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MAGNETIC DOUBLE RESONANCE STUDIES OF TRIMETHYLTIN CHALCOGENIDES

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Summary

NMR parameters for bis(trimethyltin) oxide, sulphide, selenide and telluride have been measured by ^1H—{^{13}C}, ^1H—{^{77}Se}, ^1H—{^{119}Sn}, ^1H—{^{125}Te}, and ^1H—{^{117}Sn} double resonance. Theories of ^{119}Sn magnetic shielding and one-bond coupling constants are summarised and discussed in terms of the measured parameters. It is concluded that theoretical approximate expressions often used to estimate these parameters are inadequate when the tin atom is bound to selenium or tellurium.

Introduction

The recent more general availability of suitable spectrometers has resulted in an increase of interest in the ^{13}C and ^{119}Sn NMR parameters of organotin compounds [1]. However, the factors influencing these parameters for heavier elements are in many cases only poorly understood, and it is important to have comprehensive comparative data for related series of compounds. In this paper we report coupling constants and chemical shifts involving ^{13}C, ^{77}Se, ^{119}Sn and ^{125}Te for the series of trimethyltin chalcogenides $(Me_3Sn)_2E$ (E = O, S, Se or Te). The proton spectra of the oxide, sulphide and selenide have been reported [2].

Experimental

Trimethyltin sulphide, selenide and telluride were made according to standard methods [2] and were purified by repeated distillation. Trimethyltin oxide, b.p. 48-50°C/0.03 Torr, was made by the azeotropic dehydration of trimethyltin hydroxide in boiling benzene solution. NMR spectra were obtained under the conditions stated in Table 1, with a modified JEOL C-60H instrument and using ^1H-{X} double resonance techniques described elsewhere [3-5]. Spectra recorded in the field-sweep mode were calibrated by the audio-frequency side band technique, and those recorded in the frequency-sweep mode by use of a frequency counter to determine the frequency of the audio-modulation side-band used to excite the resonance.

Results

Trimethyltin sulphide

Lines due to $Me_3{}^{119/117}SnSSnMe_3$ and $(^{13}CH_3)(CH_3)_2SnSSn(CH_3)_3$ were well resolved as satellites of the main resonance in the proton spectrum of trimethyltin sulphide (see Fig. 1) and standard heteronuclear $^1H-\{^{13}C\}$ and $^1H-\{^{119}Sn\}$ spin tickling experiments [6,7] gave the ^{13}C and ^{119}Sn resonance frequencies. The tin spectrum was sufficiently sharp for careful $^1H-\{^{119}Sn\}$ and $^1H-\{^{117}Sn\}$ tickling experiments to give ^{119}Sn and ^{117}Sn resonance frequencies to ±0.2 Hz and a value for their ratio of 1.04654122 ± 0.00000002. This is within 0.00000008 of the same ratio determined for $SnMe_4$ and for Me_2SnCl_2 and indicates the absence of any significant primary isotope effect upon the tin shielding. Lines due to $(^{13}CH_3)(CH_3)_2{}^{119}SnSSn(CH_3)_3$, present in a natural abundance of ca. 0.095%, were also observed as ^{119}Sn satellites of the ^{13}C satellites (see Fig. 1) and $^1H-\{^{13}C\}$ experiments on these [7] gave the magnitude of $^1J(^{119}Sn-^{13}C)$ and its sign relative to $^2J(^{119}Sn \cdots {}^1H)$ which is generally considered to be positive in compounds of this type [8]. [Note that $\gamma(^{119}Sn)$ is negative].

Trimethyltin telluride

In addition to the lines mentioned above, the proton spectrum of trimethyltin telluride exhibited lines due to species containing ^{125}Te (natural abundance 7.0%) and these appeared as well-resolved satellites in the proton spectrum $[^3J(^{125}Te \cdots {}^1H) = 2.9\ Hz]$. $^1H-\{^{125}Te\}$ experiments on these at the central peak

