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THE PMR SPECTRA OF FUNCTIONALLY-SUBSTITUTED ETHYLTIN COMPOUNDS

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INTRODUCTION

Investigations on the PMR spectra of ethyltin compounds[1,2] have shown that several factors affect the chemical shift data and the coupling constants *J*(Sn–C–H) and *J*(Sn–C–C–H). Substitution on either the α- or the β-carbon atom with respect to tin could shed light on some of the problems encountered in discussing the PMR spectra. Therefore a series of compounds carrying a substituent on the α- or the β-carbon atom were studied, comprising *n*-propyl-, *n*-butyl, and isopropyl-tin compounds and the respective halides, together with compounds of the type ZCH_2CH_2-SnR_3 and $(ZCH_2CH_2)_2SnR_2$ (Z = CN, C_6H_5, $COOCH_3$, $OCOCH_3$, OC_6H_5 and R = C_6H_5), and also some bromides and iodides.

EXPERIMENTAL

Synthesis of compounds

Tetraisopropyltin, tetra-n-propyltin and tetra-n-butyltin were prepared by a Grignard synthesis[3]. The corresponding dialkyltin dihalides and monoalkyltin trihalides were obtained by the usual redistribution reactions with tin tetrachloride or tin tetrabromide[4,5]. Triisopropyltin bromide and the triisopropyltin acetate hydrate were prepared according to the procedure described by Luijten and Van der Kerk[3]. Diisopropyltin diiodide was obtained by a modification of the synthesis described earlier by Cahours[6], as follows. A mixture of isopropyl iodide and excess tin powder is heated to 80° for 24 h with vigorous stirring. The reaction mass is then cooled and extracted with diethyl ether. Fractional distillation of the extract yields the diiodide (boiling point 265–268°).

For the synthesis of the functionally-substituted compounds, (ZCH_2CH_2)-SnR_3 and $(ZCH_2CH_2)_2SnR_2$, the reactions,

$$R_3SnH + CH_2{=}CHZ \rightarrow R_3SnCH_2CH_2Z$$
$$R_2SnH_2 + 2\,CH_2{=}CHZ \rightarrow R_2Sn(CH_2CH_2Z)_2\,.$$

proposed by Noltes and Van der Kerk[5,7], were used. The reaction of these compounds with molecular halogens resulted principally in displacement of one alkyl or aryl group.

$$R_3SnCH_2CH_2Z + Br_2 \rightarrow RBr + R_2BrSnCH_2CH_2Z$$

The organotin hydrides, $(C_6H_5)_3SnH$, $(n\text{-}C_3H_7)_3SnH$, $(n\text{-}C_4H_9)_3SnH$ and $(n\text{-}C_3H_7)_2$-

SnH_2, were prepared by the reduction of the appropriate organotin halides[7,8] with $LiAlH_4$.

NMR spectra

The spectra were recorded with a Varian V-4300 B spectrometer with a fixed frequency of 56.44 MHz. Details on the instrumentation and techniques used have been published previously[1]. The tin-satellite spectra were observed on the neat liquids; the chemical shift data were derived from spectra taken on 10 vol % solutions in CCl_4.

DESCRIPTION AND ANALYSIS OF SPECTRA

Spectra of n-propyltin compounds $(CH_3CH_2CH_2)_nSnY_{4-n}$

These molecules can be considered as belonging to the $A_3B_2C_2X$ type molecules, X being either ^{117}Sn or ^{119}Sn. The main signal therefore will result from the $A_3B_2C_2$ group. As the internal chemical shift, $\delta(AB)$, and the proton–proton coupling constant, J_{AB}, are nearly equal, the resulting multiplet structure is seriously distorted by second-order coupling. The resonance frequency of type C-protons is under direct influence of the inductive effect of the substituents, Y, on tin. The ratio $J(BC)/\delta(BC)$ decreases with increasing number of electronegative substituents, Y, and for $CH_3CH_2CH_2SnCl_3$ we observe a nearly pure triplet-structure.

The tin-satellite spectra, caused by coupling of B- and C-protons with ^{117}Sn and ^{119}Sn, with coupling constants, $J(BX)$ and $J(CX)$, yield weak but purely first-order spectra that can be observed on both sides of the main signal or only on one side, depending on the total frequency area covered by the former and the value of $J(BX)$ or $J(CX)$. In many cases, the satellites through coupling with ^{117}Sn and ^{119}Sn respectively, coincided.

