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ON THE CONFIGURATION OF SOME 1,1,2,2-TETRAPHENYL-1,2-DIACYLOXYDITIN COMPOUNDS IN SOLUTION

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SUMMARY

The IR spectra in the 2000–400 cm^{-1} region of 1,1,2,2-tetraphenyl-1,2-diacyloxyditin compounds, $Ph_4Sn_2(OOCR')_2$, having $R'=CH_3$, CH_2Cl, $CHCl_2$, CCl_3 or CF_3 have been recorded on the solids, Nujol mulls, and chloroform solutions. Asymmetric and symmetric stretching vibrations of the carboxylic group have been assigned. The frequencies do not change on going from the solids or Nujol mulls to the chloroform solutions in which they are monomeric.

The reaction rates of the compounds with iodine in chloroform decrease in the order $R=CH_3>CH_2Cl>CHCl_2>CCl_3>CF_3$. The reaction appears to involve electrophilic attack of iodine at a tin atom.

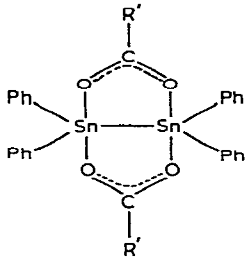
The $Ph_4Sn_2(OOCR')_2$ compounds are thought in the solid state to be polymers having bridging carboxylate groups and in solution to have carboxylate ligands bridging the two tin atoms, which are thus five-coordinated in a trigonal bipyramidal structure.

INTRODUCTION

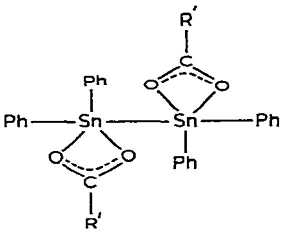
Organotin carboxylates of the general formulae $R_3SnOOCR'$ and $R_2Sn(OOCR')_2$ have been extensively investigated in recent years[1]. Structural studies have been directed towards establishing the nature of the carboxylate ligand, which can act as an intramolecular chelate[2] or as an intermolecular bridging group[1,3]. Trimethyltin carboxylates have been shown to be polymeric in the solid state, but depolymerization occurs on dissolution in an organic solvent[4-6].

We have now examined 1,2-diacyloxyditins, $[Ph_2Sn(OOCR')-Sn(OOCR')Ph_2]$ (aspects of the preparation are described in ref. 7–9) in order to establish the mode of behaviour of the carboxylate ligand.

The carboxylate group might coordinate with the tin atoms in one of these ways:



(I)



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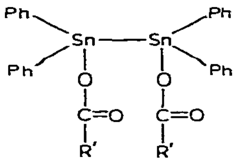

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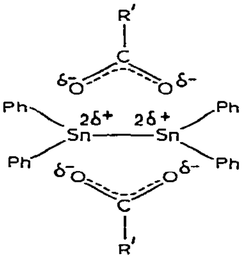

(IV)

Furthermore one cannot reject *a priori* polymeric structures involving pentacoordinated tin atoms and bridging carboxylate groups. A structure such as (I) has been suggested for the hexaacetoxyditin, $Sn_2(OOCCH_3)_6$, on the basis of its stability, which seems to depend upon two acetate ligands acting as bridging groups between the tin atoms[10].

In order to reveal the effect on the coordination of the carboxylate ligands of varying electronegativity of the acyloxy groups, we have examined the IR spectra in solid and in solution, we have determined molecular weights, and we have measured iodination rates in chloroform for the $Ph_4Sn_2(OOCR')_2$ compounds in which R′ is CH_3, CH_2Cl, $CHCl_2$, CCl_3, and CF_3.

EXPERIMENTAL

The 1,1,2,2-tetraphenyl-1,2-diacyloxyditin compounds were prepared as previously described[8], and were analysed for carbon, hydrogen and tin. Melting points (uncorrected), taken with a Gallenkamp apparatus, were as follows: acyloxy = acetate 155° (152°), monochloroacetate 147° (150°), dichloroacetate 167° (169°), trichloroacetate 169° (170°) and trifluoroacetate 164° (165°) (literature values[8] are shown in parentheses).

All chemicals and solvents used were of reagent grade. IR spectra were recorded on a Perkin–Elmer Model 621 or 457 equipped with KBr optics. Molecular weights were determined in chloroform or benzene with a Mechrolab Model 301A vapour phase osmometer. Conductivity measurements were carried out with a LKB 3216B Conductivity Bridge at 25±0.01° in an oil thermostat.

