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Diorganotin(IV) and Triorganotin(IV) Derivatives of Diphenic Acid

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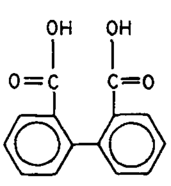
The diorganotin(IV) and triorganotin(IV) derivatives R_2SnA (R = Me, n-Pr, n-Bu, n-Oct) and $(R_3Sn)_2A$ [R = Me, Ph, cyclohexyl (Cyh); A = an anion of diphenic acid] have been prepared and characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopies. Tetrahedral tin forms a part of a diphenate cyclic ring in the diorganotin complexes with unidentate carboxylates, which have further been used for the synthesis of cyclic acid anhydrides. The soluble dinuclear triorganotin complexes (Me, Ph) possess symmetrically bonded carboxylates while the less soluble compound $(Cyh_3Sn)_2A$ has two asymmetrically bonded carboxylates. All have a trigonal bipyramidal structure with R_3Sn units remote from each other.

Keywords: diphenic acid; organotin(IV); complexes

INTRODUCTION

Organotin(IV) compounds are used as microcides, insecticides and marine antifouling agents.[1] Di- and tri-organotin(IV) derivatives of thiophene 2-carboxylic acid and aminobenzoic acid have been reported and assigned octahedral and trigonal bipyramidal geometries.[2,3] In the present case, derivatives of diphenic acid (AH_2) have been prepared to assess the bonding mode of the two carboxylate groups and have also been used to synthesize cyclic acid anhydrides.



AH_2 diphenic acid

EXPERIMENTAL

Materials and methods

Dimethyl-,di-n-butyl- and di-n-octyl-tin oxides, and trimethyl and tricyclohexyltin chlorides, were obtained from Alfa Products and Aldrich Chemicals, USA, respectively. Diphenic acid was procured from Fluka Chemika, Germany.

Preparation of sodium salt of diphenic acids

Diphenic acid (0.1 mol) and sodium hydroxide (0.2 mol) were dissolved in ethyl alcohol (95%, 50 ml) and refluxed until a clear solution resulted (pH ~7). After removing the excess of alcohol by distillation, dry benzene (20 ml) was added to remove water azeotropically using a Dean and Stark trap. The sodium salt which separated was filtered and washed several times with dry ether and dried in vacuum.

Preparation of ethyl ester of diphenic acid

The ethyl ester of diphenic acid was prepared by refluxing diphenic acid (0.1 mol) in absolute ethanol (30 ml) in the presence of two to three drops of sulphuric acid for 4 h. The solution was filtered, then poured into water, and the ester was extracted with ether and dried over anhydrous sodium sulphate.

Preparation of diorganotin(IV) complexes

Complexes **1–4** (Table 1) were prepared by dissolving diphenic acid (0.1 mol) in a mixture of dry benzene (30 ml) and absolute ethanol (10 ml) and diorganotin(IV) oxide (0.1 mol) was added. The reaction mixture was then refluxed over a water bath using a Dean and Stark trap. Dialkyltin(IV) oxide went into solution within 10–15 min to give a clear solution. Refluxing was further continued for 3–4 h and the contents were then cooled and

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Table 1 Physical and analytical data of diorganotin(IV) and triorganotin(IV) complexes of diphenic acid (AH_2)

Complex	Colour	Yield (%)	M.P. (°C)	Analysis (%): Found (Calcd)		
				C	H	Sn
1 Me_2SnA^a	Light green	71	159–161	50.04 (49.39)	3.78 (3.60)	29.98 (30.52)
2 $n\text{-}Pr_2SnA^a$	Light green	82	105–108	54.24 (53.96)	5.08 (4.94)	27.18 (26.69)
3 $n\text{-}Bu_2SnA^a$	Light green	79	65–66	56.04 (55.80)	5.86 (5.46)	25.83 (24.91)
4 $n\text{-}Oct_2SnA^a$	Light green	83	72–73	61.34 (61.57)	7.68 (7.18)	21.05 (20.35)
5 $(Me_3Sn)_2A^b$	White	76	225–230	42.74 (42.20)	4.65 (4.58)	43.31 (41.84)
6 $(Ph_3Sn)_2A^b$	White	89	124–126	62.93 (62.84)	3.84 (4.04)	26.08 (25.27)
7 $(Cyh_3Sn)_2A^b$	White	85	121–122	59.83 (61.51)	7.78 (7.58)	25.25 (24.33)

