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Complexes of Organometallic Compounds.
L. The Correlation between ^{119}Sn Mössbauer Isomer Shifts and Calculated Partial Charges on Tin in Adducts of Tin(IV) and Organotin(IV) Halides with Phosphorus and Oxygen Donors

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The relationship between Mössbauer isomer shifts, δ, and atomic charges on tin, Q_{Sn}, has been studied for homologous series $R_nSnhal_{4-n}\cdot L_2$ [n = 0–3; L_2 = donor atoms of 1,2-bis(diphenylphosphino)ethane, N,N'-ethylenebis(salicylideneimine) and N,N'-ethylenebis(acetylacetoneimine)] and $Snhal_4\cdot 2PR_3$. Semiempirical values of Q_{Sn} have been calculated by two methods based on the concept of orbital electronegativity equalization upon bond formation. Linear correlations δ/Q_{Sn} are obtained, which can be function of the coordination number of the metal atom, for terms of the series characterized by different orbital electronegativities of atoms directly bound to tin. Deviations occur for adducts $AlK_2SnCl_2\cdot L_2$ and $AlKSnCl_3\cdot L_2$, as well as for $Snhal_4\cdot 2PR_3$, on varying the nature of AlK and R radicals respectively. The inconsistencies are attributed to under- and over-estimate of inductive effects by the two methods of calculation of Q_{Sn}, respectively, with reference to the related variations of δ's.

Introduction

The Mössbauer parameter isomer shift, δ, is known to be a function of s electron density (5 s in case of tin) at the nucleus, $\psi^2(0)$:

$$\delta = (\psi_s^2(0) - \psi_a^2(0)) \times \frac{Ze^2}{R} \times \frac{4}{3}\pi R^3 \left(\frac{\Delta R^2}{R^2}\right) \qquad (1)$$

where subscripts 's' and 'a' refer to source and absorber Mössbauer nuclei, respectively, and ΔR^2 is the difference of (squared) nuclear radii in excited and ground states respectively [1a,b]. Theoretical estimates of $\psi_a^2(0)$ led to parabolic [1c, 2] as well as linear [3, 4] correlations between experimental δ s and $\psi_a^2(0)$ (or related quantities) for a number of tin derivatives. Analogous trends were detected also in semiempirical approaches, where $\psi_a^2(0)$'s are substituted by the electronegativities (or related parameters) of atoms and groups involved in bond formation into the molecule [1c]; the calculated parabolic relationships appear quasi-linear within small electronegativity ranges, due to the minor contribution by the quadratic term(s). In this context, there appeared in the literature three reports concerning tin(IV) and organotin(IV) salts and complexes (mainly with bulky ligands), where electronegativity-related parameters of all atoms and groups bound to tin were taken into account in the attempted correlations with δ values. In a pioneering work, Herber and his coworkers proposed a linear relationship between δ s and the sum of electronegativities for tin tetrahalides, several tetraorganotins and distannanes, and supposedly tetrahedral di- and tri-organotins [5]. Subsequently, Sharma, Carty *et al.* advanced an one-parameter linear correlation between Mössbauer isomer shifts and ligand atom or group electronegativities [6, 7] (later defined "operational parameters" [7]), as a function of tin coordination number; a sequence of partial isomer shift data, analogous to that of iron(II) derivatives [8], was practically set up, which was employed to predict structural characteristics, in line with the established rationalization of Mössbauer quadrupole splittings [8].

Proceeding along with the same philosophy, we recently got a linear relationship between δ's and partial atomic charges on tin, Q_{Sn}, for the members of the homologous series of 1:1 pyrazine adducts; Q_{Sn} were calculated through a valence state electronegativity equalization procedure carried out over the whole bonds into the molecule [9]. Adducts $R_nSnCl_{4-n}\cdot pyz$ (n = 1, 2) were structurally characterized according to the insertion of their δ/Q_{Sn} data points into the relationship, on the assumption of six-coordinate tin [9]. The results were in line with previous findings on δ/Q_{Sn} trends stated for the series $Snhal_4$ and $Snhal_6^{2-}$ [10]. It clearly appears that the method of calculation of Q_i we employed has the advantage of a firm theoretical basis [11–13], as well as of considering groups, bound to tin, as 'built in' any individual molecule (*vide infra*). This method suffers, of course, of the disadvantages of any two-parameter correlation, since the Q_{Sn} values come from a procedure which ignores the hyperfine factors governing δ magnitudes.

In order to check the applicability and potentiality of our approach, we planned to extend the study to further homologous series, and first selected tin(IV) adducts with 1,2-bis(diphenylphosphino)ethane, DPE, and N,N′-ethylenebis(salicylideneimine), H_2Salen, as examples of bases with phosphorus and oxygen donor atoms respectively. During the work it appeared desirable to test the influence of inductive effects on the magnitude of calculated charges; to the purpose adducts of the ligand N,N′-ethylenebis-(acetylacetoneimine), H_2Acen (where a number of compounds differ mainly for the nature of the alkyl radical bound to tin), as well as series of Snhal$_4$·2PRR′R″ adducts, were investigated. The results obtained are reported in the present paper.

Calculation of Partial Charges and Valence Bond Structures

The definition of orbital electronegativity by Jaffé *et al.* [11], and the concept of electronegativity equalization upon bond formation (the bond electronegativity [11]) are the basis of the methods here employed. The following equations are established [12] in the case of a biatomic molecule:

$$\chi_i = [(I_v + E_v)/2]_i + (I_v - E_v)_i q_i = \\ = \chi_j = [(I_v + E_v)/2]_j + (I_v - E_v)_j q_j \qquad (2)$$

$$a_i + b_i q_i = a_j + b_j q_j \qquad (2')$$

$$q_i + q_j = \text{molecular charge} \qquad (3)$$

where χ are orbital electronegativies, I_v and E_v are valence state ionization potentials and electron affinities [11] respectively, and q are partial charges residing on the i,j atoms. In polyatomic species, eqns. as (2) are set up for each bond, which allow, in conjunction with an eqn. of type (3), to estimate equilibrium values of q as well as the resulting bond electronegativity.