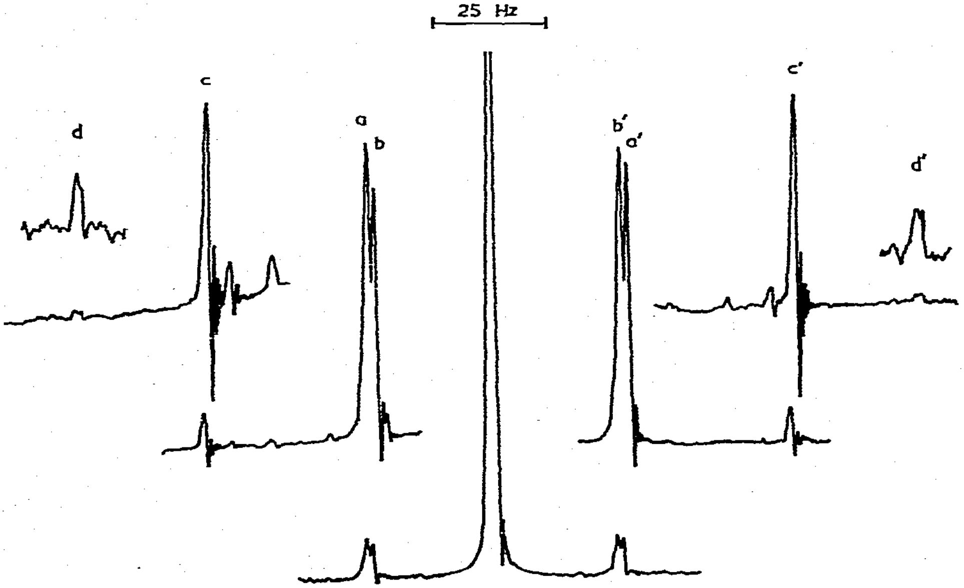

Fig. 1. Proton spectrum of trimethyltin sulphide showing at increased spectrometer gain lines due to the presence of (a) ^{119}Sn, (b) ^{117}Sn, (c) ^{13}C, and (d) $^{117/119}Sn$ and ^{13}C in the same molecule.

position gave the central ^{125}Te resonance frequency and similar experiments at the $^{119/117}$Sn satellite position gave the sign and the magnitude of $^1J(^{125}\text{Te}-^{119}\text{Sn})$ which were confirmed by $^1\text{H}-\{^{119}\text{Sn}\}$ experiments.

Trimethyltin selenide

In this compound [5] the corresponding coupling to ^{77}Se (natural abundance 7.5%) was smaller [$^3J(^{77}\text{Se} \cdots {}^1\text{H} = 1.5$ Hz] and the ^{77}Se satellites were not well resolved. However peak heights could increased by ca. 6% by irradiation at the appropriate ^{77}Se frequency and the experiments were otherwise straightforward.

Trimethyltin oxide

In trimethyltin oxide, the $^{117/119}$Sn satellites in the proton spectrum were broadened, even when the compound was rigorously purified by refluxing with metallic sodium in benzene before redistillation. However, the NMR parameters for trimethyltin hydroxide [Me_3SnOH; $\delta(^{119}\text{Sn}) = -118 \pm 1$ ppm; $^2J(^{119}\text{Sn} \cdots {}^1\text{H}) = +59.5 \pm 0.5$ Hz; $^1J(^{13}\text{C}-^1\text{H}) = 130.0 \pm 0.5$ Hz; saturated solution in dichloromethane] are so similar to those for trimethyltin oxide that the presence of small amounts of the former would be unlikely to have any significant effect. This broadening did not hinder the measurement of parameters for $(CH_3)_3{}^{119}SnOSn(CH_3)_3$ or for $(^{13}CH_3)(CH_3)_2SnOSn(CH_3)_3$, but had the effect of reducing the signal-to-noise ratio for lines due to $(^{13}CH_3)(CH_3)_2{}^{119}SnOSn(CH_3)_3$ to below the level at which successful double resonance experiments could be performed and therefore precluded the determination of $^1J(^{119}\text{Sn}-^{13}\text{C})$ for this compound.

The results are summarised in Table 1. In calculating the chemical shifts the following were used as standards: ^{13}C, $(^{13}CH_3)(CH_3)_3Si$, $\Xi = 25{,}145{,}004$ Hz; ^{77}Se, $(CH_3)_2{}^{77}Se$, $\Xi = 19{,}061{,}097$ Hz.; ^{119}Sn, $(CH_3)_4{}^{119}Sn$, $\Xi = 37{,}290{,}665$ Hz; ^{125}Te, $(CH_3)_2{}^{125}Te$, $\Xi = 31{,}511{,}513$ Hz. Chemical shifts are quoted on the convention that an increase in shielding corresponds to an algebraic decrease in

