

## SHORT COMMUNICATION

### Far infrared and $^{35}\text{Cl}$ NQR spectra of triphenyltin chloride\*

Recently molecular weight determination has shown triphenyltin chloride to be a monomer in solution<sup>1</sup>. The observed vibrational modes in the far infrared spectrum of solid triphenyltin chloride are presented in Table 1 and interpreted in terms of  $C_{3v}$  symmetry for the  $\text{C}_3\text{SnCl}$  skeleton of the molecule in the solid state.

TABLE 1

SKELETAL VIBRATIONS OF  $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}$

Description	Symmetry (point group $C_{3v}$ )	IR (solid) ( $\text{cm}^{-1}$ )
$\text{Sn}(\text{C}_6\text{H}_5)_3$ deformation	$a_1$	85
$\text{Sn}(\text{C}_6\text{H}_5)_3$ deformation	$e$	152
$\text{C}_6\text{H}_5\text{-SnCl}$ bending	$e$	180
Sn-Cl stretching	$a_1$	332
Sn- $\text{C}_6\text{H}_5$ stretching	$a_1$	230
Sn- $\text{C}_6\text{H}_5$ stretching	$e$	449 (broad)

The Sn- $\text{C}_6\text{H}_5$  degenerate stretching mode ( $e$ ) in triphenyltin chloride was observed at  $449\text{ cm}^{-1}$  (IR and Raman) in solution<sup>2</sup>. The present investigation shows this fundamental mode at the same position in the solid state. The broadening of this mode may be due to a "solid state" effect. The Raman spectrum of triphenyltin chloride in solution<sup>2</sup>, showed two more bands at  $214\text{ cm}^{-1}$  due to Sn- $\text{C}_6\text{H}_5$  stretching ( $a_1$ ) and at  $329\text{ cm}^{-1}$  due to Sn-Cl stretching ( $a_1$ ). These fundamental modes are observed here at  $230\text{ cm}^{-1}$  and at  $332\text{ cm}^{-1}$  respectively in the solid state. The bands at  $85\text{ cm}^{-1}$ ,  $152\text{ cm}^{-1}$  and  $180\text{ cm}^{-1}$  in the far infrared spectrum are attributed to two deformations ( $a_1$  and  $e$ ) and the  $\text{C}_6\text{H}_5\text{-SnCl}$  bending ( $e$ ). Thus the skeleton of  $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}$  molecule favours  $C_{3v}$  symmetry.

The  $^{35}\text{Cl}$  NQR spectrum of  $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}$  was searched in the range 12.5 to 28.5 Mc/s at  $77^\circ\text{K}$ . The apparatus used has been described by Smith and Tong<sup>3</sup>. A single resonance signal of  $^{35}\text{Cl}$  was observed at 13.690 Mc/s. The observed frequencies and calculated nuclear quadrupole coupling constants of  $^{35}\text{Cl}$  in phenyltin chlorides and tin tetrachloride are given in Table 2.

The decrease in the value of  $|e^2 \cdot Q \cdot q_{zz}|$  from  $\text{SnCl}_4$  to  $(\text{C}_6\text{H}_5)_3\text{SnCl}$  can be attributed to the increase in ionic character and enhanced  $\pi$  bonding in Sn-Cl bonds. However one expects that the contribution due to change in ionic character is more dominant than enhanced  $\pi$  bonding<sup>5</sup>.

We expect distortion of bond angles from  $109^\circ 28'$  (ref. 6) and electric field gradient at the tin nucleus in alkyl- and aryltin chlorides arising due to  $d_\pi\text{-}p_\pi$  interaction

\* This work was done at the University of Newcastle Upon Tyne.

TABLE 2

OBSERVED FREQUENCIES AND CALCULATED NUCLEAR QUADRUPOLE  
 COUPLING CONSTANTS OF  $^{35}\text{Cl}$  IN PHENYL TIN CHLORIDES

Compound	Observed frequencies (Mc/s) (77° K)	$ e^2 \cdot Q \cdot q_{zz} $ calcd. <sup>b</sup> (Mc/s)
$\text{SnCl}_4$ <sup>4</sup>	24.100	48.200
$\text{C}_6\text{H}_5\text{SnCl}_3$ <sup>5</sup>	21.166	42.332
$(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ <sup>5</sup>	16.947	33.892
$(\text{C}_6\text{H}_5)_3\text{SnCl}$ <sup>a</sup>	13.690	27.380

<sup>a</sup> Present investigation. <sup>b</sup>  $|e^2 \cdot Q \cdot q_{zz}|$  is calculated by assuming asymmetry parameter equal to zero.

and the ionic character of Sn-Cl bond. This is reflected as quadrupole splitting in Mössbauer spectra of these compounds<sup>7,8</sup>. Contrary to these expectations the experiments show no quadrupole splitting in  $(\text{C}_6\text{H}_5)_3\text{SnH}$ ,  $(\text{C}_6\text{H}_5)_3\text{SnLi}$ ,  $[(\text{C}_6\text{H}_5)_3\text{Sn}]_2$ , etc.<sup>9</sup>. This awaits a satisfactory explanation.

Triphenyltin chloride was prepared according to the method of Kocheshkov, Mad and Alexandrov<sup>10</sup>.

The infrared spectrum was recorded between  $4000\text{ cm}^{-1}$  and  $70\text{ cm}^{-1}$  on instruments previously described<sup>11</sup>.

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