Method A

Based on these principles, Jolly and Perry [13] proposed a semiempirical approach (indicated in the following as method A) where q s are calibrated through experimental XPS electron binding energies. The orbital electronegativity χ_{ij} of the atom i, forming a bond with the atom j, is expressed as follows:

$$\chi_{ij} = \chi(p)_i + \frac{S_{ij}}{(1 + \pi_{ij})^a}\,(\chi(s)_i - \chi(p)_i) + \\ + h_i\left[\frac{bq_{ij}}{(N_{ij})^a} + \sum_{K \neq j} q_{ik} + cF_i\right] \qquad (4)$$

in which $\chi(s)$, $\chi(p)$ are valence state electronegativities (in Pauling units [11]) of s and p orbitals; S_{ij}, N_{ij} and π_{ij} are the s character and the σ and π bond orders respectively; h is 0.1 $(I_v - E_v)_{av}$, being the properly weighted average of values for s and p orbitals in case of hybridization; q are charges transferred upon equalization, and F is the assumed formal charge; a, b and c are XPS calibration factors [13] (the value c = 2.7 has been used here, irrespective of the atomic number of i, j [13, 14]). The first two terms at the right hand side of eqn. (4) are equivalent to the fixed orbital electronegativity, *i.e.*, that expressed in the form $[(I_v + E_v)/2]$ in eqn. (2). The hybridization of the ij bond is accounted for by these terms through the s character and bond order parameters (this means that actual valence state values [11] are not used, and that eventual d orbital involvements are ignored [13]); the third term is clearly related to the charge-containing part of eqn. (2). The electronegativities of orbitals of any couple of atoms forming a bond are equalized ($\chi_{ij} = \chi_{ji}$, see eqn. (4)), obtaining a set of n equations in n unknowns for a molecule constituted by n + 1 atoms. Values of q are obtained by solving the system [13, 14] and the charge on individual atoms, Q, is calculated by [13, 14]:

$$Q_i = F_i + \Sigma\, q_{ik} \qquad (5)$$

It is worth remarking that Jolly's procedure yields *incomplete orbital electronegativity equalization*; as evidenced by eqn. (4), only q transferred to or from atoms i and j, and atoms directly linked to them, are accounted for in the eqn. $\chi_{ij} = \chi_{ji}$. This has the effect of building inside a molecule, say, in an alkyl chain, sets of 'blocks' of atoms whose charges appear into the equation concerning a given bond; in some way, this could correspond to consider a molecule, containing polyatomic substituents or bulky ligands, as a sequence of groups whose electronegativities have a topological dependence, which seems to be quite a correct description of the actual situation.

In order to obtain reliable Q values by this method, valence bond structures of the compounds under study must be carefully selected for atoms having a coordination number larger than four [13]. Arbitrary assignments of input parameters N_{ij} and F (eqn. (4)) must be avoided, since the latter heavily

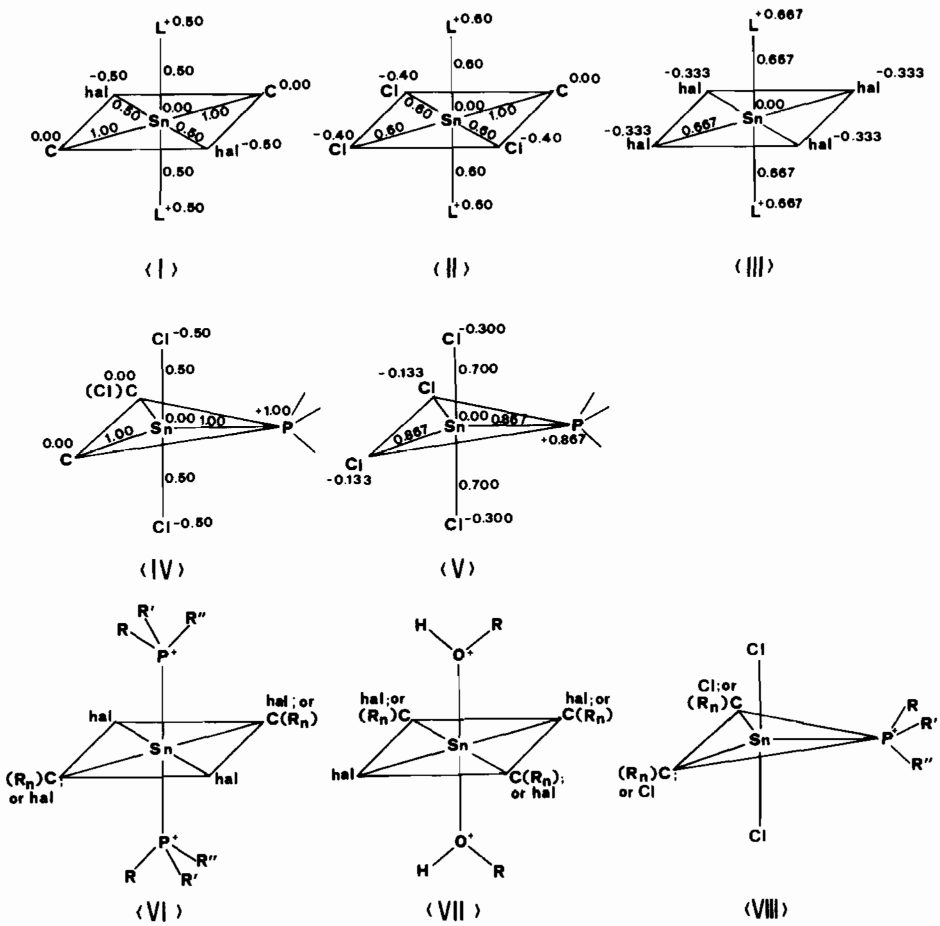
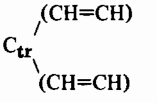
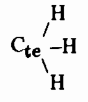
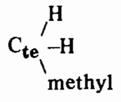


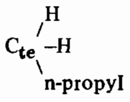
Fig. 1. Valence bond structures, in the environment of tin atoms, assumed in the calculation of partial charges by the electronegativity equalization procedures by methods A [(I)–(V)] and B [(VI)–(VIII)] (see text, Calculation). Bond orders and formal charges in (I)–(VI) are input parameters for the program CHELEQ. 'L' are atoms bound to tin, embedded into ligands here treated (L = P for phosphines, O for H_2Salen and H_2Acen). R,R' and R" in (VI) and (VIII) are atoms or groups bound to P in the individual phosphines, and R in (VII) are (ligand)/2 groups linked to O in H_2Salen and H_2Acen adducts (see Table II and legend). No configurational implications, such as the occurrence of *trans-* or *cis-*L_2 isomers in octahedral species, are considered in this context, being uninfluential in the charge estimation.