TABLE 1

NMR PARAMETERS (δppm, *J* Hz) OF $(Me_3{}^{119}Sn)_2E$ (E = O, S, ^{77}Se, ^{125}Te)[a]

Parameter	E O	 S	 ^{77}Se	 ^{125}Te
$\delta(^1\text{H})^b$	+ 0.24	+ 0.38	+ 0.58	—
$\delta(^{13}\text{C})^c$	− 1.9 ± 0.3[d]	− 0.9 ± 0.3	− 1.05 ± 0.3	− 1.9 ± 0.3
$\delta(^{119}\text{Sn})^e$	+113.1 ± 1[f]	+ 86.5 ± 0.3[g]	+ 44.5 ± 1	− 66.8 ± 1
δ(E)	—	—	− 547 ± 1[h]	−1214 ± 1[i]
$^1J(^{119}\text{Sn}-^{13}\text{C})$	*j*	−356 ± 5	− 340 ± 10	*k*
$^1J(^{119}\text{Sn}-\text{E})$	—	—	+1060 ± 10[b]	−1385 ± 10[m]
$^1J(^{13}\text{C}-^1\text{H})$	+130.1 ± 0.2[n]	+130.8 ± 0.2	+ 131.5 ± 0.5	+ 132.3 ± 0.5
$^2J(^{119}\text{Sn} \cdots {}^1\text{H})$	+ 56.2 ± 0.2[o]	+ 57.1 ± 0.2	+ 56.1 ± 0.2	+ 55.3 ± 0.3
$^3J(\text{E} \cdots {}^1\text{H})$	—	—	1.5 ± 0.3	2.9 ± 0.1

[a] For neat liquids containing 20% v/v dichloromethane. [b] Data taken from ref. 2. [c] Relative tc $Me_4Si = 0$. [d] Neat liquid −1.7; 50% v/v in dichloromethane −2.1. [e] Relative to $Me_4Sn = 0$. [f] Neat liquid +109.5; 50% v/v in dichloromethane +117.1. [g] Neat liquid +84.9. [h] Relative to $Me_2Se = 0$. [j] Not measurable (see text). [k] Not measured. [l] $^1K(\text{Sn}-\text{Se}) = -124\ \text{nm}^{-3}$. [m] $^1K(\text{Sn}-\text{Te}) = -98.1\ \text{nm}^{-3}$. [n] Neat liquid + 129.1; 50% in dichloromethane +130.7. [o] Neat liquid +58.0; 50% in dichloromethane +55.7.

chemical shift. Small variations in the parameters were observed on dilution of the samples by dichloromethane, but these were not very significant except in the case of the oxide, and can be attributed to intramolecular anisotropic effects and a degree of autoassociation, which is known to be greater for oxastannanes [9] than for the thia- and selena- analogues. The values at the greatest dilution are taken as being closest to those for a truly monomeric species.

Discussion

A. Chemical shifts

General. The magnetic shielding σ_A of a nucleus A is made up of a number of contributions (eq. 1) [10]:

$$\sigma_A = \sigma^d_{AA} + \sigma^p_{AA} + \sum_{B \neq A} \sigma^d_{AB} + \sigma^l_A + \sigma_E + \sigma_M \qquad (1)$$

σ^d_{AA}, the Lamb term, arises from the diamagnetic currents induced on the atom A by the magnetic field [11]. Although it is large, the major contributions come from the inner core electrons, and so for heavier elements changes within the valence shell will have a small effect. Thus the contribution to σ^d_{AA} for a 6*s* electron in a lead atom has been estimated at ca. 10 ppm, compared to the overall range of lead chemical shifts of ca. 7000 ppm [12]. The size of σ^d_{AA} depends on the electron density on atom A, and hence it decreases as the atoms bound to A become more electronegative. The term σ^p_{AA} is due to induced paramagnetic currents on A, and is generally considered to dominate the variations in shielding of all but the lightest nuclei [12,13]. A simplified expression for σ^p_{AA} is given in eqn. 2 [13]:

$$\sigma^p_{AA} = -(2e^2\hbar^2/3m^2c^2\Delta E)\,(\langle 1/r^3\rangle_p Q_p + \langle 1/r^3\rangle_d Q_d) \qquad (2)$$

in which ΔE is a mean excitation energy, $\langle 1/r^3\rangle_p$ is the mean inverse cube of the valence *p*-electron-nuclear distance, Q_p contains elements of the charge and bond-order matrix and is a measure of the electron imbalance in the ground state valence *p*-orbitals, and $\langle 1/r^3\rangle_d$ and Q_d are similarly defined for the valence *d*-electrons [13].

