Electronegativity-induced Quadrupole Splittings in the Mössbauer Spectra of Some Tin(IV) Compounds

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SINCE the environment of the tin atom in compounds of the type R_3SnX has less than cubic symmetry, the Mössbauer spectra of such compounds would be exected to show a quadrupole splitting. However, in several instances [*e.g.* $X = H$,[1,2] SnR_3,[3] $Ge(SnR_3)_3$,[3] $CH:CH_2$[4]] no discernible splitting has been found, and it has been suggested that the spectrum will be split only if the group X is capable of π-bonding to the tin atom.[3] We doubt this suggestion, and now present data which show that quadrupole splitting can be induced by σ-bonding (electronegativity) effects alone. Some similar data have been reported recently, but not interpreted in this way.[5]

In Table 1 are presented Mössbauer parameters for compounds of the type R_3SnX (R = Me, Ph), which fall into three groups: (a) X = Me, Ph, $CH:CH_2$, $SnMe_3$; Δ = 0 mm. sec.$^{-1}$; (b) X = CF_3, C_6F_5, C_6Cl_5, $C{\vdots}CPh$; Δ = 1·0–1·4 mm. sec.$^{-1}$; (c) X = F, Cl, Br, I; Δ = 2·2—3·9 mm. sec.$^{-1}$ The small quadrupole splittings of the second group of compounds are quite well resolved with the ^{119}Sn–Pd source. Several lines of evidence suggest that the effective electronegativities of CF_3, C_6F_5, and $C{\vdots}CPh$ are comparable to those of Cl and Br, and appreciably greater than those of Me, Ph, and SnR_3. Such evidence may be adduced from the isomer shifts of SnX_4,[6] from the Me–Sn

TABLE 1. *Mössbauer parameters for* R_3SnX[a]

Compound	δ	Δ	Γ_1	Γ_2	Ref.
Me_4Sn	1·29	0·00	0·81		b
$Me_3SnSnMe_3$	1·46	0·00	0·96		b
Me_3SnPh	1·16	0·00			2
$Me_3SnCH:CH_2$	1·30	0·00			4
Me_3SnCF_3	1·31	1·38	0·92	0·98	b
$Me_3SnC_6F_5$	1·27	1·31	0·76	0·97	b
$Me_3SnC_6Cl_5$	1·32	1·09	0·70	1·00	b
$Me_3SnC\vdots CPh$	1·23	1·17	0·76	0·92	b
Me_3SnF	1·28	3·86			2
Me_3SnCl	1·42	3·41			2
Me_3SnBr	1·49	3·25			2
Me_3SnI	1·48	3·05			2
Ph_4Sn	1·27	0·00	0·93		b
$Ph_3SnCH:CH_2$	1·28	0·00	0·98		b
$Ph_3SnC_6F_5$	1·30	0·90	1·00	1·30	b
	1·25	0·98			5
$Ph_3SnC_6Cl_5$	1·27	0·84	0·82	0·82	b
Ph_3SnF	1·25	3·53	0·84	0·90	b
Ph_3SnCl	1·31	2·56	0·88	0·97	b
Ph_3SnBr	1·37	2·48	0·84	0·98	b
Ph_3SnI	1·20	2·25	1·28	1·24	b
$PhSn(CH:CH_2)_3$	1·25	0·00	0·88		b

[a] All data are in mm. sec.$^{-1}$, and refer to *ca.* 80°K.
δ = isomer shift relative to SnO_2 at room temperature, and
Δ = quadrupole splitting, both believed accurate to better than $\pm 0{\cdot}05$ mm. sec.$^{-1}$; Γ_1 and Γ_2 are widths at half-height of the absorptions at higher and lower velocity respectively, accurate to $\pm 0{\cdot}10$ mm. sec.$^{-1}$.
[b] This work.

coupling constants in the n.m.r. spectra of Me_3SnX (ref. 7 and this work), and from Taft σ^* constants[8] (Table 2). Also, the electronegativity of CF_3 (3·29) is significantly greater than those for Me (2·30) and H (2·20).[9] Stöckler and Sano suggest that the quadrupole splittings observed in the spectra of the perfluorophenyl compounds could be due to π-donation from the ring to the tin atom.[5] However, n.m.r. data show that $SnMe_3$ does not withdraw π-density from the C_6F_5 ring,[10] which is supported by our observation that the effects, on the Mössbauer spectra, of C_6F_5 and CF_3 are very similar (CF_3 would not be expected to show an electromeric effect). We therefore attribute the quadrupole splittings of the second set of compounds to electronegativity effects. The smaller splitting observed for $X = C_6Cl_5$ than for $X = C_6F_5$ is consistent with this interpretation.

The quadrupole splittings for the halides are considerably greater than those for $X = CF_3$, *etc.* Since the electronegativities are not greatly different, additional factors must be involved. This effect cannot be due to π-bonding, since π-donation and σ-withdrawal would work in opposition,[2] and the quadrupole splitting would be reduced (unless the π-effect grossly outweighed the σ-effect, which is most unlikely). The most plausible explanation of the enhanced Δ-values is that the halides all have five-co-ordinate, polymeric structures similar to that of Me_3SnF.[11] Such a structure would give rise to a quadrupole splitting even if all five ligands were

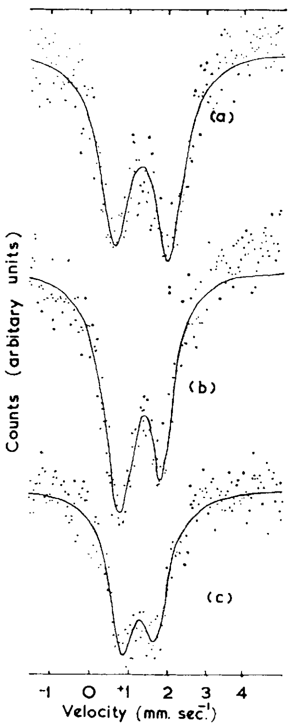

FIGURE. *Mössbauer spectra of* R_3SnX *compounds.* (a) Me_3SnCF_3, (b) $Me_3SnC_6Cl_5$, (c) $Ph_3SnC_6Cl_5$. *The solid line represents the computed spectrum.*

TABLE 2. *Electronegativity data*

X	Cl	Br	I	CF_3	C_6F_5	CC⋮Ph	Me
δ in SnX_4 (mm. sec.$^{-1}$)	0·9	1·2	1·8	—	1·0	—	1·2
$J_{^{119}Sn-Me}$ (c. sec.$^{-1}$)	58·1	57·8	57·2	60·9	59·4	60·3	54·0
Taft σ^*	1·05	1·00	0·85	0·92	—	0·48	0·00

identical. It is of interest that, apart from the fluorides, the Δ-values for Ph_3SnX are proportional to those for the corresponding Me_3SnX.

We gratefully acknowledge the award (to R.H.P.) of an S.R.C. Studentship.

(*Received, June 28th,* 1968; *Com.* 857.)

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