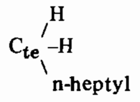
In $C(R_n)$, structures (VI)–(VIII), C is bound to Sn, and R_n to C, according to the following schemes:


Phenyl


Methyl


Ethyl


n-Butyl


n-Octyl

influence the magnitude of calculated Qs. A prior accurate knowledge of available structural and bonding characteristics is then needed for the molecules to be considered.

The 1:1 adducts R_nSnCl_{4-n}·DPE, ·H_2Salen and ·H_2Acen (n = 0–3) here investigated are very likely six-coordinate tin-containing species. A *cis*-P_2 octahedral monomeric configuration seems to occur for $SnCl_4$·DPE [15]; to derivatives of $RSnCl_3$, a solid state polymeric structure has been assigned containing 6-coordinate Sn [16], and the latter is probably the case also of Ph_2SnCl_2·DPE [17]. In the adducts of H_2Salen with organotins and $SnCl_4$, the ligand would coordinate through the oxygen atoms bridging the tin-containing moieties, in this way forming polymers with tin in an octahedral environment [18–20] (even though there is some evidence of weakening of the coordinate bond in the $BuSnCl_3$ and $OctSnCl_3$ adducts [20]); tin six-coordination would definitely take place in $SnBr_4$ and SnI_4 derivatives [21]. Finally, in the adducts of H_2Acen the bonding situation is highly probably similar to that observed in H_2Salen derivatives, [18–20] even though the occurence of N → Sn bonds, or of

TABLE I. Partial Charges on Tin (Q_{Sn}) Calculated by Electronegativity Equalization Procedures According to Methods A[a] (structures (I)–(V)) and B[a] (structures (VI)–(VIII)), and ^{119}Sn Mössbauer Isomer Shifts (δ) for Homologous Series of Tin(IV) Adducts.

Code No.	Compound[b]	Valence bond structure[c]	Q_{Sn}	δ[d]	Refs. for δ
1	$Ph_2SnCl_2 \cdot DPE$	I	+0.180	1.35; 1.31	33, 17
		IV	+0.246		
		VI	+0.078		
		VIII	+0.072		
2	$MeSnCl_3 \cdot DPE$	II	+0.206	1.18	16
		IV	+0.301		
		VI	+0.083		
		VIII	+0.080		
3	$Bu^nSnCl_3 \cdot DPE$	II	+0.207	1.19	16
		IV	+0.302		
		VI	+0.061		
		VIII	+0.046		
4	$Oct^nSnCl_3 \cdot DPE$	II	+0.207	1.20	16
		IV	+0.302		
		VI	+0.039		
		VIII	+0.017		
5	$PhSnCl_3 \cdot DPE$	II	+0.230	1.06	16
		IV	+0.325		
		VI	+0.087		
		VIII	+0.087		
6	$SnCl_4 \cdot DPE$	III	+0.290	0.72	15, 33
		VI	+0.100		
7	$SnCl_4 \cdot PCy_3$	V	+0.339	0.49	15
		VIII	−0.017		
8	$SnCl_4 \cdot PPh_3$	V	+0.343	0.59; 0.82; 1.14	15, 27, 29
		VIII	+0.109		
9	$Me_2SnCl_2 \cdot H_2Salen$	I	+0.263	1.327; 1.37	20, 18
		VII	+0.142		
10	$Bu^n_2SnCl_2 \cdot H_2Salen$	I	+0.265	1.62	18
		VII	+0.077		
11	$Ph_2SnCl_2 \cdot H_2Salen$	I	+0.311	1.233; 1.26	20, 18
		VII	+0.142		
12	$MeSnCl_3 \cdot H_2Salen$	II	+0.367	0.751; 0.86	20, 18
		VII	+0.169		
13	$Bu^nSnCl_3 \cdot H_2Salen$	II	+0.368	0.905	20
		VII	+0.125		
14	$Oct^nSnCl_3 \cdot H_2Salen$	II	+0.368	0.910; 0.95	20, 18
		VII	+0.085		
15	$PhSnCl_3 \cdot H_2Salen$	II	+0.393	0.777; 0.81	20, 18
		VII	+0.166		
16	$SnI_4 \cdot H_2Salen$	III	+0.354	0.98	21
		VII	+0.167		
17	$SnBr_4 \cdot H_2Salen$	III	+0.427	0.55	21
		VII	+0.175		
18	$SnCl_4 \cdot H_2Salen$	III	+0.471	0.34; 0.36	20, 18
		VII	+0.199		
19	$Me_2SnCl_2 \cdot H_2Acen$	I	+0.262	1.46; 1.57	22, 23
		VII	+0.102		
20	$Me_2SnBr_2 \cdot H_2Acen$	I	+0.253	1.53	22
		VII	+0.093		
21	$Et_2SnCl_2 \cdot H_2Acen$	I	+0.265	1.67	23
		VII	+0.080		
22	$Bu^n_2SnCl_2 \cdot H_2Acen$	I	+0.265	1.64; 1.66	22, 23
		VII	+0.049		

(continued on facing page)

