl_2 and Et_2SnBr_2 the distorted octahedral arrangement around each tin is completed by two secondary bonds involving the halogen atoms of two neighbouring molecules (Figures 1 and 2). Both $(CH_2Cl)_2SnCl_2$ and Ph_2SnCl_2 associate in the same chelating manner as does Et_2SnI_2; Me_2SnCl_2, however, has the second bridging-type of association. It is not readily apparent which type of bridging arrangement a system containing secondary bonds will adopt, but the chelating bridges seems to be favoured with the longer weaker bonds. Brown and Shannon [33] have attempted to classify the bridging environments in certain inorganic structures using the bond valences of the bridging atoms, and this method may be applicable to secondary-bonded systems.

The lengths of the $Sn \cdots Cl$ secondary bonds (Table 3) can be compared to that [3.486(7) Å] for quinolinium trichlorodimethylstannate(IV) where this bond links two $Me_2SnCl_3^-$ ions into dimeric units.[34] The cation here is very important since in $[Me_2Sn(terpyridyl)][Me_2SnCl_3]$ the anion shows no $Sn \cdots Cl$ contacts <3.7 Å;[35] nor does the ion $[Me_3SnCl_2]^-$ in $[Mo_3(\eta^5\text{-}C_5H_5)S_4][Me_3SnCl_2]$, although it does contain a very long Sn–Cl distance (2.696 Å).[23]

The $Sn \cdots Br$ secondary bond in Et_2SnBr_2 has the same length [3.774(5) Å] as the intramolecular interaction of bromine with tin in (4-bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-buta-1,3-dienyl)dimethyltin bromide (resulting in an axially substituted trigonal bipyramid with equatorial organic groups).[27] In that compound also, the C(butadienyl)–Sn–Me angle has opened to 129.0° and Me–Sn–Me to 112.7°. A series of analogous 4-chloro- and 4-bromo-compounds has been investigated in which Sn–Ph replaces Sn–Br. In these compounds, the interaction is drastically weakened so that the $Sn \cdots Cl$ (4.28) and $Sn \cdots Br$ distances (4.35 Å) are both greater than the sum of the two corresponding van der Waals radii. The difference in the two $Sn \cdots Br$ distances is 0.57 Å. Similarly the C(butadienyl)–Sn–Me angles are reduced to 116.5 (4-chloro) and 117.1° (4-bromo).[36]

Factors affecting Intermolecular Interactions.—A CNDO calculation of the valence-electron distribution in a series of Sn^{IV} compounds has shown that for isolated halogeno(dimethyl)stannanes the 5*s* and 5*p* orbital occupancies are strongly dependent on the electronegativity of the halogen.[37] Although the methyl groups donate electrons to the tin, they are unable to replace all the electron density removed by the halogen atoms, leaving a slightly electron-deficient tin atom which can then form secondary bonds. The decreasing electronegativity of the halogens and decreasing overlap with the more diffuse orbitals on bromine and iodine would then qualitatively explain the observed strengths of the secondary interactions. There is also a clear

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connection between secondary-bond strength and the nature of the organic group.

In Me_2SnCl_2, Et_2SnCl_2, and Et_2SnBr_2 the secondary bonding is considerably stronger than in Ph_2SnCl_2. The effect of replacing methyl by ethyl in R_2SnCl_2 is to strengthen the intermolecular bonding by shortening the secondary bond from 3.54(5) to 3.461(4) (mean) Å with the corresponding C–Sn–C angle opening out from 123(4) to 134.0(6)°. These angles are still considerably less than in the more-associated dimethyltin pseudohalide compounds $Me_2Sn(CN)_2$ [148.7(3.5)°] and $Me_2Sn(NCS)_2$ [145.9(1.4)°]. The phenyl group produces a significant weakening of the secondary interaction as can be seen from Table **3** and from the dimethyl(tetraphenylbutadienyl)tin compounds already mentioned. This is presumably due to the ability of the phenyl group to involve available orbitals on the tin atom in inductive and mesomeric interactions so that they cannot overlap effectively with further orbitals. Similarly, the chloromethyl-group, with a reasonably strong inductive effect, also weakens the secondary bonding. However, the C–Sn–C angle of 135(6)° in $(CH_2Cl)_2SnCl_2$ compared with 123.9(2) and 127.0(2)° in the two crystallographically independent Ph_2SnCl_2 molecules suggests a stronger interaction in the former. If the viewpoint of Bokii *et al.*[6] is accepted, the difference of 4° between the C–Sn–C angles in the two Ph_2SnCl_2 molecules is directly attributable to secondary-bonding effects.

Hybridisation Models and Other Physical Measurements.—The C–Sn–C angle is important when describing any tin hybridisation model and in interpreting other physical measurements made on tin. Sham and Bancroft,[18] using a simple theoretical model, have correlated the ^{119}Sn Mössbauer quadruple splittings with the C–Sn–C angle in a number of distorted Me_2Sn^{IV} compounds. They find that Me_2SnCl_2 and $Me_2Sn(NO_3)_2$ lie in intermediate positions between the two predicted curves for Me_2SnL_2 and Me_2SnL_4. Recent Mössbauer results have also shown that the amount of tin 5*s* character in the bonds from tin to transition metals and organic groups in the series of compounds $X_nR_{3-n}SnM$ [X = Cl, Br, or C_6F_5; R = Me or Ph; M = $Mn(CO)_5$ or $Fe(CO)_2(\eta\text{-}C_5H_5)$] decreases in the order: $Sn\text{–}Fe(CO)_2(\eta\text{-}C_5H_5) > Sn\text{–}Mn(CO)_5 > Sn\text{–}Me > Sn\text{–}Ph > Sn\text{–}C_6H_5 > Sn\text{–}Cl \approx Sn\text{–}Br$. By use of this series they have rationalised the known distortions from tetrahedral geometry in several tin compounds.[38]

The values of the coupling constants $J(^{119}Sn\text{–}CH_3)$ also indicate that the *s* character in the Sn–Me bonds decreases substantially as the C–Sn–C angle decreases.[39] There should be a corresponding increase in the Sn–C distance, which is not always readily seen owing to the difficulty of determining this distance accurately. The idea of a linear relationship between the $J(^{119}Sn\text{–}CH_3)$ values and the percentage *s* character in the Sn–C bonds was advanced by Holmes and Kaesz [40] but has been criticised by McFarlane.[41] van den Berghe and van der Kelen [42] have since suggested that the coupling constants are proportional to the percentage *s* character of sp^n hybrid orbitals only, since any *d* orbital involvement in bonding would increase orbital overlap and hence bond strength, whilst not increasing the amount of *s* character of the hybrid orbital.

In *trans*-octahedral complexes, the bonding may, therefore, be described in terms of sp_z hybridisation of the tin with p_x and p_y orbitals used in the equatorial bonds.[43] The resulting equatorial bonds should then be longer than those observed for tetrahedral compounds as is generally found (*cf.* Ph_2SnCl_2 and Et_2SnCl_2). In the present compounds (**1**)—(**3**), which are clearly intermediate between tetrahedral and *trans*-octahedral, the tin hybridisation must be intermediate between sp^3 and sp and involvement of the 3*d* orbitals is possible. The Mössbauer parameters and other physical measurements have been made on the present compounds as well as on a series of related mixed-halogen species.[44]

We thank Dr. D. A. Armitage for samples of the diethyltin halides, and the S.R.C. for a research studentship (to J. F. S.) and a grant for the diffractometer (to N. W. A.).

[6/1562 *Received*, 9*th August*, 1976]

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