

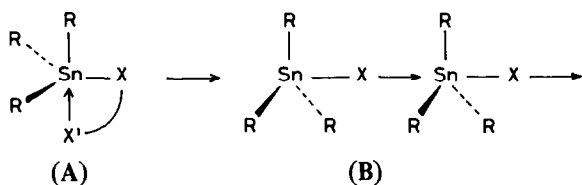
### Tricyclohexyltin Compounds: Structural Implications of $^{119}\text{Sn}$ NMR Chemical Shifts

STEPHEN J. BLUNDEN and ROBIN HILL

International Tin Research Institute, Fraser Road, Greenford, UB6 7AQ, U.K.

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Tricyclohexyltin compounds,  $\text{Cy}_3\text{SnX}$ , 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  $^{119}\text{Sn}$  NMR spectroscopy, since, to date, there is a paucity of reliable structural information regarding this class of organotins, and an almost total absence of  $^{119}\text{Sn}$  NMR data.

Table I shows the Mössbauer isomer shift,  $\delta$ , and quadrupole splitting,  $\Delta E_Q$ , parameters for the compounds studied.

1- $\text{Cy}_3\text{Sn}(1,2,4\text{-triazole})$  has been shown crystallographically [6] to have a polymeric intermolecularly associated structure (B), and this geometry is reflected [7] in the value of  $\Delta E_Q$  (Table I).  $\{\text{NBu}_4\}^+\{\text{Cy}_3\text{SnCl}_2\}^-$ , however, although probably being monomeric, has a 5-coordinate tin atom geometry, with a planar  $\text{Cy}_3\text{Sn}$  moiety and consequently shows a similar value for  $\Delta E_Q$ . In contrast,  $\text{Cy}_3\text{Sn}(2\text{-mercaptobenzothiazole})$  has recently been shown crystallographically to exist as a slightly distorted tetrahedral monomer [8] and, in consequence [7], a smaller  $\Delta E_Q$  ( $2.22 \text{ mm s}^{-1}$  [8]) is observed. The  $\Delta E_Q$  value obtained for  $(\text{Cy}_3\text{Sn})_2\text{O}$  suggests a similar tin atom configuration.

Although the tricyclohexyltin derivatives  $\text{Cy}_3\text{SnX}$  ( $X = \text{Cl}, \text{Br}, \text{I}$  and  $\text{O}_2\text{CMe}$ ) have been reported [9-11] to exist as discrete tetrahedral monomers in the solid state, the magnitudes of  $\Delta E_Q$  imply [7] that these compounds are better considered as weakly-

TABLE I.  $^{119}\text{mSn}$  Mössbauer Data.

Compound	$\delta^{a,b}$ ( $\text{mm s}^{-1}$ )	$\Delta E_Q^a$ ( $\text{mm s}^{-1}$ )
1- $\text{Cy}_3\text{Sn}(1,2,4\text{-triazole})$	1.52	3.32
$\text{Cy}_3\text{SnCl}$	1.70 (1.64) <sup>c</sup>	3.66 (3.49) <sup>c</sup>
$\text{Cy}_3\text{SnBr}$	1.65 (1.63) <sup>c</sup>	2.97 (2.90) <sup>c</sup>
$\text{Cy}_3\text{SnI}$	1.65 (1.64) <sup>c</sup>	2.88 (2.77) <sup>c</sup>
$\text{Cy}_3\text{SnOH}$	1.43 <sup>d</sup> (1.40) <sup>c</sup> (1.46) <sup>e</sup>	3.07 <sup>d</sup> (2.99) <sup>c</sup> (2.98) <sup>e</sup>
$\text{Cy}_3\text{SnO}_2\text{CMe}$	1.61 (1.57) <sup>c</sup>	3.46 (3.27) <sup>c</sup>
$\text{Cy}_3\text{SnO}_2\text{CPh}$	1.52	2.87
$\{\text{NBu}_4\}^+\{\text{Cy}_3\text{SnCl}_2\}^-$	1.60	3.47
$\text{Cy}_3\text{Sn}(\text{trop})$	1.39	2.67
$\text{Cy}_3\text{Sn}(\text{of})$	1.36 <sup>f</sup>	2.81 <sup>f</sup>
$(\text{Cy}_3\text{Sn})_2\text{O}$	1.34	1.55

<sup>a</sup>Error =  $\pm 0.05 \text{ mm s}^{-1}$ . <sup>b</sup>Relative to  $\text{Ba}^{119\text{m}}\text{SnO}_3$ . <sup>c</sup>Ref. [3]. <sup>d</sup>Recorded as a mixture of  $\text{Cy}_3\text{SnOH}$  and  $(\text{Cy}_3\text{Sn})_2\text{O}$ . <sup>e</sup>Ref. [4]. <sup>f</sup>Ref. [5].

bridged 5-coordinate polymers (B), as has been proposed previously for these compounds by Maddock and Platt [3] and for the two carboxylates,  $\text{Cy}_3\text{Sn}(\text{O}_2\text{CCX}_3)$  ( $X = \text{H}, \text{F}$ ) by Harrison *et al.* [12]. The magnitudes of  $\Delta E_Q$  for  $\text{Cy}_3\text{SnOH}$  and  $\text{Cy}_3\text{SnO}_2\text{-CPh}$  also imply structure (B) in the solid state.