TABLE I. *(continued)*

Code No.	Compound[b]	Valence bond structure[c]	Q_{Sn}	δ[d]	Refs. for δ
23	$Ph_2SnCl_2\cdot H_2Acen$	I	+0.311	1.34	22, 23
		VII	+0.109		
24	$MeSnCl_3\cdot H_2Acen$	II	+0.366	0.91	22
		VII	+0.126		
25	$Me_3SnCl\cdot H_2Acen$	VII	+0.081	1.38	22
26	$Bu^nSnCl_3\cdot 2PPh_3$	II	+0.209	1.23	28
		VI	+0.068		
27	$SnI_4\cdot DP$	III	+0.179	1.18	29
		VI	+0.084		
28	$SnBr_4\cdot 2PBu^n_3$	III	+0.244	1.03	27
		VI	−0.029		
29	$SnBr_4\cdot 2POct^n_3$	III	[e]	0.94	29
		VI	−0.058[f]		
30	$SnBr_4\cdot 2PPhMe_2$	III	+0.246	1.13	29
		VI	+0.080		
31	$SnBr_4\cdot 2PPh_3$	III	+0.251	0.63[g]; 0.95	26, 6
		VI	+0.089		
32	$SnBr_4\cdot DP$	III	+0.251	1.21	29
		VI	+0.089		
33	$SnCl_4\cdot 2PEt_3$	III	+0.285	0.84; 0.87	27, 15
		VI	+0.030		
34	$SnCl_4\cdot 2Pr^n_3$	III	+0.285	0.89	15
		VI	−0.002		
35	$SnCl_4\cdot 2PBu^n_3$	III	+0.285	0.85; 0.87	15, 29, 27, 26
		VI	−0.021		
36	$SnCl_4\cdot 2POct^n_3$	III	[e]	0.72	29
		VI	−0.053[f]		
37	$SnCl_4\cdot 2PPhEt_2$	III	+0.288	0.86; 0.88	27, 15
		VI	+0.060		
38	$SnCl_4\cdot 2PPhMe_2$	III	+0.287	0.85; 0.91	15, 29
		VI	+0.099		
39	$SnCl_4\cdot 2PPh_2Et$	III	+0.290	0.63	15
		VI	+0.082		
40	$SnCl_4\cdot 2PPh_2Me$	III	+0.289	0.79; 0.81	27, 15
		VI	+0.100		
41	$SnCl_4\cdot DME$	III	+0.290	0.69	27
		VI	+0.100		
42	$SnCl_4\cdot 2PEt_2(SPr^n)$	III	+0.290	0.82	34
		VI	+0.012		
43	$SnCl_4\cdot 2P(\textit{iso}\text{-}Pr)_2(SMe)$	III	+0.290	0.83	34
		VI	+0.012		
44	$SnCl_4\cdot 2PPh_3$	III	+0.292	0.56; 0.75; 0.78	29, 15, 27
		VI	+0.101		
45	$SnCl_4\cdot DP$	III	+0.292	1.05	29
		VI	+0.101		
46	$SnCl_4\cdot 2PPh_2(C{\equiv}CMe)$	III	+0.295	0.77	15
		VI	+0.123		
47	$SnCl_4\cdot 2PEt_2Cl$	III	+0.295	0.75	34
		VI	+0.092		
48	$SnCl_4\cdot 2PEt(SPr^n)_2$	III	+0.295	0.62	34
		VI	−0.001		
49	$SnCl_4\cdot 2PPh_2(NMe_2)$	III	+0.297	0.83	34
		VI	+0.092		
50	$SnCl_4\cdot 2PEt(Cl)(SPr^n)$	III	+0.299	0.70	34
		VI	+0.058		
51	$SnCl_4\cdot 2P(SPr^n)_3$	III	+0.299	0.66	34
		VI	−0.012		

(continued overleaf)

TABLE I. *(continued)*

Code No.	Compound[b]	Valence bond structure[c]	Q_{Sn}	δ[d]	Refs. for δ
52	$SnCl_4 \cdot 2PEt(NMe_2)_2$	III	+0.301	0.85	34
		VI	+0.060		
53	$SnCl_4 \cdot 2PPh_2(OMe)$	III	+0.305	0.81	15
		VI	+0.131		
54	$SnCl_4 \cdot 2P(NMe_2)_3$	III	+0.308	0.74	34
		VI	+0.072		
55	$SnCl_4 \cdot 2P(OMe)_3$	III	+0.333	0.63	34
		VI	+0.251		

[a] See text, Calculation. Q_{Sn} data from method B refer to the electronegativity factors a = 7.90 and b = 5.01 for tin; valence states of other atoms in the molecule, and group electronegativities, are in Table II and legend to the Table. [b] Codes: DPE, $Ph_2P(CH_2)_2PPh_2$; DP, $(o\text{-}Ph_2P)_2C_6H_4$; DME, $Ph_2PCH_2PPh_2$; Cy, cyclohexyl; in the calculations by method B, DPE and DME are taken as 2 $[P^+(Ph_2Me)]$, and DP as 2 $[P^+(Ph_3)]$. Compound 8 could be dimeric. [c] See Fig. 1 and Calculation, this work. [d] mm s^{-1}, with respect to R.T. $BaSnO_3$, $CaSnO_3$ or SnO_2. [e] Not calculated. Taken as that of No 28 and 35, respectively. [f] Values estimated by hand calculations, since the Gauss-Seidel solution did not converge in the computer run. [g] Probably refers to $SnBr_4 \cdot 2P(O)Ph_3$; not taken into account in the graphs.

monomeric species, has been previously inferred [22, 23].

