THE INFRARED SPECTRA OF ETHYLTIN COMPOUNDS IN THE REGION 2–45 μ

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The spectra of some ethyltin compounds, obtained by both infra-red[1–17] and Raman techniques[18,19], have been described in a number of publications but they are scattered through the literature and are largely concerned with the organic part of the molecules. In this work, we have investigated the infra-red spectra of a range of ethyltin compounds and have attempted to assign the bands and correlate these with the physical characteristics of the compounds concerned.

EXPERIMENTAL

Infra-red measurements

All spectra were recorded using Grubb Parsons Spectromaster and DM4 grating spectrometers covering the ranges 2–25 μ and 15–45 μ respectively. Solid materials were investigated as nujol mulls or in potassium bromide discs and liquids as capillary films. Standard potassium bromide plates were used as supports in the region 2–25 μ and 0.03" thick high-density polyethylene sheeting (as supplied by Iridon Limited) was used in the 15–45 μ region.

Spectra were all recorded directly after preparation of materials and specimens prepared in the dry box.

Preparation of compounds

Compounds were all prepared by established procedures[20–26] and characterized by melting point, boiling point, refractive index and chemical analysis[25–27]. Literature methods were found to be satisfactory for the preparation of all compounds, though when handling bis(triethyltin) oxide and triethyltin hydroxide, it was found to be necessary to take extreme care to remove all carbon dioxide from the atmosphere to prevent the formation of the corresponding carbonate; and for the preparation of ethyltin tribromide from diethyltin dibromide, it was found necessary to use a sealed-tube technique to obtain high yields.

DISCUSSION

Characteristic vibrations of ethyltin compounds

Direct comparison of the range of compounds Et_nSnX_{4-n} is complicated by the fact that the diethyltin compounds and the triethyltin derivatives are solids while the other compounds are liquids. However, comparison of the spectra of the liquid and solid triethyltin compounds shows that the physical state does not affect the position of the bands to any great extent. Some broadening of the bands is observed, probably because of lattice interactions and, as observed by Vyshinskii[14], there is in some instances a splitting of the band at 10.4 μ in the solids. In all cases, there was no significant shift of any of the bands associated specifically with the ethyl group, *i.e.* the remainder of the molecule behaves as an inert, heavy mass. Significant changes in band position were noticed, however, with those bands associated with the tin–carbon bond, and for particular groups of compounds these lie in the ranges:

	Et_4Sn	Et_3SnX	Et_2SnX_2	$EtSnX_3$
$Sn–C_2H_5$ rock	15.1	14.9–15.2	14.6 –14.7	14.6–14.7
$Sn–C_2H_5$ asym. str.	19.95	19.3–19.8	18.8 –19.4	19.4–20.1
$Sn–C_2H_5$ sym. str.	—	20.4–20.75	20.25–20.6	—
Sn–C–C bend	36.5	36 –37.6	37 –38	36.5–39

These values cover all the compounds investigated except where there has been a considerable shift of the band due to the presence of a bulky group – *e.g.* the $SnEt_3$ group in hexaethylditin – or a very electronegative group as in triethyltin fluoride or sulphate.

As can be seen, the differences between the bands for different groups are not great, but they are large enough to characterize the groups concerned.

As will be discussed, the absence of a symmetric Sn–Et stretching band in some compounds is due to an increase of symmetry within the Et_nSn group making such bands forbidden. In the case of the triethyltin compounds, the pyramidal group tends towards a planar triangular arrangement and with the diethyltin compounds, the angular group tends towards a linear arrangement. In the case of the triethyltin derivatives, it is noticeable that there is a reduction in the separation between the two bands and a reduction in intensity of the symmetric stretching frequency as the compounds become more "ionic".

1. Alkyltin compounds (Table 1)

The tetraethyltin molecule is of point group T_d, thus we should expect to find only one infra-red active band associated with tin–carbon stretching in the region considered. In accord with this, we find the asymmetric stretching band at 19.95 μ. With hexaethylditin, where we have two $SnEt_3$ groups of point group C_{3v} presumably free to rotate about the tin–tin bond, we note two bands which we assign to the asymmetric stretch at 20.15 μ and the symmetric stretch at 21.05 μ.