Iodination rates in chloroform were measured spectrophotometrically[11,12]. The absorbance of I_2 at λ_{max} 520 nm, $\varepsilon = 820$ (in $CHCl_3$) against time was recorded by means of a Unicam SP 800 spectrophotometer fitted with SP 820 control unit and

SP 825 programme controller accessories suitable for kinetic work. Values of k ($l \cdot mole^{-1} \cdot sec^{-1}$) are accurate to within ±3%.

Analysis of the ditin solutions were carried out by coulometric titration method as previously described[13].

RESULTS

Molecular weights and conductivity measurements

Molecular weights are shown in Table 1. In the concentration range used, *viz.* 2.5–20 mg/ml, all the compounds were monomeric in the solvents used.

Measurements on 10^{-3} M solutions (in benzene/ethanol, 75/25, v/v) at 25° showed that solutions of all compounds were non-conducting.

TABLE 1

MOLECULAR WEIGHTS OF 1,1,2,2-TETRAPHENYL-1,2-DIACYLOXYDITINS IN CHLOROFORM AND BENZENE

At 37° in the concentration range 2.5–20 mg/ml.

R′	Solvent	Mol.wt. found (calcd.)
CH_3	$CHCl_3$	645 (664)
	C_6H_6	654 (664)
CH_2Cl	$CHCl_3$	735 (733)
	C_6H_6	740 (733)
$CHCl_2$	$CHCl_3$	803 (802)
CCl_3	$CHCl_3$	860 (871)
CF_3	$CHCl_3$	760 (772)

Infrared spectra

The IR spectra in the 2000–400 cm^{-1} region of the $Ph_4Sn_2(OOCR')_2$ compounds were recorded on the solids (KBr discs), Nujol mulls and chloroform solutions (optics KBr, 0.1 mm). Assignments of the asymmetric and symmetric stretching vibrations of the carboxylic groups are shown in Table 2. Fig. 1 shows the IR spectra of the diacetate compound in the (COO) absorption region in Nujol mull and in $CHCl_3$. The (COO) asymmetric and symmetric stretching frequencies are linearly related to the Taft inductive constants[14] σ^* of the R′ carboxylate organic group as shown in Fig. 2.

Reaction of 1,1,2,2-*tetraphenyl*-1,2-*diacyloxyditins with iodine, bromine and silver ions*

The stoichiometry of the reaction of $Ph_4Sn_2(OOCCH_3)_2$ and bromine,

TABLE 2

IR WAVENUMBERS (cm^{-1}) OF 1,1,2,2-TETRAPHENYL-1,2-DIACYLOXYDITINS, $Ph_4Sn_2(OOCR')_2$, IN THE CARBOXYLIC REGION[a]

R′	Medium	ν_a(COO)	ν_s(COO)
CH_3	Nujol	1530	1405
	Solid	1530	1405
	$CHCl_3$	1530	1405
	C_2Cl_4	1530	1405
CH_2Cl	Nujol	1560	1395
	$CHCl_3$	1565	1390
$CHCl_2$	Nujol	1585	1385
	$CHCl_3$	1590	1380
CCl_3	Nujol	1610	1350
	$CHCl_3$	1615	1350
CF_3	Nujol	1625	
	$CHCl_3$	1625	
	Solid	1625	

[a] All bands are strong.

$$Ph_4Sn_2(OOCCH_3)_2 + Br_2 \rightarrow 2\ Ph_2Sn(OOCCH_3)Br$$

first reported by Kuivila[15], was confirmed for all the examined compounds by the coulometric titration method[13]. In addition, it was shown that these compounds can be titrated quantitatively with one mole of iodine or two moles of silver ions. This behaviour is quite similar to that found for the hexaalkyl- and hexaarylditins[13,16].

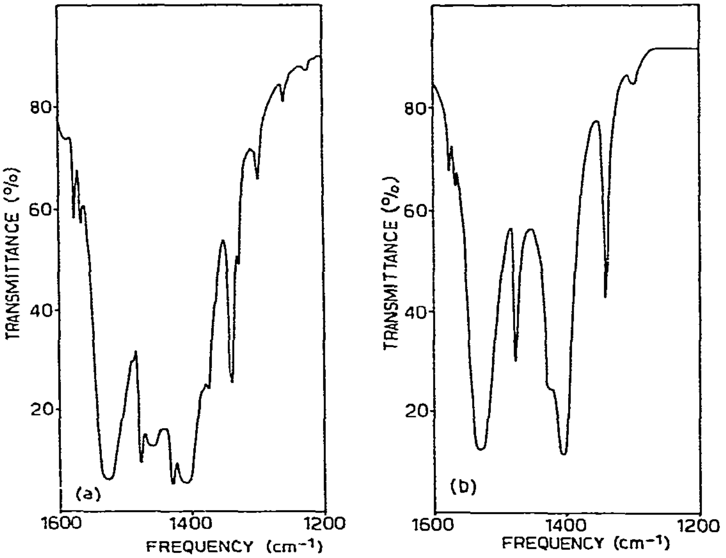

Fig. 1. IR spectra of $Ph_4Sn_2(OOCCH_3)_2$ in the carboxylic region. *a*. in Nujol mull; *b*. in chloroform solution.