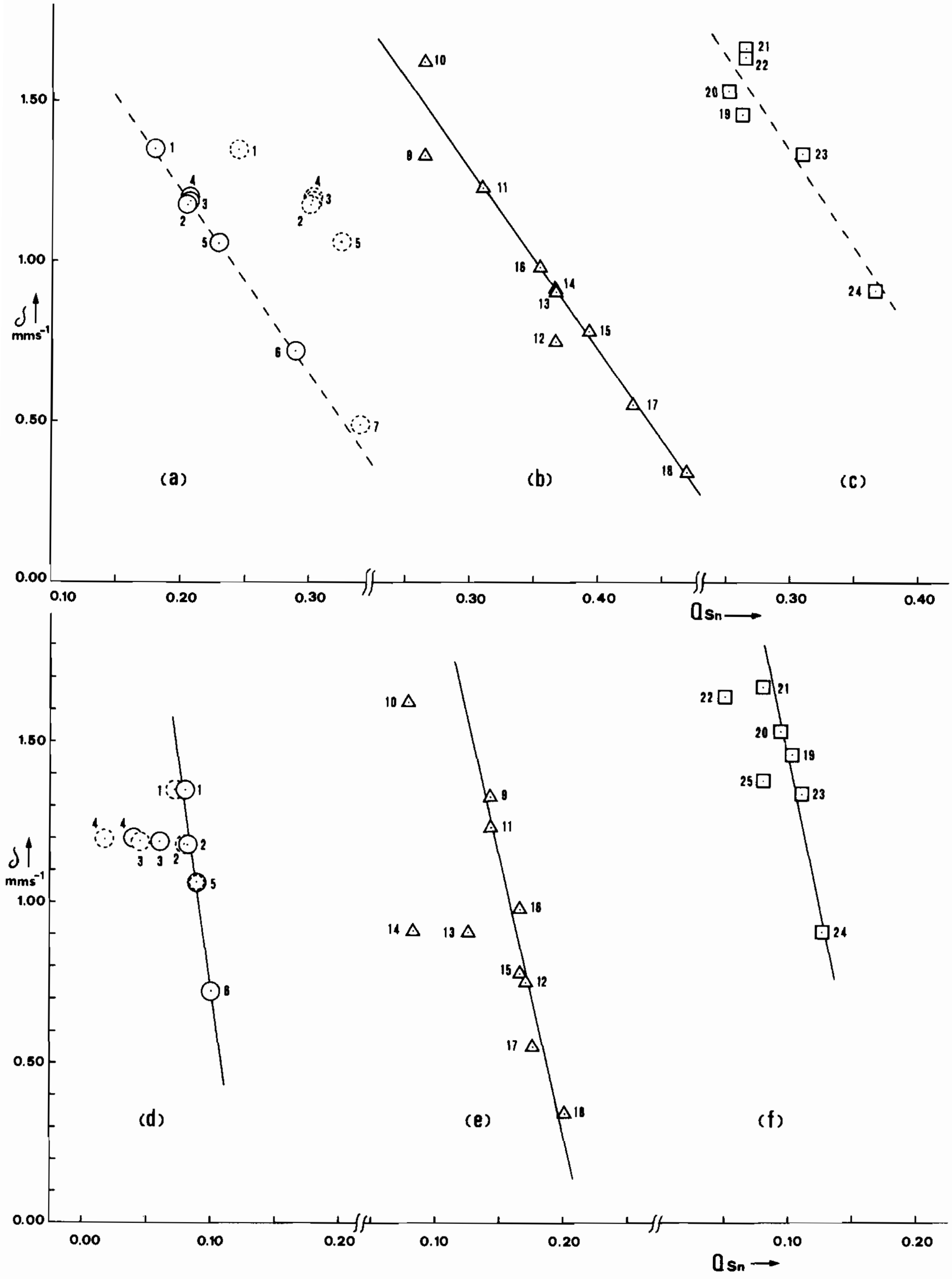
Octahedral type structures have been reported for phosphanes, $Snhal_4 \cdot 2PR_3$, and also $BuSnCl_3 \cdot 2PPh_3$, preferentially with *trans*-P_2 atoms, and *cis*-P_2 where required by the nature of the ligand (see for example, refs. 15, 24–29, and refs. therein). The only known five-coordinate adduct seems to be $SnCl_4 \cdot PCy_3$ [15].

We consequently assume, in tin environments of the compounds here studied, the valence bond structures (I)–(III), Fig. 1. The only configurational implication concerns the linearity of the C Sn C skeleton in (I), according to previous findings and proposals [18, 19, 22, 23]. The assumption of bond order Sn–C = 1.0 in (I) and (II) is in consonance with experimental evidence and related rationalizations [30]. Structure (III) reflects an equivalent involvement of Sn s and p orbitals in the six bonds [13].

Eventual five-coordinate structures, (IV) and (V) in Fig. 1, have been assigned by the same reasoning. These structures imply trigonal bipyramidal configurations, the metal atom s character being concentrated in the trigonal plane in (IV), while equally distributed among the five bonds in (V) [13]. Phosphine substituents are assumed to lie in equatorial position according to the observation that the most electronegative groups and atoms are actually axial in trigonal bipyramidal configurations [31]. In fact, if Mulliken electronegativities are taken into account for a qualitative estimate, it follows that the value of $Cl_{s^2p^2p^2p}$ (9.38) is larger than that of $P_{te^2tetete}$ (8.91) as well as of groups PR_3 and P^+R_3 (as obtainable by method B, see Table II) [11].

Using the input data N_{ij}, F for tin environment reported in Fig. 1 (and usual values [13] in the rest of the molecules), transferred partial charges, as well as equilibrium partial charges, have been computed by using the Fortran IV program CHELEQ [13, 14], which has been modified in order to account correctly for structures (I)–(V). The results are reported in Table I, and employed in Figs. 2 and 3.

Fig. 2. (*Facing page*). Correlation δ/Q_{Sn} (Mössbauer isomer shift *vs.* partial charge on tin) for homologous series of 1:1 tin (IV) and organotin (IV) adducts, (see text, Table I and Fig. 1). The ligands are the following:
(a): ○: DPE, 6 coordinate Sn, structures (I)–(III); ◌: DPE and PCy_3, 5 coordinate Sn, structure (IV) for adducts of organotin moieties, and structure (V) for $SnCl_4 \cdot PCy_3$. (b): △: H_2Salen, and (c): ▣: H_2Acen, 6 coordinate structures (I)–(III). (d), (e), (f): same as in (a)–(c), structures (VI)–(VIII). Isomer shift data and code No's: see Table I. Q_{Sn} data (Table I): (a)–(c), from method A; (d)–(f), from method B; see Calculation. Lines in the Figure are least squares fits of data points (6 coordinate species), excluding the following (see text): (b): adducts of $AlkSnCl_3$ and Alk_2SnCl_2; (d)–(f): adducts of Bu^nSnCl_3, Oct^nSnCl_3, $Bu^n_2SnCl_2$, Et_2SnCl_2 and Me_3SnCl. Related least squares equations are: (b): $\delta = -5.63\ Q_{Sn} + 2.98$ (r = 0.999); (d): $\delta = -28.23\ Q_{Sn} + 3.53$ (r = 0.998); (e): $\delta = -17.30\ Q_{Sn} + 3.72$ (r = 0.961); (f): $\delta = -19.44\ Q_{Sn} + 3.40$ (r = 0.976). Cases (a) and (c) have not been considered, due to the limited number of data points available for the linear correlation. For all data in each series, including also the white tin value (δ = 2.56 mm s^{-1}, Q_{Sn} = 0.00, see text), it is obtained: (a): $\delta = -6.43\ Q_{Sn} + 2.54$ (r = 0.999); (b): $\delta = -4.78\ Q_{Sn} + 2.65$ (r = 0.986); (c): $\delta = -4.20\ Q_{Sn} + 2.62$ (r = 0.972). (d): $\delta = -14.87\ Q_{Sn} + 2.27$ (r = 0.883); (e): $\delta = -9.40\ Q_{Sn} + 2.32$ (r = 0.892); (f): $\delta = -11.08\ Q_{Sn} + 2.45$ (r = 0.937).