With both compounds, bands were observed at about 15 μ and 36 μ which were assigned to the Sn–Et rock and Sn–C–C bend respectively.

These results are essentially in agreement with those of other workers[3–6], but with tetraethyltin differing from those of Kaesz and Stone who find an additional band at 11.18 μ which is presumably due to an impurity.

2. Ethyltin oxides (Table 2)

Great care was needed in handling the triethyl compounds because of the ease with which they absorb carbon dioxide from the atmosphere – the spectrum reported earlier for the hydroxide[1] is in fact the spectrum of the carbonate. These compounds

TABLE 1

ASSIGNMENTS FOR ETHYLTIN COMPOUNDS

$SnEt_4$	Sn_2Et_6	*Assignment*
2.34 vw	2.33 vw	CH_3 sym. stretch
3.45 vs	2.43 vs	CH_3 asym. str.
		CH_2 out of phase stretch
3.50 vs	3.50 vs	CH_2 in phase str.
3.56 m	3.56 m	
3.68 w	3.67 w	
5.10 vvw	—	
5.4 vvw	5.4 vvw	
6.0 vvw	6.0 vvw	
6.2 vvw	6.25 vvw	
6.85 s	6.85 s	CH_3 asym. def.
7.05 ms	7.0 m	CH_2 bending
7.2 s	7.25 s	CH_3 sym. def.
7.6 vvw	—	
8.1 m	8.1 m	CH_2 wagging
8.45 ms	8.45 s	CH_2 twisting
9.9 vs	9.85 vs	CH_2 twisting
10.4 s	10.45 ms	$C-CH_3$ rocking
10.6 ms	10.05 s	$C-CH_3$ rocking
15.1 vs	15.2 vs	$Sn-CH_2$ rocking
10.95 vs	20.15 vs	$Sn-C_2H_5$ asym. stretch
—	21.05 vs	$Sn-C_2H_5$ sym. stretch
36.5 ms	39.0 m	Sn–C–C bend

TABLE 2

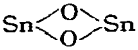
ASSIGNMENTS FOR ETHYLTIN OXIDES

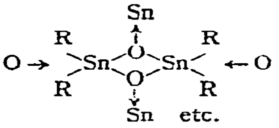
Bands not specifically associated with the ethyl group

$(Et_3Sn)_2O$	Et_3SnOH	Et_2SnO	*Assignment*
—	2.8 vw	—	Free OH
—	6.55 vw	—	H–O–H (?)
—	11.3 s	—	Sn–OH def.
13.0 vs	13.0 s	—	Sn–O–Sn asym. str.
15.2 vs	15.1 vs	15.0 s	$Sn-C_2H_5$ rock
—	—	17.5 vs	Sn–O–Sn asym. str.
19.65 vs	19.6 vs	18.8 s	$Sn-C_2H_5$ asym. str.
20.6 s (sh)	20.6 m (sh)	20.3 m	$Sn-C_2H_5$ sym. str.
25.4 w	25.5 w	24.0 w	Intermol. Sn–O bonding
37.0 m	37.5 m	—	Sn–C–C bend.

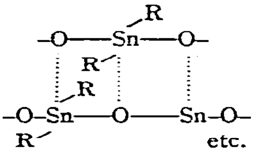
were consequently handled in a glove box containing nitrogen which had been freed from carbon dioxide by passage through a column packed with "Carbabsorb".

Bis(triethyltin) oxide is a high-boiling liquid (b.p. 147°/5 mm) which is converted into triethyltin hydroxide – a low-melting solid (m.p. 50°) – by adding an equimolar quantity of water; while the hydroxide is converted into the oxide by storing over calcium chloride or by vacuum distillation.