Unfortunately, it is difficult to distinguish between a tetrahedral  $\text{R}_3\text{SnX}$  geometry and a 5-coordinate *cis*- $\text{R}_3\text{SnX}_2$  configuration on the basis of  $\Delta E_Q$  values [7]. However, the tricyclohexyltin derivative of tropolone  $\text{Cy}_3\text{Sn}(\text{trop})$  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*- $\text{R}_3\text{SnX}_2$  configuration, since the alternative *mer*-structure would be expected to have a larger  $\Delta E_Q$  value [7].

$^{119}\text{Sn}$  NMR chemical shifts,  $\delta(^{119}\text{Sn})$ , (Table II) are indicative of coordination number, an increase of which is accompanied by a shift to low frequency [14]. Since  $(\text{Cy}_3\text{Sn})_2\text{O}$  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  $\delta(^{119}\text{Sn}) = -7.9$  ppm. Therefore, the values obtained for the compounds  $\text{Cy}_3\text{SnX}$  ( $X = \text{Cl}, \text{Br}, \text{I}, \text{OH}, \text{O}_2\text{CMe}$  and  $\text{O}_2\text{CPh}$ ) indicate that, in solution, they are no longer weakly associated polymers, but discrete monomeric units. In contrast,  $\text{Cy}_3\text{Sn}(\text{trop})$  has a  $\delta(^{119}\text{Sn})$  value of

TABLE II.  $^{119}\text{Sn}$  NMR Chemical Shifts.

Compound	Solvent	Concentration	$\delta$ ( $^{119}\text{Sn}$ ) <sup>a</sup> (ppm)
( $\text{C}_3\text{H}_5\text{Sn}$ ) <sub>2</sub> O	Toluene	10% w/v	-7.9
$\text{C}_3\text{H}_5\text{SnOH}$	Toluene	10% w/v	1.5 <sup>b</sup>
$\text{C}_3\text{H}_5\text{SnCl}$	Toluene	10% w/v	65.1
$\text{C}_3\text{H}_5\text{SnBr}$	Toluene	10% w/v	69.1
$\text{C}_3\text{H}_5\text{SnI}$	Toluene	10% w/v	56.7
$\text{C}_3\text{H}_5\text{SnO}_2\text{CMe}$	Toluene	10% w/v	-1.3
$\text{C}_3\text{H}_5\text{SnO}_2\text{CPh}$	Pet ether	10% w/v	1.8
1- $\text{C}_3\text{H}_5\text{Sn}(1,2,4\text{-triazole})$	Toluene	~2% w/v (satd.)	-23.5
$\text{C}_3\text{H}_5\text{Sn}(\text{trop})$	Toluene	10% w/v	-62.8
$\text{C}_3\text{H}_5\text{Sn}(\text{of})$	Toluene	0.06 M	-27.4 <sup>c</sup>
$\{\text{NBu}_4\}^+\{\text{C}_3\text{H}_5\text{SnCl}_2\}^-$	Toluene	20% w/v	-85.6
	Toluene	10% w/v	-78.1
	Toluene	5% w/v	-68.5

<sup>a</sup> $\delta$  ( $^{119}\text{Sn}$ ) values are relative to  $\text{Me}_4\text{Sn}$  and are accurate to  $\pm 0.2$  ppm.

<sup>b</sup>Recorded as a mixture of  $\text{C}_3\text{H}_5\text{SnOH}$  and  $(\text{C}_3\text{H}_5\text{Sn})_2\text{O}$ .

<sup>c</sup>Ref. [5].

-62.8 ppm, approximately 55 ppm to low frequency of  $(\text{C}_3\text{H}_5\text{Sn})_2\text{O}$  and suggests that the pentacoordinate structure of the former species is retained in solution. The tricyclohexyltin derivative of 3-hydroxyflavone,  $\text{C}_3\text{H}_5\text{Sn}(\text{of})$ , has been reported [5], on the basis of a reduced carbonyl stretching frequency, to also have a *cis*- $\text{R}_3\text{SnX}_2$  structure. The  $\delta$  ( $^{119}\text{Sn}$ ) value of -27.4 ppm [5] suggests, however, that intramolecular chelation by the ligand is relatively weak.

The  $^{119}\text{Sn}$  NMR chemical shift of  $\{\text{NBu}_4\}^+\{\text{C}_3\text{H}_5\text{SnCl}_2\}^-$  was found to be strongly concentration dependent (Table II). At infinite dilution, the expected chemical shift would be approximately 65 ppm, corresponding to free  $\text{C}_3\text{H}_5\text{SnCl}$ , while extrapolation of the measured shifts to a limiting value, indicates  $\delta$  ( $^{119}\text{Sn}$ ) for the 5-coordinate  $\{\text{C}_3\text{H}_5\text{SnCl}_2\}^-$  ion to be approximately between -90 and -100 ppm.

The  $\delta$  ( $^{119}\text{Sn}$ ) value of -23.5 ppm recorded for 1- $\text{C}_3\text{H}_5\text{Sn}(1,2,4\text{-triazole})$  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  $^{119}\text{Sn}$  NMR spectrum of a technical sample of  $\text{C}_3\text{H}_5\text{SnOH}$  in toluene showed two resonances, corresponding to the presence of both  $\text{C}_3\text{H}_5\text{SnOH}$  and  $(\text{C}_3\text{H}_5\text{Sn})_2\text{O}$ . Subsequent investigation revealed that it was extremely difficult to obtain pure samples of either of these compounds. For example, treating  $\text{C}_3\text{H}_5\text{SnCl}$  with an equimolar amount of NaOH, resulted in mixture of  $\text{C}_3\text{H}_5\text{SnOH}$  and  $(\text{C}_3\text{H}_5\text{Sn})_2\text{O}$ . 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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