Spectra of the n-butyltin compounds $(CH_3CH_2CH_2CH_2)_nSnY_{4-n}$

These spectra are of the $A_3B_2C_2D_2X$ type. The signals of the B- and C-protons are unresolved in most cases, yielding an ill-defined multiplet. The A-protons yield a seriously distorted triplet but the D-proton signal structure approaches that of a slightly distorted triplet with increasing number of substituents, Y, on tin. The tin satellite signals yield the same general pattern as observed in the n-propyltin compounds.

Spectra of the iso-propyltin compounds $[(CH_3)_2CH]_nSnY_{4-n}$

The isopropyl group yields spectra of the A_6B type. The ideal first-order multiplet structure for small values of $J(AB)/\delta(AB)$ is approached with increasing number of electronegative substituents as $\delta(AB)$ increases, and $J(AB)$ remains practically constant.

The $J(^{117/119}Sn-H_\beta)$ satellites could be observed on both sides of the main signal. The $J(^{117/119}Sn-H_\alpha)$ satellite signals however escaped observation due to the unfavourable intensity-relation and probably also because their value was too small to allow them to emerge from the main signal.

Spectra of β-functionally substituted ethyltin compounds

The β-functionally substituted ethyl group, CH_2CH_2Z, bonded on tin should yield a PMR spectrum belonging to the A_2B_2X pattern. As Z is in most instances an electronegative substituent, the value of $\delta(AB)$ is large and the spectrum consists of two nearly undisturbed triplets. In most spectra the corresponding tin-satellites with separations $J(Sn-H_\alpha)$ and $J(Sn-H_\beta)$ could be easily observed, although the former were sometimes hidden under the main signal.

All these PMR spectral parameters are collected in Tables 1 and 2. For ease of tabulation, the protons of the alkyl group bonded to tin are indexed with the greek letters, α, β, etc., along the alkyl chain, starting from the tin atom. The same method of designation is used for the substituted ethyl group protons.

TABLE 1

PMR SPECTRAL DATA OF n-PROPYL-, ISOPROPYL- AND n-BUTYLTIN-COMPOUNDS

Compound	τ_α	τ_β	τ_γ	$J(^{117/119}Sn-H_\alpha)$ (*cps*)	$J(^{117/119}Sn-H_\beta)$ (*cps*)
$[(CH_3)_2CH]_4Sn$	8.61	8.61			61
$[(CH_3)_2CH]_3SnBr$	8.25	8.55			81.5/84
$[(CH_3)_2CH]_3SnOOCCH_3 \cdot H_2O$	8.31	8.59			79/82.5
$[(CH_3)_2CH]_2SnI_2$	7.72	8.45			123/128
$[CH_3(CH_2)_2]_2SnCl_2$	8.09	8.09	8.77	47/48.4	115/119.5
$[CH_3(CH_2)_2]_2SnBr_2$	7.99	8.07	8.80		114.5/119.5
$[CH_3(CH_2)_2]_2SnCl_3$	7.55	7.97	8.68	81/85	217.5/227.5
$[CH_3(CH_2)_3]_2SnCl_2$	8.15	8.15			102/106
$[CH_3(CH_2)_3]SnCl_3$	7.70	8.14		85/88	200/210

DISCUSSION

Chemical shift data

Chemical shift data of isopropyl-, n-propyl- and n-butyltin compounds. The data collected in Table 1 show that both τ_α and τ_β decrease with increasing number of substituents other than alkyl on tin. Moreover, it is observed that τ_α for tri-isopropyltin bromide is smaller than for the acetate, and that τ_α for di-isopropyltin dibromide is smaller than for the dichloride. This is obviously an analogous situation to that of the ethyltin compounds[1,2] and the chemical shifts are apparently determined simultaneously by the inductive effect and the neighbour anisotropy effect.

For the n-butyltin compounds, both τ_α and τ_β are larger than in the corresponding n-propyltin compounds. This might be due to the increasing diamagnetism of the carbon chain with increasing chain length.

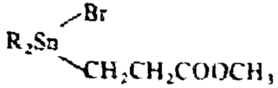
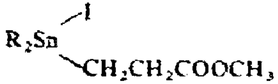
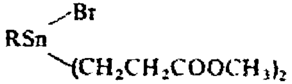
A comparison of the τ_α-values of the ethyltin compounds with those of the isopropyltin compounds and of their τ_β-values with those of the n-propyltin compounds, reveals that

$$\tau_{\alpha\ \text{ethyl}} > \tau_{\alpha\ \text{isopropyl}}$$
$$\tau_{\beta\ \text{ethyl}} > \tau_{\beta\ \text{n-propyl}}$$