There are a number of approximations involved the derivation of this equation [13] but expressions of this form have been used with some success in the interpretation of chemical shifts of first and second row elements, and also as a basis for discussing the shielding of heavier nuclei [5,14—16]. σ^p_{AA} is of opposite sign to σ^d_{AA} and can be regarded as arising from opposition by the substituents on A to the diamagnetic circulation by the mixing in of excited states. Thus for example, major contributions to the total magnetic shielding of a tin nucleus in an sp^3-hybridized $\mathrm{Sn^{IV}}$ compound can be considered as being due to σ^d_{AA} for the hypothetical $\mathrm{Sn^{4+}}$ ion reduced by appropriate contributions from *p*-electron terms in σ^p_{AA}.

$\Sigma\sigma^d_{AB}$ arises from electronic circulation associated with other atoms in the molecule and is proportional to the reciprocal of the distance between A and B and might be quite significant [17] in the shielding of lighter nuclei, e.g. ^{13}C, which have a comparatively small chemical shift range. σ^l_A is due to circulation of electrons not associated with any particular atom, for example in aromatic hydrocarbons. It may be anisotropic and can amount to a few ppm, and is therefore mainly of significance for lighter elements. σ_{E} is included to account for the effects of any permanent or induced electric dipole in the molecule which will distort the electronic structure and produce changes in the shieldings discussed above. This contribution has not been extensively investigated for nuclei other than the proton [18], but it may be important when a nucleus is surrounded by a large number of polarizable electrons. σ_{M} results from interaction with the environment in a non-chemical sense, and may include reaction field effects, dispersion forces, magnetic and electric anisotropies, etc., and in many cases can be neglected in studies of series of closely-related molecules.

Chalcogen shielding. The bonding at the chalcogen atom in the compounds examined in this work presumably involves sp^n hybridisation, and therefore Q_d, the *d*-orbital component of the paramagnetic term σ^p_{AA} for the selenium and tellurium shieldings will be zero and variations will therefore be due to contributions from the *p*-orbital component Q_p. Electron donating substituents on the chalcogen will cause it to approach more closely the sp^3 closed shell configuration of the E^{2-} ion, and so Q_p will be small and the total shielding large. Any concomitant changes in σ^d_{AA} would be expected to be positive, and further augment an increase in shielding. In the bis(trimethyltin) selenide and telluride, in which the chalcogens are bounded by two electropositive tin atoms, the measured ^{77}Se and ^{125}Te shieldings are therefore high — the highest yet measured. The point plotted for these two chemical shifts does not deviate appreciably from the linear relationship established between ^{77}Se and ^{125}Te shieldings in a series of analogous compounds [5], which is regarded as confirming both the similarity of Se and Te bonding in a range of compounds, and the validity of eqn. 2 [5] for describing the shielding of these elements.