[a] Crystallized from benzene. [b] Crystallized from benzene + absolute ethanol

solvent was removed by distillation under reduced pressure. Light green solids were obtained in the case of Me_2SnA, $n\text{-}Pr_2SnA$ $n\text{-}Bu_2SnA$ and $n\text{-}Oct_2SnA$ complexes, which were recrystallized from dry benzene.

Preparation of triorganotin(IV) complexes

complexes **5–8** (Table 1) were prepared by dissolving the sodium salt of diphenic acid (0.1 mol) in a mixture of dry benzene (30 ml) and absolute ethanol (10 ml) and triorganotin(IV) chlorides (0.2 mol) were added. The reaction mixture was refluxed for 5–6 h, during which a white solid (NaCl) separated out. The contents were then cooled and filtered. The process of refluxing and filtration was repeated two or three times until all of the sodium chloride was separated. The solvent was removed by distillation under reduced pressure to leave a white solid in the case of methyl, phenyl and cyclohexyl (Cyh) derivatives, which were recrystallized from a mixture of dry benzene and absolute ethanol (3 : 1 ratio).

Physical measurements

Elemental analyses were carried out by the Microanalytical Service, R.S.I.C., Punjab University, Chandigarh, India. Tin was estimated as oxide (SnO_2).[4] Infrared spectra in Nujol were recorded on a Perkin–Elmer 1430 spectrophotometer in all cases. The ^1H and ^{13}C NMR spectra were recorded on a Brucker AC200 spectrometer using TMS as internal standard.

RESULTS AND DISCUSSION

Dialkyltin(IV) and trialkyltin(IV) derivatives have been prepared by reaction of dialkyltin(IV) oxide and trialkyltin(IV) chloride with diphenic acid (AH_2) and its sodium salt in a 1 : 1 and 2 : 1 molar ratio respectively (Eqns [1] and [2]).

$$AH_2 + R_2SnO \rightarrow R_2SnA + H_2O \qquad [1]$$

$$ANa_2 + 2R_3SnCl \rightarrow (R_3Sn)_2A + 2NaCl \qquad [2]$$

They were characterized by elemental analysis and infrared, ^1H and ^{13}C NMR spectroscopy. Complexes **1–7** (Table 2) are soluble in chloroform, benzene and absolute ethanol. The tricyclohexyl complex is insoluble in chloroform, dichloromethane and absolute ethanol and soluble in benzene. Analytical and physical data are given in Table 1.

Infrared spectra

Infrared spectra of diphenic acid (AH_2) and the complexes were recorded in Nujol in the range 4000–400 cm^{-1}. The stretching frequencies of

Table 2 Infrared spectral data (Nujol, 4000–400 cm^{-1}) of diorganotin(IV) and triorganotin(IV) complexes of diphenic acid

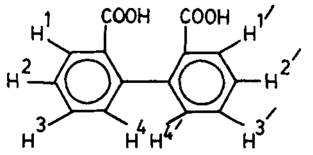
Complex	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	ν(Sn—C)	ν(Sn—O)
AH_2	1665s	1355s	310	—	—
ANa_2	1600s	1405s	205	—	—
AEt_2	1685s	1290s	395	—	—
1 Me_2SnA	1700s	1380s	320	580m	460m
2 n-Pr_2SnA	1650s	1380s	270	580m	470m
3 n-Bu_2SnA	1700s	1380s	320	550m, 590m	465m
4 n-Oct_2SnA	1730s	1385s	335	535m, 585m	420m
5 $(Me_2Sn)_2A$	1590s	1390s	200	555m, 590m	430m
6 $(Ph_3Sn)_2A$	1615s	1385s	230	—	—
7 $(Cyh_3Sn)_2A$	1620s, 1635m	1380s, 1345s	240, 290	490m, 415m	430m

