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Tricyclohexyltin Compounds: Structural Implications of ^{119}Sn NMR Chemical Shifts

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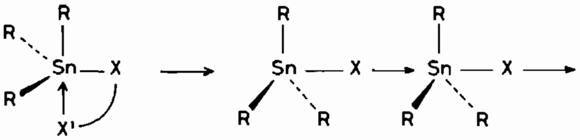
Tricyclohexyltin compounds, Cy_3SnX, are known [1] to possess good acaricidal activity, and the hydroxide and 1-N-1,2,4-triazole are both in commercial use. It has recently been found, however, that, in cases where the anionic radical, X, results in the formation of a 5-coordinate intramolecularly chelated monomer (**A**) a significant reduction in biological activity may occur [2]. Therefore, as part of an investigation into structure/activity relationships for triorganotin biocides, a series of tricyclohexyltin compounds has been investigated, in the solid state, by Mössbauer spectroscopy, and in solution, by ^{119}Sn NMR spectroscopy, since, to date, there is a paucity of reliable structural information regarding this class of organotins, and an almost total absence of ^{119}Sn NMR data.



(**A**) (**B**)

Table I shows the Mössbauer isomer shift, δ, and quadrupole splitting, ΔE_Q, parameters for the compounds studied.

1-Cy_3Sn(1,2,4-triazole) has been shown crystallographically [6] to have a polymeric intermolecularly associated structure (**B**), and this geometry is reflected [7] in the value of ΔE_Q (Table I). $\{NBu_4\}^+\cdot\{Cy_3SnCl_2\}^-$, however, although probably being monomeric, has a 5-coordinate tin atom geometry, with a planar Cy_3Sn moiety and consequently shows a similar value for ΔE_Q. In contrast, Cy_3Sn(2-mercaptobenzothiazole) has recently been shown crystallographically to exist as a slightly distorted tetrahedral monomer [8] and, in consequence [7], a smaller ΔE_Q (2.22 mm s^{-1} [8]) is observed. The ΔE_Q value obtained for $(Cy_3Sn)_2O$ suggests a similar tin atom configuration.

Although the tricyclohexyltin derivatives Cy_3SnX (X = Cl, Br, I and O_2CMe) have been reported [9–11] to exist as discrete tetrahedral monomers in the solid state, the magnitudes of ΔE_Q imply [7] that these compounds are better considered as weakly-bridged 5-coordinate polymers (**B**), as has been proposed previously for these compounds by Maddock and Platt [3] and for the two carboxylates, $Cy_3Sn(O_2CCX_3)$ (X = H, F) by Harrison *et al.* [12]. The magnitudes of ΔE_Q for Cy_3SnOH and Cy_3SnO_2CPh also imply structure (**B**) in the solid state.

TABLE I. ^{119m}Sn Mössbauer Data.

Compound	δ [a,b] (mm s^{-1})	ΔE_Q [a] (mm s^{-1})
1-Cy_3Sn(1,2,4-triazole)	1.52	3.32
Cy_3SnCl	1.70 (1.64) [c]	3.66 (3.49) [c]
Cy_3SnBr	1.65 (1.63) [c]	2.97 (2.90) [c]
Cy_3SnI	1.65 (1.64) [c]	2.88 (2.77) [c]
Cy_3SnOH	1.43 [d] (1.40) [c] (1.46) [e]	3.07 [d] (2.99) [c] (2.98) [e]
Cy_3SnO_2CMe	1.61 (1.57) [c]	3.46 (3.27) [c]
Cy_3SnO_2CPh	1.52	2.87
$\{NBu_4\}^+\{Cy_3SnCl_2\}^-$	1.60	3.47
Cy_3Sn(trop)	1.39	2.67
Cy_3Sn(of)	1.36 [f]	2.81 [f]
$(Cy_3Sn)_2O$	1.34	1.55

[a] Error = ±0.05 mm s^{-1}. [b] Relative to $Ba^{119m}SnO_3$. [c] Ref. [3]. [d] Recorded as a mixture of Cy_3SnOH and $(Cy_3Sn)_2O$. [e] Ref. [4]. [f] Ref. [5].