Tin shieldings. Changes in the shielding of the tin atom can similarly be discussed on the basis of the paramagnetic contribution σ^p_{AA}. The measure of the electron imbalance in the valence *p*-orbitals, Q_p, has a maximum value of 2 when two *p*-orbitals are filled and one empty, or vice versa, and is zero when all are full or all are empty [13]. These extreme situations will not arise with approximately sp^3 hybridized tin, but it can be seen how differences in electronegativity between substituents will increase σ^p_{AA} and thus decrease the shielding. This accounts for the low-field tin chemical shift of ca. 115 ppm in trimethyltin oxide, and also for the non-linearity of plots of $\delta(^{119}\mathrm{Sn})$ against n for series of compounds $\mathrm{X}_{4-n}\mathrm{SnY}_n$ where X and Y are of significantly different electronegativities [1]. The tin chemical shifts of the chalcogenides move the higher field as the atomic number of the chalcogen increases, corresponding to a decrease in the electron imbalance about tin as the electronegativity of the chalcogen decreases. The increase in tin shielding from oxide to telluride is however bigger than would be expected on this basis alone, and in the telluride the tin nucleus is considerably more shielded than in tetramethyltin, which indicates that other factors become dominant as the atomic number of chalcogen substituents on tin increases. Dramatic high-field shifts have also been observed when tin is bound to other heavy atoms such as iodine [1], rhenium [19], etc., and similar, though not so large, effects are observed for ^{29}Si shielding in silicon compounds [15,20]. A contribution from the diamagnetic term $\Sigma\sigma^d_{\mathrm{AB}}$ would depend upon the atomic number of the substituent atom, and this has been considered as significant in the ^{13}C shielding in haloalkanes [17]. However, the necessary variation with the atomic number of the shielded atom is not usually found and as this term is inversely proportional to internuclear distance its importance will decrease as the atomic radius of the shielded atom increases. Thus this term should be relatively unimportant in the interpretation of large changes in ^{119}Sn chemical shifts [3]. Diamagnetic contributions from the anisotropy of the Sn—Te bonds are more difficult to assess, but the small ^{119}Sn chemical shift anisotropy, $\sigma_{\parallel}$—$\sigma_{\perp}$, in methyltin triiodide, and negligible differences in ^{199}Hg chemical shift anisotropies between methylmercuric chloride, bromide and iodide would suggest that these are insignificant [21], as are any electric field effects σ_E since the Sn—Te bond will not be particularly polar. The effect of *d*-orbital occupancy on the terms of eqns. 1 and 2 is difficult to assess in these systems, but $p\pi$—$d\pi$ bonding is probably negligible for the Sn—Te bond, and certainly so, for example, in Sn—Re compounds, and so $p\pi$—$d\pi$ contributions to σ^d_{AA} in these cases will be zero, as will those to σ^p_{AA} via the Q_d terms. (It has been proposed that $d\pi$—$d\pi$ bonding can account for features of ^{119}Sn shielding observed in molecules with a tin—transition metal bond [19], but this will not arise in the molecules studied in this work).

It is clear that only the paramagnetic term will be able to account for the high-field chemical shifts which are found when the tin atom is bound to a heavy atom, but that eqn. 2 cannot predict this effect. The main approximations used in the derivation of eqn. 2 are the use of an average electronic excitation energy and the neglect of orbitals other than centred on the atom whose nuclear shielding is being considered. For molecules of the type considered in this work the first of these assumptions is reasonable but the second is probably less justified (and indeed is used only because of the unavailability of information on more suitable orbitals). Ramsey's full expression [22] for σ^p_{AA} makes neither of these assumptions, and in particular contains terms which are related to the mutual polarizabilites of the orbitals of the central atom and its substituents. Some of these contributions may be negative and if these are large then a reduced paramagnetic term will result with a corresponding increase in the shielding of the central atom. That is, a large polarizable atom such as iodine or tellurium will produce less distortion of the tin outer orbitals and hence will impair the diamagnetic electronic circulation to a smaller extent.

Carbon shielding. The carbon atoms in these various molecules all have the same local environment, and their chemical shifts show only a small variation within the series. The decrease in shielding from telluride to sulphide may reflect the long-range residual diamagnetic and electron-releasing effects of the chalcogen; the reversal of this trend with the oxide however, shows that other effects, such as a contribution to the electric field effect σ_E from the increasingly polar E—Sn—E system, or possibly an increasing incidence of $p\pi$—$d\pi$ bonding, may also be significant.

Proton shielding. The proton chemical shifts show the opposite trend to that expected both on the basis of the long-range inductive effect of the chalcogens, the diamagnetic effect of the chalcogens, and any σ_E effect of the polar Sn—E bond. This trend has been noted before not only for some of these compounds [2], but also for methyltin and methylsilicon halides [23], and has generally been ascribed to the magnetic anisotropy of the metal—halogen bond.

B. Coupling constants

General. Treatments [24,25] of one-bond spin—spin coupling constants involving Group IVB elements indicate that the Fermi contact interaction should dominate, and most experimental results [26] have been taken to indicate that the mean excitation energy approximation embodied in eqn. 4 is valid. In this equation ${}^1K$ is the reduced coupling constant (defined by $K(\mathrm{XY}) = 4\pi^2 J(\mathrm{XY})/$-

$${}^1K(\mathrm{XY}) = (4e^2\mathrm{h}^2/9m^2\mathrm{c}^2\Delta E)\psi^2_{\mathrm{X}}(0)\psi^2_{\mathrm{Y}}(0)\alpha^2_{\mathrm{X}}\alpha^2_{\mathrm{Y}} \qquad (4)$$