interest are those of COO, Sn—C and Sn—O (Table 2). Absence of a broad band due to OH of COOH in the 2800–2500 cm^{-1} region shows deprotonation of the carboxylic group. The mode of bonding of the carbonyl group can be assessed by the magnitude of separation ($\Delta\nu$) of the ν_{asym} and ν_{sym} of the carboxylate group. For complexes **1–4**, the $\Delta\nu$ values, are comparable with that of the ethyl ester and suggest unidentate bonding of the carboxylate to tin(IV),[5] while in complexes **5–7** the $\Delta\nu$ values are comparable with that of the sodium salt and suggest a bidentate nature of the carboxylates.[6,7] In the case of $(Cyh_3Sn)_2A$ the two carboxylatyes are bonded asymmetrically to each tin, as indicated by the presence of two $\nu(COO)_{asym}$ and two $\nu(COO)_{sym}$ values. The presence of only one ν(Sn—C) band in complexes **1** and **2** indicates a linear configuration while in the other complexes the presence of two ν(Sn—C) bands shows the non-linear *trans* arrangement of

Table 3 ^1H NMR spectral data of diorganotin(IV) and triorganotin(IV) complexes of diphenic acid (δ, ppm)

	Biphenyl[a]			Sn—R	
Complex	H^1, $H^{1'}$	H^2, $H^{2'}$, H^3, $H^{3'}$	H^4, $H^{4'}$	—(CH_2)—	CH_3
AH_2[b]	7.97–7.93 (d, 2H)	7.48–7.37 (m, 4H)	7.20–7.16 (d, 2H)	—	—
1 Me_2SnA[c]	7.95–7.91 (d, 2H)	7.43–7.35 (t, 4H)	7.24–7.19 (t, 2H)	—	1.25 (s, 6H)
2 (n-Pr_2SnA[c]	7.98–7.95 (d, 2H)	7.48–7.38 (t, 4H)	7.25–7.15 (t, 2H)	1.39–1.18 (m, 8H)	0.80–0.74 (t, 6H)
3 n-nBu_2Sna[c]	7.99–7.95 (d, 2H)	7.46–7.37 (t, 4H)	7.23–7.14 (t, 2H)	1.39–1.17 (m, 12H)	0.85–0.77 (t, 6H)
4 n-Oct_2SnA[c]	7.96–7.93 (d, 2H)	7.46–7.33 (t, 4H)	7.24–7.16 (t, 2H)	1.39–1.16 (m, 28H)	0.90–0.75 (t, 6H)
5 $(Me_2Sn)_2A$[c]	8.08–8.02 (d, 2H)	7.45–7.32 (m, 4H)	7.15–7.09 (m, 2H)	—	1.41–1.23 (m, 18H)
6 $(Ph_3Sn)_2A$[c]	7.46–6.85 (m, 38H)	—	—	[d]	[d]

[a] Numbering is according to:



[b] Spectra recorded in $CDCl_3 + DMSO\text{-}d^6$ (4:1). [c] Spectra recorded in $CDCl_3$. [d] $SnPh_3$ protons overlapped by diphenyl protons.

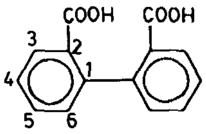
Table 4 ^{13}C NMR spectral data of diorganotin(IV) and triorganotin(IV) complexes of diphenic acid (δ, ppm)

	Biphenyl[a]						Sn—R[a]							
Complex	C_1	C_2	C_3	C_4 and C_5	C_6	COO	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
AH_2[b]	130.74	143.11	130.22	129.58	126.67	168.51	—	—	—	—	—	—	—	—
Aet_2[c]	131.30	143.46	130.40	129.62	127.14	167.41	—	—	—	—	—	—	—	—
1 Me_2SnA[c]	130.08	142.98	129.95	128.35	127.10	175.82	—	—	—	—	—	—	—	—
2 n-Pr_2SnA[c]	131.42	143.09	130.18	129.92	127.10	174.74	18.23	18.05	17.58	—	—	—	—	—
3 n-Bu_2SnA[c]	131.12	143.12	130.04	130.01	126.95	175.53	26.38	26.13	25.12	13.47	—	—	—	—
4 n-Oct_2SnA[c]	130.96	143.08	130.10	129.89	126.82	172.97	33.27	31.88	29.27	29.08	25.60	24.56	22.68	14.12
5 $(Me_3Sn)_2A$[c]	131.52	144.47	130.85	130.25	129.72	172.74	—	—	—	—	—	—	—	—
6 $(Ph_3Sn)_2A$[c]	130.02	136.22	129.06	128.79	128.13	171.65	—	—	—	—	—	—	—	—