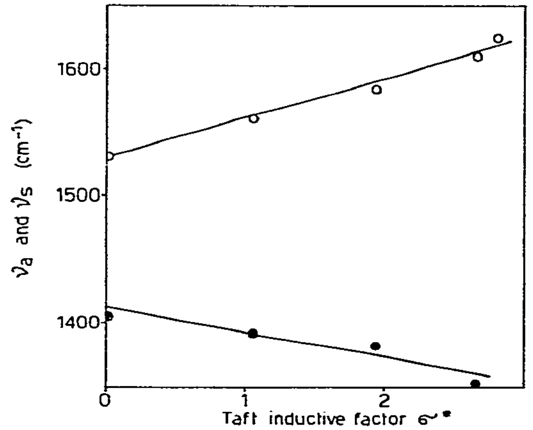

Fig. 2. Correlation between the carboxylic asymmetric (open circles) and the symmetric (black circles) stretching frequencies (wavenumbers, cm^{-1}) and the Taft inductive constants σ* of the R′ organic carboxylate groups.

Rate constants of the reactions of 1,1,2,2-*tetraphenyl*-1,2-*diacyloxyditins with iodine in chloroform*

Table 3 lists the rate constants $k(l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1})$ obtained at 25±0.1° for the reactions of the 1,2-diacyloxyditins and iodine in chloroform. The reactivities of the $Ph_4Sn_2(OOCR')_2$ compounds fall in the order (R′=)$CH_3 > CH_2Cl > CHCl_2 > CCl_3 > CF_3$. Thus the rate decreases with increase in the electron-withdrawing power of the R′ groups. Hexaphenylditin was shown to react with iodine more rapidly than the carboxylates under the conditions used.

TABLE 3

RATE CONSTANTS k FOR THE REACTION OF 1,1,2,2-TETRAPHENYL-1,2-DIACYLOXYDITINS, $Ph_4Sn_2(OOCR')_2$, AND IODINE IN CHLOROFORM AT 25°

R′	k (l·mole^{-1}·sec^{-1})
CH_3	[a]
CH_2Cl	32
$CHCl_2$	4.0
CCl_3	2.8
CF_3	1.9

[a] Too fast to be measured under our experimental conditions.

DISCUSSION

The (COO) asymmetric stretching vibration bands of the ditin compounds are found in the range of the frequencies generally attributed[17] to a coordinate [structures (I) and (II)] or ionic (IV) carboxylate group. Thus the carboxylate ester-like structure (III) seems to be ruled out. The ionic structure (IV) must also be ruled out because the compounds do not conduct in alcohol/benzene solution. The bridged structure (I) and the chelated structure (II) represent the remaining possible forms of these compounds, which are monomeric in chloroform and benzene solution (*cf.* Table 1).

IR spectra are generally not helpful in distinguishing between chelating and bridging carboxylate groups, but, nevertheless, the IR spectra of the examined compounds, especially when considered along with those for related systems[2,10] seem to us to favour structure (I) rather than (II).

The single sharp unsplit band associated with the ν_a(COO) vibration indicates that solid-state interactions within the lattice are not significant or balance out. Furthermore no change in the (COO) vibration frequencies occurs on passing from the solid state to solution, and thus the configuration of the carboxylate ligand seems to be the same in both states. The existence in chloroform of monomers having the same (COO) configuration as in the solid state could be ascribed to attributed depolymerization of a polymer in which the tetraphenylditin moieties are held together by carboxylate groups which bridge in the way observed for trialkyltin[1,3–5,18,19] and trivinyltin[20] carboxylates. This view is supported by a preliminary result of an X-ray examination of the $Ph_4Sn_2(OOCCH_3)_2$ structure: the two observed tin–tin atom distances of 2.6 and 2.8 Å seem to be consistent with acetate groups bridging the tin atoms intramolecularly and intermolecularly, respectively[21].