The propyl compounds can be considered as derived from ethyl compounds wherein an α-hydrogen, or a β-hydrogen has been replaced by a methyl group. The methyl group obviously causes a downfield shift. In the chloro-and bromo-methyltin com-

TABLE 2

CHEMICAL SHIFT DATA OF β-FUNCTIONALLY SUBSTITUTED ETHYLTIN COMPOUNDS

	τ_α	τ_β			τ_{CH_3}	$J(^{117,119}Sn-H_\alpha)$	$J(^{117,119}Sn-H_\beta)$		
	$R=C_6H_5$	$R=C_6H_5$	$R=n\text{-}C_3H_7$	$R=n\text{-}C_4H_9$		$R=C_6H_5$	$R=C_6H_5$	$R=n\text{-}C_3H_7$	$R=n\text{-}C_4H_9$
$R_3SnCH_2CH_2Cn$	8.39	7.58	7.55	7.56		49.5/51.5	53.5/55.5	44.5/46.5	44/46
$R_3SnCH_2CH_2C_6H_5$	8.25	7.04	7.25			53.5/55.5	59/61	48/50	
$R_3SnCH_2CH_2COOCH_3$	8.45	7.39	7.58	7.58	$R=C_6H_5$ 6.64 $R=n\text{-}C_3H_7$ 6.44 $R=n\text{-}C_4H_9$ 6.45	56	75	56/58	56/58
$R_3SnCH_2CH_2OC_6H_5$	8.13	5.82				61.5/63.5	62/64		
$R_3SnCH_2CH_2OCOCH_3$	8.21	5.64			8.35	54/56	53/55		
$R_3SnCH_2CH_3$*	8.56	8.63				80/83	54.5/56.5		
$R_2Sn(CH_2CH_2COOCH_3)_2$			7.50		6.38			95	
$R_2Sn(CH_2CH_2CN)_2$			7.41					48	
 $R_2Sn(Br)(CH_2CH_2COOCH_3)$				7.28	6.28				83
 $R_2Sn(I)(CH_2CH_2COOCH_3)$	8.16	7.25			6.33				
 $RSn(Br)(CH_2CH_2COOCH_3)_2$			7.23		6.29			77	
$RSn(Br)_2(CH_2CH_2COOCH_3)$	8.06	7.12			6.20		136/142		
$Br_2Sn(CH_2CH_2COOCH_3)_2$	$\tau_\alpha=8.06$	$\tau_\beta=7.15$			$\tau_{CH_3}=6.25$		$J(^{117,119}Sn-H_\beta)=147.5/154$		

* Data taken from ref. 2.

pounds[9] we have observed that the neighbour anisotropy contribution of the halogen–carbon bond to the methylene resonance is negligible compared to the inductive effect of the halogen. We therefore assume that these shifts are mainly due to the negative inductive effect (deshielding) of the methyl group. The electronegativity of this group was estimated by several investigators: Ranft[10], 2.64 (from $J(^{13}C\text{–}H)$; Gordy[11], 2.33 and 2.32 (from force constants and quadrupole coupling constants, respectively).

Chemical shift data of β-functionally substituted ethyltin compounds. An examination of the data of Table 2 shows that in all molecules $\tau_\beta < \tau_\gamma$. Moreover, τ_β increases as a function of the nature of the substituent, Z, in the order $OCOCH_3 < OC_6H_5 < COOCH_3 < CN$ and the known group-electronegativities show a decreasing trend in the same order. The τ_β-values are therefore obviously determined by the inductive effect of the substituent, the neighbour anisotropy effect being negligible. Only in the $R_3SnCH_2CH_2C_6H_5$ compound might there also be a slight downfield shift due to the ring current effect. The increasing trend in τ_β-values for compounds $R_3SnCH_2CH_2Z$ with identical Z, but where R is successively, C_6H_5, n-C_3H_7, n-C_4H_9, is clearly due to the decreasing group electronegativity of R, although the ring current effect of the phenyl groups might also yield a small contribution.

A comparison of the chemical shift values of the methoxy-group protons in the compounds studied shows that the shielding is higher for $R = C_6H_5$ than for $R =$ n-C_3H_7 or n-C_4H_9. The inductive effect of R can be discarded as a possible explanation, because of the distance and because the opposite effect should have been observed. If it is assumed, however, that the $CH_2CH_2COOCH_3$ group is curled, so that the OCH_3 group comes into the neighbourhood of the phenyl groups, the ring current diamagnetism on the former would result in a shift to higher field as is observed. Indirect evidence for this spatial configuration is to be found in the fact that the replacement of C_6H_5 by Br or I shifts the methoxy-proton resonance to lower values. In this case only the neighbour anisotropy effect of the Sn–Br, or Sn–I bond could explain this shift.