[a] Numbering is according to:

1 2 3 4 5 6 7 8

$SnCH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$



[b] Spectra recorded in $CDCl_3$ + DMSO-d^6 (4 : 1). [c] Spectra recorded in $CDCl_3$.

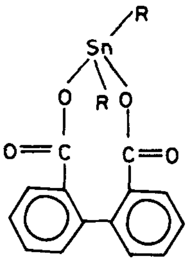


Figure 1

the R groups. The Sn—O bands are assigned in the region 500–400 cm^{-1}.[5]

NMR spectra

The ^{1}H NMR spectrum of the acid (AH_2) was recorded in a mixture of $CDCl_3$ and DMSO-d^6 (4:1) while the spectra of the soluble complexes were recorded in $CDCl_3$ solution and the data are given in Table 3 (δ, ppm). The absence of a single resonance due to the COOH proton at 9.42 ppm in the spectra of the complexes shows deprotonation. The position of the biphenyl protons remains unchanged in the complexes as compared with that in AH_2. In the methyl complex **1** (Table 3) the presence of a singlet indicates the equivalence of both the methyl groups while a non-planar arrangement of methyl groups is indicated in the case of the trimethyltin derivative from the presence of a multiplet. In complexes **2**, **3**, **4** and **6** a triplet due to methyl and a complex pattern due to the remaining alkyl group protons are observed. In the triphenyltin derivative there is ovelapping of the phenyl protons of the diphenic acid with the phenyl protons of the organotin moiety. The integration area is equivalent to the number of protons calculated from the expected structure in all the complexes.

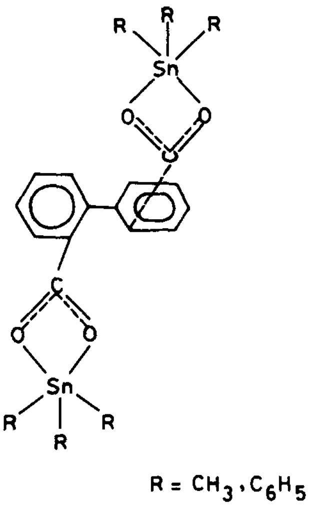


Figure 2

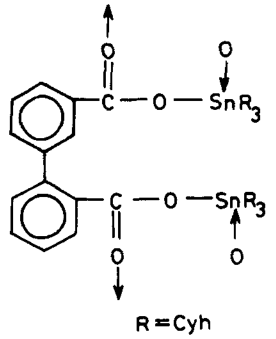


Figure 3

The ^{13}C NMR spectrum of diphenic acid (AH_2) has been recorded in solution in a mixture of $CDCl_3$ and DMSO-d^6 (4:1) while the spectra of its ethyl ester (AEt_2) and of the soluble complexes have been recorded in $CDCl_3$ and the data are given in Table 4 (δ, ppm). The number of signals found corresponds with the presence of magnetically non-equivalent carbon atoms. The positions of phenyl carbon signals in the complexes remain almost unchanged. The carboxylate carbon signal shifts to lower field in complexes **1–7** as compared with that in the acid (AH_2), indicating the participation of the carboxylate group in coordination with tin(IV).[7] The identification of alkyl/phenyl carbons in all the complexes confirms complexation.

CONCLUSION

The IR and NMR data support a tetrahedral structure (Fig. 1) for the diorganotin diphenates with a unidentate carboxylate and *trans* R groups, and a trigonal bipyramidal five-coordinate structure for the trimethyl and triphenyltin(IV) complexes (Fig. 2) with two symmetrically bonded carboxylates and for the tricyclohexyl compound (Fig. 3), which has two asymmetrically bonded carboxylates.

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