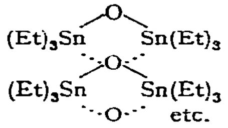
The spectra of bis(triethyltin) oxide and triethyltin hydroxide are very similar, the major difference being the appearance of a band at 11.3 μ in the hydroxide spectrum, this we have assigned to Sn–OH deformation. The two bands at 13.0 μ and 25.5 μ are reduced in intensity as we pass from the oxide to the hydroxide, but they are present in the spectrum of the hydroxide even when this contains an excess of water. These chemical and spectral characteristics support the view put forward by Harada[20] that the hydroxide is best regarded as the hydrated oxide. The band at 13.0 μ is readily assigned to the Sn–O–Sn asymmetric stretch. With diethyltin oxide – which is an amorphous, high-melting solid – there is a band at 24 μ which corresponds to the band at 25.5 μ in the triethyltin compounds. Shimanouchi[13] noticed similar bands at approximately 25 μ for a range of dialkyltin oxides and attributed these to the stretching of an  ring. His work is supported to some extent by the recent Mössbauer spectra of Gol'danskii[28], who explains his results in terms of structure (I) where the tin is five-coordinate in each case and forms four and eight-membered rings with oxygen atoms. Here, we would expect each of the tin atoms to be in a similar environment and provide only a single infra-red band or two bands of similar type. From the present results, it would seem more likely that the dialkyltin



(I)



(II)



(III)

oxides have a linear, polymeric structure with weaker bonding between the polymer chains, similar to that suggested by Reichle[29] for alkyltin oxides [see structure (II)]. The sharper band at 17.5 μ can be explained as being due to the asymmetric Sn–O–Sn stretch while the broad band at 24 μ is accounted for by weak bonds between the oxygen atoms of one chain with the tin atoms of the next. Reverting to the triethyltin compounds, we see that the band at 15 μ can be assigned to the Sn–O–Sn asymmetric stretch, while the weaker, broader band at 25 μ is due to interaction between molecules, building up a ribbon structure of the type (III). The hydroxide may then be considered to consist of ribbons of triethyltin oxide molecules cross-linked by water molecules.

The corresponding triphenyltin oxide and hydroxide are both substances with comparatively low melting points, which may be interconverted only with comparative difficulty, whose spectra show considerable differences[30–32], the oxide showing bands at 12.90 and 41.67 μ attributed to the symmetric and asymmetric stretching of Sn–O–Sn respectively. The hydroxide, on the other hand, shows bands at 2.76 μ, 10.96 and 11.15 μ, and 21.93 μ attributed to OH stretch, OH deformation and tin–oxygen stretching respectively. Thus, it would seem that in this instance the compounds may be regarded as separate oxide and hydroxide (*cf.* ref. 35). With the corresponding methyl compounds[23,24], it has been suggested that the hydroxide exists as a dimer in solution (though it is unfortunate that the interesting region between 3.5 μ and 17.5 μ could not be investigated because of the lack of a suitable solvent in this range) and as a linear polymer in the solid state. The position of the Sn–O–Sn stretching band in the methyltin compounds is a little more doubtful because of the close proximity of the Sn–Me rocking band (12.5–13.0 μ).

In a recent publication, Cummins[35] reported the spectra of a number of organotin oxides over a comparatively limited range. He was able to differentiate these into two groups, the mono- and di-organotin oxides (A), which are all high-melting, polymeric materials, and the low-melting triorganotin oxides (B). He concluded that in oxides of group (A), the asymmetric stretching band lay in the range 17.36–18.28 μ whilst group (B) oxides showed an asymmetric stretching band at 12.9 μ, these were the only bands reported and it is unfortunate that a wider wavelength range was not investigated. The results obtained in the present investigation are essentially in agreement with those of Cummins. However, Cummins further concluded that the bis(triorganotin) oxides are simple anhydrides of the corresponding hydroxides, which as we have seen above is not so in all cases.

3. Triethyltin sulphate and carbonate (Table 3)

With the sulphate, we can unambiguously assign the bands at 9.3, 16.35 and 22.2 μ to the S–O asymmetric stretching, and the asymmetric and symmetric deformation bands respectively[37]. Because of the tetrahedral (T_d) symmetry of the sulphate ion, we would not expect the symmetric S–O band to be infra-red active.

TABLE 3

BIS(TRIETHYLTIN) CARBONATE AND SULPHATE

Bands not specifically associated with the ethyl group.

