^{119}Sn Mössbauer Quadrupole Splittings in Polyhalogenoaryltin Compounds

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PARISH and PLATT[1] have shown that quadrupole splitting in the Mössbauer spectra of tetraco-ordinate Sn^{IV} compounds can arise from differences in ligand electronegativity only, contrary to earlier suggestions.[2] We present Mössbauer and n.m.r. results which give additional insight into the features of electronegativity-induced quadrupole splittings.

The compounds reported here fall into three groups (Table): Me_3SnX [compounds(I)—(VII)], $(Me_3Sn)_2X$ [(VIII)—(X)], and Me_2SnX_2 [(XI) and (XII)], where X is an aryl group with halogen substituents. With the exception of (II), all compounds show a resolvable quadrupole splitting Δ. Compound (II) exhibits a single line, some 30—40% broader than the lines for the other compounds, suggesting unresolved splitting in this case. This is substantiated by the fact that the observed spectrum was not accurately Lorentzian in shape. Both tetra- and penta-fluorophenyl derivatives (III) and (IV) show well-defined splittings, that for (IV) being greater. These results are as one would expect if the splittings are caused by differences in electronegativity between Me and X. The o-($C_6H_4{\cdot}CF_3$) compound (VI) is interesting in that the ring itself is not halogenated. It appears that a strong electron-withdrawing group in the *ortho*-position is also sufficient to bring about splitting. The possibility of an intramolecular interaction between the CF_3 group and the tin atom cannot be rigorously excluded, but is very unlikely, since it would require the presence of pentacoordinate tin, which would produce a much greater splitting than is observed.[1]

Mössbauer parameters and ^{119}Sn–Me *coupling constants*[a]

Compound	δ[b]	Δ	Γ_1	Γ_2	J(^{119}Sn–Me)[c] (Hz)	Ref.[d]
	(mm.sec.$^{-1}$)					
(I) Me_3SnPh	1·16	0			54·6	5
(II) $Me_3Sn{\cdot}C_6H_4{\cdot}F$-$p$	1·23	0	1·27		54·5	
(III) $Me_3Sn{\cdot}C_6F_4{\cdot}H$-$p$	1·24	1·08	0·87	0·89	58·0	
(IV) $Me_3Sn{\cdot}C_6F_5$	1·27	1·31	0·97	0·76	58·8	1
(V) $Me_3Sn{\cdot}C_6Cl_5$	1·32	1·09	1·00	0·70	56·8	1
(VI) $Me_3Sn{\cdot}C_6H_4{\cdot}CF_3$-$o$	1·21	0·66	0·80	0·81	55·6	
(VII) $Me_3Sn{\cdot}CF_3$	1·31	1·38	0·98	0·92	60·9	1
(VIII) 1,2-$(Me_3Sn)_2{\cdot}C_6F_4$	1·26	0·85	0·90	0·82	54·9	
(IX) 1,4-$(Me_3Sn)_2{\cdot}C_6F_4$	1·20	1·20	0·77	0·74	58·2	
(X) 1,4-$(Me_3Sn)_2{\cdot}C_6Cl_4$	1·26	1·10	0·93	0·88	57·0	
(XI) $Me_2Sn{\cdot}(C_6F_5)_2$	1·23	1·56	0·94	0·92	65·6	
	1·25	1·48				3
(XII) $Me_2Sn{\cdot}(C_6F_4Br$-$o)_2$	1·25	1·41	0·80	0·87	63·4	

[a] For this work, isomer shift δ and quadrupole splitting Δ are $\pm$ 0·03 mm.sec.$^{-1}$, and full half maximum line-width Γ is $\pm$ 0·05 mm. sec.$^{-1}$. Subscript 2 refers to the higher velocity absorption. All Mössbauer data refer to 80°K.

[b] Relative to SnO_2 at 80°K.

[c] $\pm$0·2 Hz.

[d] This work unless otherwise noted.

The splitting found for 1,4-$(Me_3Sn)_2{\cdot}C_6F_4$ and 1,4-$(Me_3Sn)_2{\cdot}C_6Cl_4$ are again consistent with an interpretation based on electronegativity differences. More interesting perhaps is the rather large difference between the 1,2- and 1,4-substituted $(Me_3Sn)_2{\cdot}C_6F_4$ compounds [(VIII) and (IX)]. This suggests a marked dependence of quadrupole splitting upon substitution at various positions of the aryl group attached to the tin atom. These results also make it appear unlikely that there is any significant steric interaction between the Me_3Sn groups in (VIII), since this would lead to a substantially increased splitting.

The Me_2SnX_2 derivatives [(XI) and (XII)] exhibit the largest quadrupole splittings of the compounds studied. The lower value for (XII) compared to (XI) illustrates the importance of the *ortho*-substituent and is again consistent with electronegativity considerations. Furthermore it suggests the absence of intramolecular tin–bromine interaction in (XII).

We have noted in the two polyhalogenoaryl series, Me_3SnX and $(Me_3Sn)_2X$, an approximate linear relation between quadrupole splittings and n.m.r. Me–^{119}Sn coupling constants (Table). A correlation between coupling constants and isomer shifts δ in the series $Me_{4-n}SnH_n$ has been discussed[4] in terms of variations in s-electron density at the tin nucleus. No such correlation is apparent in the present case, δ being essentially constant. We feel the observed correlation is not fortuitous, and offer the following explanation.

The differential isomer shift is a function of only $|\psi_{Sn}(0)|^2$, whereas the Me–Sn coupling constant depends upon the product $|\psi_{Sn}(0)|^2 \times |\psi_{Me}(0)|^2$. Since δ is approximately constant here, J(^{119}Sn–Me) will be roughly proportional to $|\psi_{Me}(0)|^2$. Now electronegativity differences will cause rehybridisation of the tin sp^3 bonding orbitals, which apparently leaves $|\psi_{Sn}(0)|^2$ essentially unchanged, but alters the *disgribution* of s-electron density about Sn. That is, the fractional s-character of each of the (equivalent) Sn–Me bonds will differ from the value 0·25 required for Me_4Sn, although the total s-electron density about Sn is not significantly altered (δ 1·29 for Me_4Sn[1]). This would cause a change in $|\psi_{Me}(0)|^2$, hence J(^{119}Sn–Me), and at the same time would establish the field gradient responsible for the quadrupole splitting. The linear relation between Δ and $J(^{119}\mathrm{Sn{-}Me})$ is not unreasonable on this basis. A much more stringent test of this interpretation would be a comparison of Δ with $J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C})$ coupling constants, which are more directly affected by changes in Sn–C bond character. Unfortunately these coupling constants are not at present available.

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[1] R. V. Parish and R. H. Platt, *Chem. Comm.*, 1968, 1118.
[2] T. C. Gibb and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1966, 43.
[3] H. A. Stöckler and H. Sano, *Trans. Faraday Soc.*, 1968, **64**, 577.
[4] L. May and J. J. Spijkerman, *J. Chem. Phys.*, 1967, **46**, 3272.
[5] M. Cordey-Hayes, R. D. Peacock, and M. Vucelic, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1177.