It is revealing to compare the IR results for the $Ph_4Sn_2(OOCCH_3)_2$ compounds with those for some related systems. It can be seen (*cf.* Table 4) that splitting of the carboxylic stretching vibration appears for the following compounds: $Sn_2Cl_4(OOCCH_3)_2$ and $Sn_2(OOCCH_3)_6$. The splitting of 20 cm^{-1} in the former could be attributed to crystal effects, as suggested for molybdenum(II) carboxylates in which a splitting of the ν_a(COO) band of ca. 8–18 cm^{-1} occurs[22], but the splitting of 80 cm^{-1} in the latter is better explained by postulating a difference in the force constants for the chelating and bridging acetate groups. This is consistent with the probable structures of these compounds in the solid state: in $Ph_4Sn_2(OOCCH_3)_2$, as in $Sn_2Cl_4(OOCCH_3)_2$, the two carboxylate ligands have a bridging configuration, as is shown in the structures (A) and (B) (Fig. 3); in the case of the solid hexaacetoxyditin, chelating carboxylate groups must be present in addition to bridging groups which give rise to a polymeric structure.

TABLE 4

CARBOXYLIC ASYMMETRIC STRETCHING VIBRATIONS OF SOME TIN ACETATES AND PROBABLE RELATED ACETATE CONFIGURATION

Compound	ν_a(cm^{-1}) and (COO) configuration			Ref.
	ester-like	chelating	bridging	
$Ph_4Sn_2(OOCCH_3)_2$			1530	this work
$Cl_4Sn_2(OOCCH_3)_2$			1510, 1490	10
$Sn_2(OOCCH_3)_2$		1590	1510	10
$(CH_3)_2Sn(OOCCH_3)_2$		1607		2
$Sn(OOCCH_3)_4$	1725	1625		10

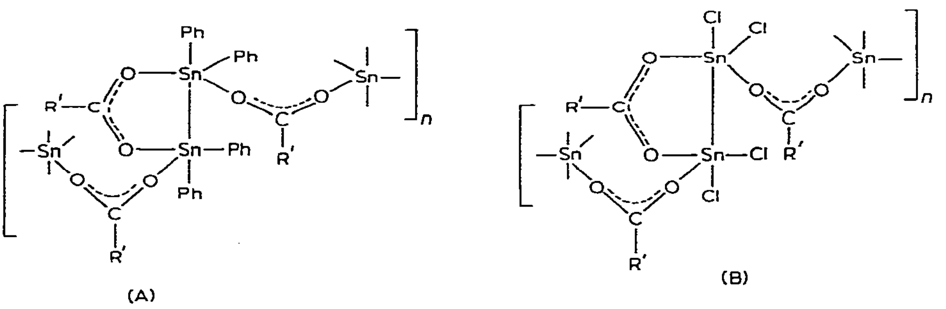

Fig. 3. Probable configuration of the carboxylate ligands in the solid state for (A) 1,1,2,2-tetraphenyl-1,2-diacetoxyditin, (B) 1,1,2,2-tetrachloro-1,2-diacetoxyditin.

The 1510 cm^{-1} band can be attributed to a stretching vibration of a bridging carboxylate group and that at 1590 cm^{-1} to a chelating one. This is in agreement with IR data for the dimethyltin diacetate for which the ν_a(COO) at 1607 cm^{-1} was attributed to a chelating acetate group[2], and to those in monomeric dipropyl- and dibutyltin diacetate, which also contain chelating carboxylic groups*. Furthermore the bands at 1625 and 1725 cm^{-1} present in the case of tin tetraacetate[10], can be interpreted as (COO) vibrations involving a chelating and an ester-like acetate configuration, respectively. Table 4 lists the ν_a(COO) wavenumbers and lists the configuration of the carboxylate ligands in the compounds concerned.

The shift of the (COO) asymmetric stretching vibration from 1530 to 1625 cm^{-1}, on passing from the diacetate to the bis(trifluoroacetate) compound (*cf.* Table 2) can be attributed to the increase of the electronegativity of the R′ group (*cf.* Fig. 2).

We conclude that, for the ditin compounds studied, a polymeric structure involving bridging carboxylate groups is the most probable in the solid state. The bridging configuration of the carboxylate ligands is maintained in solution, so that the monomeric structure in chloroform of these compounds is (I), in which the two carboxylate ligands bridge the two tin atoms, the latter thus being five-coordinated in a trigonal bipyramidal configuration.

The rate constants obtained for the coordination in chloroform are not sufficient to indicate the mechanism of the reaction. However, the decrease in rate with increasing electron-withdrawing power of the R′ groups is consistent with electrophilic attack by iodine at tin, as in hexaalkyl- and hexaarylditins[16]. The lower reactivity of this class of compounds with respect to the hexaphenylditin [*cf.* our data and ref. 16; $k=740$ l·mole^{-1}·sec^{-1} at 27° in cyclohexane] is consistent not only with the greater electron-withdrawing power of the carboxylate groups which replace two of the phenyl groups of Ph_6Sn_2, but can also be associated with stabilization of the tin–tin bond, brought about by the two intramolecular bridging carboxylate ligands as depicted in structure I.

ACKNOWLEDGEMENT

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* See ref. 1 of ref. 2.

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