$(Et_3Sn)_2SO_4$	$(Et_3Sn)_2CO_3$	*Assignment*
—	6.65 vs	C–O str.
—	7.4 vs	C–O–O asym. str.
9.3 vs	—	S–O asym. str.
—	9.35 s	C–O–O sym. str.
9.9 ms	9.9 s	CH_2 twist + S–O sym. str. (?)
—	12.0 s	C–O–O out of phase rock
—	13.3 m	C–O–O bend & planar rock
—	13.85 m	
14.8 s	14.9 vs	Sn–C_2H_5 rock
16.35 m	—	S–O deformation
19.1 s	19.3 vs	Sn–C_2H_5 asym. str.
20.4 vw	20.35 m	Sn–C_2H_5 sym. str.
22.2 mw	—	S–O deformation
—	26.3 ms	Sn...O weak bending
36.0 s	41.5 ms	Sn–C–C bend.

However, if the symmetry were destroyed, we would expect to find this band in the region of 10 μ. The band at 9.9 μ could possibly be this band, however, as we have seen with the other ethyltin compounds, this band is accounted for by the C–C stretching band and the C–CH_3 rocking band and there is no significant difference in intensity for this band in the case of the triethyltin sulphate than with other ethyltin compounds, thus it seems unlikely that this band is due to the sulphate group. Further, no band is observed in the region of 30 μ as we would expect if there were any weak tin–oxygen bonding. Bands have been assigned to the symmetric and asymmetric stretching frequencies of the tin–ethyl group, although the symmetric stretching band is much weaker and exists only as a shoulder, thus it would seem that we have a pyramidal, almost planar, triethyltin ion and discrete sulphate ions. This is in contrast to the earlier report by Sato and Okawara[8], who claim to find four bands associated with the sulphate and explain this in terms of the reduced symmetry (C_{2v}) of the sulphate group with coordination between the tin of the triethyltin group and the oxygens of the sulphate group.

With triethyltin carbonate on the other hand, six bands are found which can unambiguously be assigned to a distorted carbonate group having C_{2v} symmetry and in addition, a band is found at 26.3 which can be assigned to weak tin–oxygen bonding. Both symmetric and asymmetric stretching frequencies are observed for the triethyltin group. These results are essentially in accord with those of Sato and Okawara[8] and can be explained in terms of pyramidal triethyltin groups linked by carbonate groups.

4. Triethyltin carboxylates (Table 4)

Because of the number of bands associated with the ethyl group, it is much more difficult, in the case of the triethyltin carboxylates, to assign bands unambiguously to the carboxylate group than with the other tin carboxylates which have been investigated[8,38,41]. In all cases, comparison was made with the corresponding sodium salts for the assignment of specific bands. Bands were observed between 19.2 and 19.35 μ and 20.4 and 20.55 μ in all cases, indicating that the triethyltin group is pyramidal. Further, all exhibit a band in the region 36–37.5 μ which, by comparison with the other ethyltin compounds can be assigned to Sn–C–C bending. The propionate and benzoate show additional bands at 28.5 μ, and 22.8 and 24 μ respectively. The 22.8 μ band is certainly associated with the benzene ring, while the other bands could be associated with weak tin-oxygen bonding. Okawara and Ohara[39] when investigating the spectra of methyl, ethyl and propyl formates and acetates found a band at approximately 35 μ – the limit of their instrument – in each instance, which they attribute to weak tin-oxygen bonding. This figure seems to be somewhat higher than earlier reported for this type of bonding[8]. Their results differ further from those reported here in that they find only the asymmetric ethyl–tin stretching band – though with the ethyl compound there is a slight shoulder – and interpret the spectra as being that of planar trialkyltin groups linked by carboxylate bridges.

TABLE 4

TRIETHYLTIN ACYLATES

Bands not specifically associated with the ethyl group.