Method B

Calculations of partial charges by the original eqns. (2) and (3) have been also performed. Apart from tin (*vide infra*), tabulated values of I_v and E_v pertaining to the appropriate valence states [11] have been employed, according to valence bond formulas. The adducting atoms (formally P^+ and O^+ upon coordination) have been taken as sp^3 hybridized. In case of multiple bonds, only σ values of the parameters I_v and E_v have been considered, which seems a reasonably good approximation [32]. Whenever needed, group electronegativity values (independent

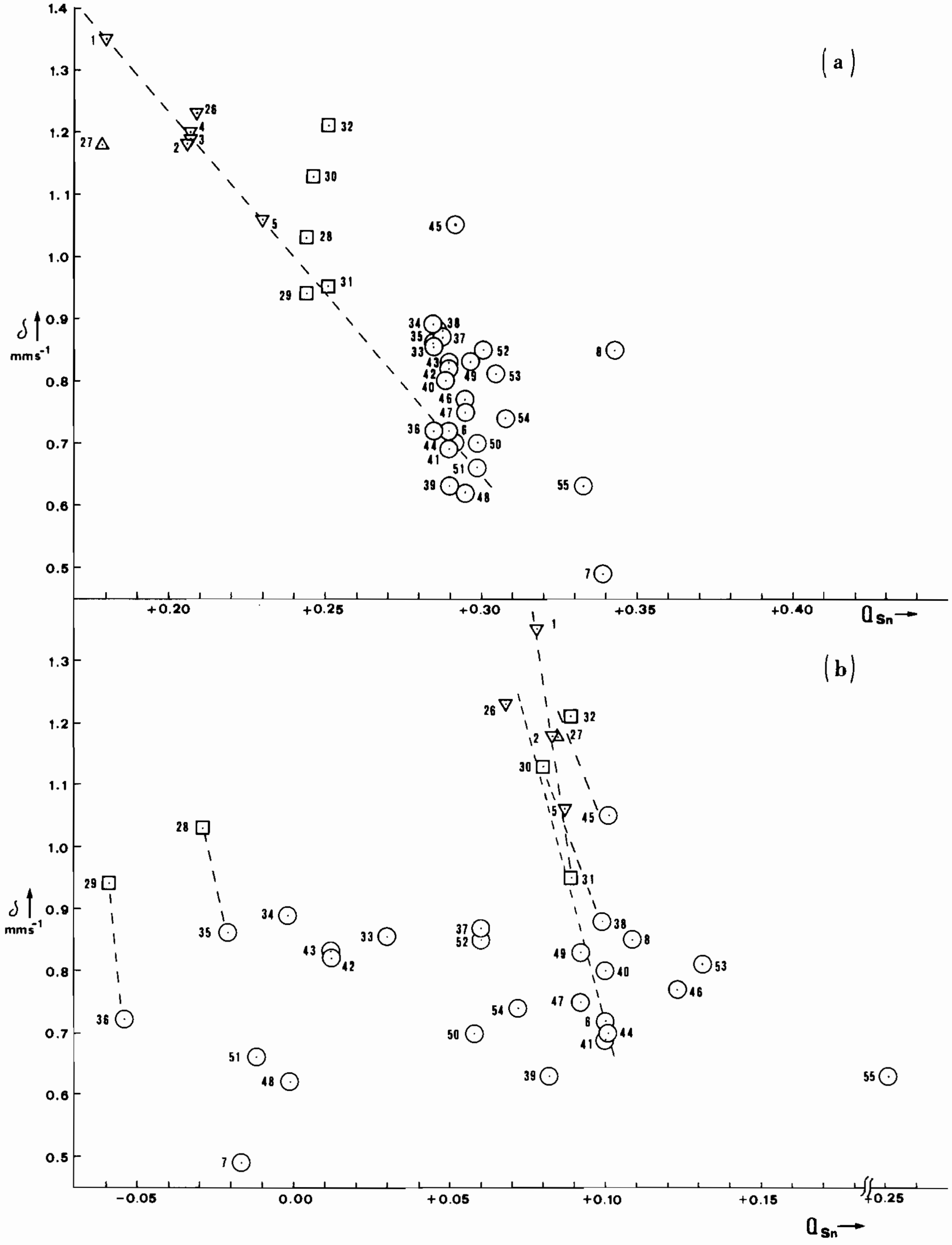


Fig. 3. Plots δ/Q_{Sn} for adducts $Snhal_4 \cdot 2PR_3$. Data points refer to: △: $SnI_4 \cdot 2PR_3$; ⊡: $SnBr_4 \cdot 2PR_3$; ⊙: $SnCl_4 \cdot 2PR_3$ (and $SnCl_4 \cdot PR_3$); ▽: $R_nSnCl_{4-n} \cdot 2PR_3$ (n = 1, 2), including some data of DPE adducts for comparison purposes. Adducts are considered to contain six-coordinate Sn, except $SnCl_4 \cdot PR_3$, see Table I. Isomer shift data and code No's, see Table I. Partial charges, Q_{Sn} are calculated according to: (a), method A; (b), method B (see text, Calculation).

TABLE II. Group Electronegativities Calculated by Method B (text, see Calculation).

Group[a]	a[b]	b[c]
$(CH_2)_2CH_3$	7.41	1.30
$(CH_2)_3CH_3$	7.42	1.00
$(CH_2)_6CH_3$	7.42	0.59
$(CH_2)_7CH_3$	7.42	0.52
C_6H_{11}	7.45	0.77
CH=CH	7.96	3.31
C_6H_4–CH=N–CH_2[d]	8.22	0.84
$(CH_3)C(=CH–C(CH_3)=N–CH_2)$[e]	7.92	0.83
SCH_3	7.38	2.45
$S(CH_2)_2CH_3$	7.41	1.15
$C{\equiv}CCH_3$	8.32	2.22
$N(CH_3)_2$	7.78	1.46
OCH_3	8.56	2.75

[a] Values for CH_3, C_2H_5, *iso*-C_3H_7 and C_6H_5 have been taken from the literature [12, 32]. Tabulated I_v and E_v data have been used in the equalization procedure (eqns. (2) and (3)), assuming the appropriate valence states [11] for: C: te te te te, tr tr tr π (σ), di di ππ(σ); N: tr^2 tr tr π (σ), te^2 te te te; S: s^2 p^2 p p; O: te^2 te^2 te te. The electronegativities of groups P^+R_3 and HO^+R (see Discussion and legend to Fig. 1, this paper), not reported here, have been obtained by equalizing pertinent data in this Table (and literature) to parameters pertaining to P^+ (te te te te) and O^+ (te^2 te te te) [11]; when applicable, data for hal (s^2 p^2 p^2 p) [11] have been used. [b] $(I_v + E_v)/2)$. [c] $(I_v - E_v)$. [d] $(H_2Salen)/2$. [e] $(H_2Acen)/2$.

from the bonds made by the group into the given molecule) have been calculated according to established procedures, based on eqns. (2) and (3) [12, 32]. The obtained data are listed in Table II. Complete electronegativity equalization, extended to all bonds involving atoms and groups in the molecule, has been assumed, which certainly does not reflect the actual bonding situation. Mathematically, this corresponds to get, from (2) and (3), a set of n equations in n unknowns for a molecule with n bonds, where all Q but one (the latter obtained subsequently by difference from the known total molecular charge) are contained in each equation of the set.