The effect of halogen substitution on tin, on the other chemical shift values is analogous to that observed for the ethyltin compounds[1,2], *i.e.*, the inductive and neighbour anisotropy effects are both active.

Coupling constants

Coupling constants for the isopropyl-, n-propyl- and n-butyl compounds. The ethyl-, n-propyl- and n-butyl compounds listed in Table 1 can be considered as derivatives of the corresponding methyltin compounds in which one hydrogen atom has been replaced by a methyl, an ethyl or a propyl group, respectively. The changes in the electronic configuration around tin are very small in such cases, and, consequently, the $J(Sn\text{–}H_\alpha)$ values are close to those observed in the analogous methyltin compounds. In the discussion of the $J(Sn\text{–}H_\beta)$ values, the isopropyl-, n-propyl and n-butyltin compounds will be treated as derivatives of the corresponding ethyltin compounds where an α- or a β-hydrogen atom is replaced by a CH_3 or a C_2H_5 group. The data of Table 1 indicate that the $J(Sn\text{–}H_\beta)$ values in isopropyltin compounds are as a rule smaller than those in the corresponding ethyltin compounds[1,2]. The chemical shift data already point to a decreased electron density around the remaining hydrogen nuclei after such a substitution. Furthermore, the data of Table 1 show that $J(\mathrm{Sn{-}H}_\beta)$ decreases in the sequence, ethyl > n-propyl > n-butyl. These experimental data suggest that alkyl-substitution on either α- or β-positions in the carbon chain bonded to tin results in a decreased electron density on the β-positions and that this could be the origin of the decrease of the $J(\mathrm{Sn{-}H}_\beta)$ coupling constants. This would mean that an empirical relation for the $\mathrm{Sn{-}H}_\beta$ coupling constants, such as that derived for $\mathrm{Sn{-}H}_\alpha$ coupling constants in ethyltin compounds[2], should hold a term for the electron density around the coupling proton ($\Phi^2_{\mathrm{H}}(0)$). In other words, this means that in this case also, Fermi-contact interaction is the predominant coupling mechanism. The important difference in the $J(\mathrm{Sn{-}H}_\beta)$ values for n-propyl- and n-butyltin compounds, which have nearly identical electronic structures around the coupling nuclei, can be ascribed to different contributions of the electron orbital term to the coupling constant. This term is indeed strongly dependent on the spatial configuration of the molecule and hence on the position of the β-protons with respect to the Sn–X bond[2].

Coupling constants for β-functionally substituted ethyltin compounds. The $J(\mathrm{Sn{-}H}_\beta)$ values (listed in Table 2) for triphenyltin compounds are in all cases higher than those for trialkyltin compounds. As the group electronegativity of phenyl is larger than that of a straight chain alkyl group, this observation suggests that the factor, $\Phi^2_{\mathrm{Sn}}(0)$, is more important in the former compounds. This factor also increases on substitution of an R group by Br, and again there result higher coupling constants. Moreover, these couplings are seen to be smaller in $ZCH_2CH_2Sn(C_6H_5)_3$ than in $CH_3CH_2Sn(C_6H_5)_3$. As all the substituents, Z, under investigation have been shown to withdraw electrons from around the β-protons, these data confirm the importance of a term $\Phi^2_{\mathrm{H}}(0)$, as explained above.

Let us now compare the $J(\mathrm{Sn{-}H}_\beta)$ values for $(CH_3OOCCH_2CH_2)_2SnBr_2$ with those for $(CH_3CH_2)_2SnBr_2$. In both instances, the term $\Phi^2_{\mathrm{Sn}}(0)$ can be assumed to be equal, but $\Phi^2_{\mathrm{H}}(0)$ will be smaller in the former compound. Nevertheless, the coupling in β-substituted products is higher than in the ethyltin compound, suggesting that Fermi contact interaction is not the only mechanism contributing to the coupling. A contribution of the electron orbital term, due to a higher anisotropy in the screening tensor for the β-protons in the dicarbomethoxyethyl compounds, could explain this difference.

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SUMMARY

A series consisting of isopropyl-, n-propyl, n-butyl and β-functionally substituted ethyltin compounds, has been investigated by PMR spectroscopy. The relative importance of the inductive effect, the neighbour anisotropy effect and the ring current effect in the chemical shift data, in compounds containing the phenyl group, is discussed.

Arguments are put forward to show that the trends in the coupling constants

data are largely dependent on the Fermi contact interaction mechanism but that the electron orbital term also yields a relatively important contribution.

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