Unfortunately, it is difficult to distinguish between a tetrahedral R_3SnX geometry and a 5-coordinate *cis*-R_3SnX_2 configuration on the basis of ΔE_Q values [7]. However, the tricyclohexyltin derivative of tropolone Cy_3Sn(trop) has been reported [13] to have a 5-coordinate tin atom, with a bidentate tropolone chelate. Therefore, it is proposed that, in the solid state, this compound possesses a *cis*-R_3SnX_2 configuration, since the alternative *mer*-structure would be expected to have a larger ΔE_Q value [7].

^{119}Sn NMR chemical shifts, $\delta(^{119}Sn)$, (Table II) are indicative of coordination number, an increase of which is accompanied by a shift to low frequency [14]. Since $(Cy_3Sn)_2O$ has been shown to be four coordinate in the solid state, in the absence of solvent coordination this structure is expected to be maintained, and in toluene solution $\delta(^{119}Sn) = -7.9$ ppm. Therefore, the values obtained for the compounds Cy_3SnX (X = Cl, Br, I, OH, O_2CMe and O_2CPh) indicate that, in solution, they are no longer weakly associated polymers, but discrete monomeric units. In contrast, Cy_3Sn(trop) has a $\delta(^{119}Sn)$ value of

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TABLE II. ^{119}Sn NMR Chemical Shifts.

Compound	Solvent	Concentration	δ (^{119}Sn)^{a} (ppm)
$(Cy_3Sn)_2O$	Toluene	10% w/v	−7.9
Cy_3SnOH	Toluene	10% w/v	1.5^{b}
Cy_3SnCl	Toluene	10% w/v	65.1
Cy_3SnBr	Toluene	10% w/v	69.1
Cy_3SnI	Toluene	10% w/v	56.7
Cy_3SnO_2CMe	Toluene	10% w/v	−1.3
Cy_3SnO_2CPh	Pet ether	10% w/v	1.8
1-Cy_3Sn(1,2,4-triazole)	Toluene	~2% w/v (satd.)	−23.5
Cy_3Sn(trop)	Toluene	10% w/v	−62.8
Cy_3Sn(of)	Toluene	0.06 M	−27.4^{c}
$\{NBu_4\}^+\{Cy_3SnCl_2\}^-$	Toluene	20% w/v	−85.6
	Toluene	10% w/v	−78.1
	Toluene	5% w/v	−68.5

$^{a}\delta$(^{119}Sn) values are relative to Me_4Sn and are accurate to ±0.2 ppm. ^{b}Recorded as a mixture of Cy_3SnOH and $(Cy_3Sn)_2O$. ^{c}Ref. [5].

−62.8 ppm, approximately 55 ppm to low frequency of $(Cy_3Sn)_2O$ and suggests that the pentacoordinate structure of the former species is retained in solution. The tricyclohexyltin derivative of 3-hydroxyflavone, Cy_3Sn(of), has been reported [5], on the basis of a reduced carbonyl stretching frequency, to also have a *cis*-R_3SnX_2 structure. The δ(^{119}Sn) value of −27.4 ppm [5] suggests, however, that intramolecular chelation by the ligand is relatively weak.

The ^{119}Sn NMR chemical shift of $\{NBu_4\}^+\cdot\{Cy_3SnCl_2\}^-$ was found to be strongly concentration dependent (Table II). At infinite dilution, the expected chemical shift would be approximately 65 ppm, corresponding to free Cy_3SnCl, while extrapolation of the measured shifts to a limiting value, indicates δ(^{119}Sn) for the 5-coordinate $\{Cy_3SnCl_2\}^-$ ion to be approximately between −90 and −100 ppm.

The δ(^{119}Sn) value of −23.5 ppm recorded for 1-Cy_3Sn(1,2,4-triazole) suggests that a certain degree of intermolecular association is retained in solution. However, more information needs to be acquired for Sn–N bonded species before this can be confirmed, since a concentration study was precluded by the low solubility of this compound in toluene.

It is of interest to note that a ^{119}Sn NMR spectrum of a technical sample of Cy_3SnOH in toluene showed two resonances, corresponding to the presence of both Cy_3SnOH and $(Cy_3Sn)_2O$. Subsequent investigation revealed that it was extremely difficult to obtain pure samples of either of these compounds. For example, treating Cy_3SnCl with an equimolar amount of NaOH, resulted in mixture of Cy_3SnOH and $(Cy_3Sn)_2O$. Clearly, further structural studies are required so that a better understanding of the significance of tin Mössbauer and NMR data of tricyclohexyltin compounds may be obtained. However, these preliminary studies will assist in the elucidation of structure/activity relationships to be reported at a later date.

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