As far as valence bond formulas for this method are concerned, (VI)–(VIII) in Fig. 1, sp^3d^2 and sp^3 d hybridized tin, 6- and 5-coordinate respectively, is considered without any implication of particular configurations, or preferential Sn orbital participations in individual bonds.

Calculations of group electronegativities and of Q_i by method B have been performed by the aid of '*ad hoc*' Fortran IV computer programs; the results are reported in the Tables I and II, and Q_i values are employed in the plots of Figs. 2 and 3.

It must be recalled that, contrary to literature data concerning essentially organic compounds [12, 13, 32], Q_{Sn} values here computed (Table I) are largely empirical. Due to the uncertainties in selecting valence bond structures in method A, as well as sp^3d^2 tin orbital electronegativities in method B, our Q_{Sn}, and related Q_i charges, suit only to the scope of correlating δ's and, in general, charge-dependent experimental quantities, with theoretically justified parameters in some way proportional to valence state electronegativities.

Discussion

The correlations δ *vs.* Q_{Sn} for the homologous series here studied are reported in Fig.2. Isomer shift data from our laboratory (at 77.3 K, usually affected by the standard error ±0.01 mm s^{-1} [35]) have been preferentially used in the plots. For H_2Salen adducts, average values from T dependent studies [20] have been preferred (see Table I).

In the case of Q_{Sn} from method A, lines (a)–(c), it clearly appears that: i) Q_{Sn} values for $AlkSnCl_3$ and Alk_2SnCl_2 adducts are practically constant, irrespective of the nature of the alkyl radical, while the related δ's more or less vary according to the inductive effects of these groups (see also Table I); ii) ignoring data points of $AlkSnCl_3$ and Alk_2SnCl_2 derivatives, linear correlations occur, as evidenced by lines (a) and (b); iii) Q_{Sn} magnitudes, and consequently the insertion into the correlations, depend sensibly on the assumed coordination number and valence bond structure (see for example Fig. 2(a), data points for R_nSnCl_{4-n} derivatives).

The relative insensitivity, with respect to inductive effects, of empirical partial charges from method A has been already noticed [13]; on the other hand, the practical invariance here detected was not predictable on previous grounds. From trends commented under ii) and iii), it would be inferred that the factors determining the magnitudes of Q_{Sn} from method A (*i.e.*, the valence state electronegativities of atoms bound to tin, as well as the right assignment of the number of bonds to the metal atom and the consequent smooth, appropriate changes in electron populations to be attributed to these bonds) are generally varying parallel to the actual changes on tin s and p charge clouds, which are experimentally registered in the individual Mössbauer isomer shift values. It then follows that these δ *vs.* Q_{Sn} correlations may be employed to the purpose of structural assignments within homologous series, in consonance with previous findings [9]; on the other hand, a word of caution has to be said in cases where inductive effects do operate.

The correlations in Fig. 2(a)–(c) deserve further comments. In 2(a), partial charge on tin, by this method of computation, becomes more positive on decreasing the coordination number, *i.e.*, phosphorus would release negative charge to tin upon bond formation (which, in the present context, is due to the peculiar set of s and p electronegativities of P used in the computations [13, 14]). Besides, line 2(a) would imply that assigned valence bond structures, (I)–(III), are in some way actual for the DPE adducts here considered, in consonance with previous assumptions (see text, Calculation). In this particular case, the derivatives of $AlkSnCl_3$ insert into the correlation too, due to the occurrence of limited variation of δ with the nature of the alkyl radical. Lastly, the data point of the probably pentacoordinated species $SnCl_4 \cdot PCy_3$ (see Calculation) would in some way insert into the line of octahedral type compounds (Fig. 2(a)). It is difficult to say whether this circumstance has a physical significance, and consequently whether structure (V) is actual for this compound. We are inclined to think that the agreement is incidental, being convinced that these δ *vs.* Q_{Sn} relationships strongly depend, *inter alia,* on gradual changes of tin hybridization through the series.

As far as H_2Salen adducts are concerned (Fig. 2 (b)), the generally good correlation obtained is in favour of a structural identity of tin environment in all derivatives, which could well be the assumed six-coordinate configuration with bridging ligand and oxygen donor atoms (see text, Calculation; curiously, the only member of the series for which the structure above is known from X-ray diffractometry, $Me_2SnCl_2 \cdot H_2$Salen, [19] does not enter into the correlation, which is probably due to the unreliability of its calculated Q_{Sn} value, as discussed previously). No definite conclusions may be advanced for H_2Acen adducts in view of the few data points available. These are essential, on the other hand, in stating the near independence of Q_{Sn} from inductive effects.

It is worth mentioning here that lines δ/Q_{Sn} in Fig. 2(a)–(c) extrapolate satisfactorily to the data point of tin metal [36] (see legend to the Figure). Although this is physically correct [1c, 10], due to the octahedral environment of tin metal, we hesitate to further comment, and infer, for example, the correctness of Q_{Sn} extracted by method A; in fact, we observed that δ *vs.* Q_{Sn} (method A) for $Snhal_6^{2-}$ complex anions does not contain the white tin point.