HCOO	*CH_3COO*	*C_2H_5COO*	*C_6H_5COO*	*Assignment*
6.3 vs	6.45 vs	6.5 vs	6.45 s	COO asym. str.
7.4 vs	7.3 ms	7.3 vs	7.3 vs	COO sym. str.
12.9 s	—	12.8 vw	—	COO deform.
14.9 vs	15.1 vs	14.95 vs	14.9 s	Sn–C_2H_5 rock.
19.2 vs	19.2 vs	19.3 vs	19.35 s	Sn–C_2H_5 asym. str.
20.4 m	20.55 m	20.4 ms (sh)	20.4 mw	Sn–C_2H_5 asym. str.
—	—	—	22.8 m	Benzene ring
—	—	28.5 s	24 mw (sh)	Sn...O coordn.
36.2 m	40.0 m	37.5 ms	36.5 m	Sn–C–C bend

5. *Ethyltin sulphides* (*Table 5*)

From Table 5 it is obvious directly that there is a much greater similarity between the structures of the bis(triethyltin) sulphide and diethyltin sulphide than there is between the corresponding oxides. This is also evident from the physical form of the substances, whereas diethyltin oxide is a polymeric solid, the sulphide is a low-melting solid, the bis(triethyltin) compounds in both cases being high-boiling liquids. With both sulphides, bands are found which can be attributed to ethyl–tin symmetric and asymmetric stretching and two further bands are found that can be attributed to the symmetric and asymmetric Sn–S–Sn stretching. Harada[20] has shown that diethyltin sulphide exists as a trimer (presumably cyclic) and in this form we would expect the Sn–S–Sn bond angle to be very similar to that of the triethyltin compound, accounting for the similarity in position and intensity of the bands.

TABLE 5

ETHYLTIN SULPHIDES

Bands not specifically associated with the ethyl group.

$(Et_3Sn)_2S$	Et_2SnS	*Assignment*
15.2 vs	14.7 vs	Sn–C_2H_5 rock
19.8 vs	19.1 ms	Sn–C_2H_5 asym. str.
20.7 s	20.3 s	Sn–C_2H_5 sym. str.
27.0 vs	27.2 vs	Sn–S–Sn asym. str.
31.4 s	30.3 vs	Sn–S–Sn sym. str.
37.6 m	37.0 m	Sn–C–C bend

6. *Ethyltin halides* (*Table 6*)

From spectral studies of the inorganic tin halides[15,42–47], we would expect to find tin–halogen stretching bands in the following regions; tin–fluorine (16–20 μ), tin–chlorine (24–34 μ), tin–bromine (35–45μ) and tin–iodine (60–70 μ). Directly, we see that tin–iodine bands lie outside the range investigated here.

Both fluorides investigated are white, infusible powders. The other halides are liquids in the case of the triethyl and monoethyl compounds and low melting solids with the diethyl compounds. Thus, from their physical states we would expect to find differences between the spectra of the fluorides and the other halides.

With both the fluorides, we observe only a single band which can be associated with tin–ethyl stretching, suggesting that as with the corresponding methyl compounds[28,49] there is a planar $SnEt_3$ group and a linear $SnEt_2$ group either bridged by fluorine atoms or in a lattice with fluorine ions. With triethyltin fluoride we have no bands in the region expected for tin–fluorine stretching; with the difluoride, there is a sharp peak at 17.95 μ consistent with tin–fluorine stretching. In both cases, there is a broad band at 29 μ suggesting the bridging of tin atoms by fluorine atoms. X-ray evidence[49] has shown that trimethyltin fluoride consists of chains of almost planar trimethyltin groups bridged by fluorine atoms, the chains being held together by weak van der Waals forces. Clark *et al.* also note a weak band at 19.4 μ in addition to that at 18.02 μ reported earlier[28] and use this to support their claim that the trimethyltin group is non-planar, but they do not make mention of any band that can be associated

TABLE 6

ETHYLTIN HALIDES

Bands not specifically associated with the ethyl group. X = halogen.