$\gamma_{\mathrm{X}}\gamma_{\mathrm{Y}}\mathrm{h}$ to avoid dependence on individual nuclear properties), ΔE is a mean electronic excitation energy, $\psi^2(0)$ is the valence *s*-electron density at the nucleus and α^2 is the *s*-character of the hybrid orbital used to form the X—Y bond. On the basis of this equation, ${}^1K(\mathrm{XY})$ would always be positive, would increase with an increase in electron density on X or Y, and also would increase with an increase in *s*-character of the hybrid orbital used to form the X—Y bond. For ^{119}Sn the magnetogyric ratio γ is negative, and therefore K and J for tin bonded to nuclei with positive γ (e.g. ^{1}H, ^{13}C, ^{19}F) will be of opposite sign.

Tin—carbon and tin—proton coupling constants. ${}^1K$(SnC) increases from +30.2 to +31.6 nm^{-3} from the selenide to the sulphide as the electronegativity of the chalcogen increases, this being consistent with an increase in charge density on the tin and/or a decreasing isovalent diversion of *s*-character into the tin—chalcogen bond. The latter argument also holds for the concomitant decrease in ${}^1J({}^{119}\mathrm{Sn}—{}^1\mathrm{H})$ observed for the sequence telluride, selenide and sulphide, although an alternative hyperconjugative process has been advanced to explain similar trends in methyltin and methylsilicon halides [27]. The change in magnitude of ${}^1J({}^{119}\mathrm{Sn}—{}^{13}\mathrm{C})$ is parallelled by the changes in ${}^2J({}^{119}\mathrm{Sn} \cdots {}^1\mathrm{H})$ in accord with the approximately linear correlation observed for a series of methyltin compounds [8,28].

The trends in ${}^1J({}^{119}\mathrm{Sn}—{}^{13}\mathrm{C})$ and ${}^2J({}^{119}\mathrm{Sn}—{}^1\mathrm{H})$ for the telluride, selenide and sulphide noted in the previous paragraph are diminished or reversed for the oxide, but not for the hydroxide, which again suggests that for the oxide other effects, such as an increased electric field effect due to the far Sn—O bond, $p\pi—d\pi$ bonding, or steric interaction as the size of the intermediate chalcogen is reduced, become significant. It is worth noting in this context that ${}^2J({}^{29}\mathrm{Si} \cdots {}^1\mathrm{H})$ for the trimethylsilicon halides decreases in magnitude as the halide electronegativity increases, which has been interpreted both on the basis of halogen—silicon $p\pi—d\pi$ bonding and on the basis of bond angle change due to steric crowding [2,23,27].

Tin—chalcogen coupling constants. The reduced coupling constants ${}^1K$(Sn—Se) and ${}^1K$(Sn—Te) measured for the selenide and telluride are large and negative, which conflicts with the predictions of eqn. 4 and suggests that it is not generally applicable. Measurements of ${}^1K$(SnH), ${}^1K$(SnB), ${}^1K$(SnC), ${}^1K$(SnN), ${}^1K$(SnF), ${}^1K$(SnSi), ${}^1K$(SnP), ${}^1K$(SnSn) and ${}^1K$(SnW) confirm this [8], and suggest that the expression [24] given in eq. 5 is more valid, in which π_{XY} is the mutual polarisability [29] of the *s*-orbitals of the atoms X and Y and is the change in

$${}^1K(\mathrm{XY}) = (4e^2\mathrm{h}^2/9m^2\mathrm{c}^2)\psi^2_{\mathrm{X}}(0)\psi^2_{\mathrm{Y}}(0)\pi_{\mathrm{XY}} \qquad (5)$$

electron density in the *s*-orbital of one atom which arises when the energy of the other *s*-orbital changes. The sign of K is that of π_{XY} which depends on the relative energies of the various excited states, and is positive when β_{XY}, the *s*-overlap integral between X and Y, is large (and eqn. 4 is a good approximation). As β_{XY} becomes smaller, additional excitations, of which some make negative contributions, become important, and π_{XY} can become quite small as is observed for certain hexaorganotins [1]. For very small β_{XY} the mutual polarizability and hence ${}^1K_{XY}$ will be negative, and this will occur for selenium or tellurium bound to tin because the valence *s*-orbitals of these two elements are of much lower energy than the tin 5*s*-orbital.

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