In consideration of the relative insensitivity of method A in accounting for inductive effects, we decided to test the response of the original approach, eqns. (2) and (3), method B in Calculation. In this context, we faced the problem of 5d orbital electronegativity of tin, there being, to our knowledge, no literature estimates. If the values $a_d = [(I_v + E_v)/2)]_d = 2.7$ and $b_d = (I_v - E_v)_d = 2.0$ are used [10] (which is assumed to correspond to $a_{sp^3d^2} = 4.4$ and $b_{sp^3d^2} = 3.0$ [37]), partial charges Q_{Sn} larger than +1.0 are calculated by method B, either according to the valence bond structures (VI) and (VII) (Fig. 1), or employing a 'seven atom' formulation (in the latter, calculated electronegativities of groups R, and P^+R_3 or HO^+R, Calculation and Table II, are equalized to the value of sp^3d^2 tin; for example, in DPE adducts Q_{Sn} are in the range +1.15 to +1.25 in the first case, structures (VI) and (VII), and +1.25 to +1.40 in the second). The correlations δ/Q_{Sn} obtained in these ways are quite far by including the tin metal point; the latter in some way occurs if the tin factors $a_{sp^3d^2} = 7.90$ and $b_{sp^3d^2} = 5.01$ are used in the equalization procedure (see legend to Fig. 2), which implies that Sn d and s p^3 orbital electronegativities are corresponding (quite an unrealistic assumption; the factors above come from tabulated $Sn_{te\,te\,te\,te}$ I_v and E_v data [11]). Anyway, we observed that the same general trend holds in δ/Q_{Sn} correlations for our adducts whatsoever a and b values are taken for tin, using valence bond formulas with P^+, O^+ explicitly linked to Sn (VI and VII, Fig. 1) or inserted into P^+R_3 and HO^+R groups; the only difference is that, in the latter cases, the steepness of the line is lowered. Consequently, we report in Fig. 2 (d)–(f) representative trends inherent in the use of method B partial charges, where Q_{Sn} data refer to parameters $a_{sp^3d^2} = 7.90$ and $b_{sp^3d^2} = 5.01$ and to structures (VI) and (VII) for six-coordinate Sn.

It clearly appears in Fig. 2 that Q_{Sn} from method B, (d)–(f), are varying in a lesser range than those from method A, (a)–(c), in case of linearly correlated data points. Due to this effect, or perhaps to the choice of electronegativity parameters, data points for the lower mono- and dialkyltins are now participating to the linear δ/Q_{Sn} correlations. On the other hand, it is clearly seen that adducts of butyl and octyltin, as well as of trimethyltin, lie definitely out of the lines, which means that Q_{Sn} charges from method B overemphasize the inductive effects of these radicals with respect to that detected by s and p charge clouds and registered through the respective Mössbauer isomer shifts.

Besides, the Q_{Sn} values pertaining to five-coordinate Sn, structure (VIII), do not differ much from the six-coordinate ones, which does not allow structural deductions. It is obvious that, whenever the procedure by Huheey and Watts is employed [10, 37], the electronegativity parameters of Sn sp^3d vary considerably with respect to the sp^3d^2 ones, being now a = 5.30 and b = 3.51; this induces a large dependence of Q_{Sn} from coordination number, the charge for 5 coordinate species being consistently lesser. The direction of this variation, contrary to that detected by method A (*vide*), is in consonance with the concept of charge attraction by P upon coordination, which results in the present calculations from the large orbital electronegativity parameters a and b of P^+ (from literature I_v and E_v data [11]).

At this point of our study, it seemed opportune to determine how Q_{Sn} respond to inductive effects of groups not directly linked to tin, with respect to inductive influences evidenced by Mössbauer isomer shifts. To the purpose, the large selection of members of the series $Snhal_4 \cdot 2PR_3$, reported in the literature, has been taken into account (Table I), where R groups bound to phosphorus are widely varying in nature and properties (Table II). Accordingly, δ values in this series seem to depend, *inter alia,* on the electronegativity of groups PR_3 [6, 15, 26, 27, 34]. One-parameter linear relationships have been proposed to hold between δ and $\Sigma\chi$, including χ_{PR_3} [6]; a two-parameter approach, δ *vs.* $\Sigma\sigma^*$ (the latter being the summation of Taft constants of R in PR_3), would yield a linear correlation, although the coefficient is rather poor [34].

The results obtained by our approaches are given in Table I, and plotted in Fig. 3, (a) and (b). Mathematical averages are employed in the Figure whenever replicated isomer shift data were available in the literature (Table I). The value 0.95 [3] has been used for $SnBr_4 \cdot 2PPh_3$.

It is evident from Fig. 3(a), (b) that trends commented previously essentially repeat in the present context. Q_{Sn} from method A underestimate, while data from method B overestimate, the inductive effects sensed by changes in isomer shifts. In the first case, Fig. 3(a), data points are grouped according to the nature of the halide, while in the second, 3(b), points are spread out according to the inductive effects of R in PR_3; the latter is responsible also for the failure of $SnCl_4 \cdot PCy_3$ in belonging to the DPE relationship ($Q_{Sn} = -0.017$).

It is worth commenting further the data in Fig. 3(b), where the electronegativity parameters a = 7.90 and b = 5.01 for sp^3d^2 tin, structure (VI) in Fig. 1, have been used, in consonance with the discussion in the preceding . The trends of Fig. 3(b) repeat essentially when a = 4.40 and b = 3.00 are employed, apart from the Q_{Sn} magnitudes (ranging from +1.04 and +1.44 in the case of calculations according to structure (VI)), as well as for both couples of a and b parameters in case of 'seven atom' calculations, using in the equalization procedure the electronegativities of P^+R_3 groups (Table II; Q_{Sn} are now within +1.10 to +1.65 for a = 4.40 and b = 3.00). Deductions above, based on Fig. 3(b), are then generally valid in case of method B Q_{Sn} charges.

In conclusion, it may be observed that the two-parameter correlations δ *vs.* Q_{Sn} here treated seem to be applicable in the rationalization of Mössbauer isomer shifts within homologous series. Much care has to be exercised in dealing with compounds where the metal atom is subjected to inductive effects, such as the various alkyltins and phosphino adducts here investigated, due to the wrong response of both computational methods with respect to effects sensed by 5s and p electrons of tin and reflected into the magnitude of the respective isomer shifts*. The procedure needed to build-up δ/Q_{Sn} plots seems to be easily and widely applicable, and accessible to experimentalists, taking into account also the availability of the Fortran IV CHELEQ program [13]. It would be predicted that Q_{Sn} calculations in other series would generate peculiar charge magnitudes, and consequently independent δ/Q_{Sn} straight lines, especially by using method B charges. In using method A, sets of lines could coincide in case of comparable magnitudes of orbital electronegativities and atomic parameters I_v and E_v of the ligand atoms bound to tin.

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*Similar limitations have been detected also in connection with Fe complexes [38].

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