Et_3SnX	*Et_2SnX_2*	*$EtSnX_3$*	*Assignment*
Fluorides			
14.9 s	14.6 vs		Sn–C_2H_5 rock
—	17.95 s		Sn–F str.
19.0 s	19.85 s		Sn–C_2H_5 asym. str.
29.0 vs	29.0 vs		Sn–F bridging
36.5 ms	35.0 ms		Sn–C–C rock
Chlorides			
14.95 vs	14.6 vs	14.6 vs	Sn–C_2H_5 rock
19.3 vs	18.9 m	19.4 s	Sn–C_2H_5 asym. str.
20.5 ms	20.25 s	—	Sn–C_2H_5 sym. str.
30.7 s	28.45 s	27.4 vs	Sn–Cl asym. str.
	30.5 s		Sn–Cl sym. str.
	33.8 s		
36.0 mw	33.8 s	36.5 m	Sn–C–C bend
		39.0 m	?
Bromides			
15.0 vs	14.6 mw	14.6 vs	Sn–C_2H_5 rock
19.6 vs	19.3 ms	19.65 s	Sn–C_2H_5 asym. str.
20.7 s	20.5	—	Sn–C_2H_5 sym. str.
—	29.0 m	—	?
36.0 ms	37.0 s	36.3 vs	Sn–C–C bend
	41.3 s	39.0 s (sh)	Sn–Br asym. str.
		44.5 m	Sn–Br sym. str.
Iodides			
14.95 vs	14.7 vs	14.7 vs	Sn–C_2H_5 rock
19.55 vs	19.4 m	20.1 m	Sn–C_2H_5 asym. str.
20.75 s	20.6 s	—	Sn–C_2H_5 sym. str.
37.0 s	38.0 m	39.0 m	Sn–C–C bend

with tin–fluorine stretching. Thus, it seems likely that triethyltin fluoride has a structure very similar to the methyl compound, namely chains of planar triethyltin groups linked by fluorine bridges, the band at 29 μ accounting for the bonding within the chains. The bands observed for diethyltin fluoride suggest a similar structure, with chains of linear diethyltin groups linked by fluorine bridges with another fluorine atom at right angles to the chain, accounting for the band at 17.95 μ expected of tin–fluorine stretching.

With the other halides, in contrast, the triethyltin compounds show two bands associated with tin–ethyl stretching indicating that these compounds are made up of pyramidal triethyltin groups linked covalently to halogen atoms. With the chloride, a tin–chlorine stretching band is observed at 30.7 μ but no corresponding band is observed for the other halides.

With the dihalides, two tin–ethyl stretching bands are observed indicating that there is an angular arrangement of the ethyl groups. Two tin–chlorine stretching bands were observed – at 28.45 and 30.5 μ – while a third band at 33.8 μ is difficult to explain, but could conceivably be caused by a tin–chlorine lattice interaction or by the Sn–C–C bend. A tin–bromine frequency was observed at 41.3 μ.

With the monoethyltin trihalides, a single tin–ethyl stretching band is observed in each case. Only a single – very strong – tin–chlorine stretching band is observed – at 27.4 μ – but a further peak is obtained at 39 μ which is difficult to explain. A peak has, however, been found in the Raman spectra of diethyltin dichloride[18] and the trichlorostannite ion[16] in this position. Two tin–bromine peaks were observed, at 39.0 and 44.5 μ.

In all cases, there is a diminution of the relative intensity and a shift to lower wavelengths of the ethyl–tin stretching bands as we move from the tri- to di- to mono-ethyl halides and with the chloride, we notice an increase in intensity and a shift to lower wavelengths of the tin–chlorine band with increase in the number of chlorine atoms in the molecule.

Apart from reporting the spectra for analytical purposes[1], other workers have reported exclusively on the spectra of the ethyltin chlorides. Taimsalu and Wood[17] investigated triethyltin chloride together with a range of methyltin chlorides (the results of the latter agreeing very well with the corresponding Raman spectral results for the same compounds) in the range 3.3–200 μ and give results essentially in agreement with those reported here. Butcher *et al.*[10] investigated diethyltin dichloride and report lower values for the tin–chlorine stretching bands – 27.86 and 28 μ respectively. Savidan[18] reported data from the Raman spectrum of diethyltin dichloride but made no attempt to interpret these. It would seem that a band at 29.5 μ is due to tin–chlorine stretching.

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SUMMARY

The infra-red spectra of a number of ethyltin compounds have been investigated in the region 2–45 μ and assignments made for each of the bands. Of the bands associated with the tin-carbon bond, Sn–CH_2 rocking has been found to lie between 14.6 and 15.2 μ; the asymmetric Sn–C_2H_5 stretch between 18.8 and 19.6 μ; the symmetric Sn–C_2H_5 stretch between 20.25 and 20.6 μ and the Sn–C–C bend between 36 and 37.5 μ.

Various other structural features are discussed in terms of the groups concerned.

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