

BENZYL COMPOUNDS

V*. THE FAR INFRARED AND RAMAN SPECTRA OF *para*-SUBSTITUTED BENZYL TIN COMPOUNDS

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SUMMARY

The infrared and Raman spectra of some $(Y-C_6H_4CH_2)_nSnCl_{4-n}$ ($Y = F, Cl$, and $n = 3, 2$) compounds have been studied and frequency assignments proposed.

para-Substitution has little influence on the Sn-Cl stretching vibration but causes a slight decrease in the frequency of the Sn-C stretching vibration.

INTRODUCTION

As a part of a study of the vibrational spectra of benzyl derivatives^{1,2,3} we have analyzed the infrared and Raman spectra of some $(Y-C_6H_4CH_2)_nSnCl_{4-n}$ ($Y = F, Cl$ and $n = 3, 2$) compounds. Special attention has been paid to the influence of *para* substitution on the skeletal vibrations and the conformational behaviour of the benzyltin molecules.

EXPERIMENTAL

The synthesis of tetrabenzyltin has been described in a previous report⁴. The various benzyltin halides were prepared by direct synthesis from tin metal and organic halides following the procedure elaborated by Sisido *et al.*⁵.

The infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer. The compounds were studied as solids in nujol mulls between CsI windows, and as solutions in cyclohexane, benzene and acetone in an adjustable infrared cell with CsI windows using several sample thicknesses. A Coderg PH₁ spectrometer equipped with He/Ne gas laser OIP model 181E was used for the Raman study of the solid compounds and the solutions in benzene and acetone.

The relevant experimental data are collected in Tables 1 and 2.

RESULTS AND DISCUSSION

Analysis and interpretation of the vibrational spectra are based on the concept

* For part IV see ref. 3.

TABLE 1
 FUNDAMENTAL FREQUENCIES OF THE $YC_6H_3CH_2Z$ MOIETY^a

$(FC_6H_4CH_2)_3SnCl$	$(FC_6H_4CH_2)_2SnCl_2$	$(ClC_6H_4CH_2)_2SnCl$	$(ClC_6H_4CH_2)_2SnCl_2$	Assignment
637 p (634 w) 637 (633 m)	638 p (635 w) 634 (635 w, 633 (sh))	651 p (647 s) 646 (647 vs, 651 (sh))	652 p (646 s) 651 (651 s)	X-sens
511, 499 p (504 vs, 495 (sh)) 506, 492 (504 vs, 491 vs)	511, 500 p (506 s, 498 (sh)) 494 (508 w, 493 vs)	634 (sh) (631 vw) 634 (631 w) 480, 470 p (479 vs, 470 (sh)) 481, 467 (479 vs, 464 s)	~635 (sh) (~630 vw) 633 (630 vw) 473 p (482 vs, 472 (sh)) 465 (479 m, 464 vs)	α (CCC) 6b ϕ (CC) 16b + ν (Sn-C) ?
469 p (465 m) 469 (466 s, 459 s)	470 p (465 m) 469 (466 s)	394 p (392 w) 392 (393 w)	(395 w) 398 (397 m)	α (CCC) 6a
418 p (417 m) 412 (413 m)	(416 m) (418 m)	~360 (sh) (~360 (sh)) 369 (362 w)	355 p (~360 (sh)) 362 (361 w)	δ (CX) ν_{29}
~350 335 (339 m, 331 (sh))	~350 ~340 (sh) (~340 (sh))	295 p (300 m) ~300 (~300 (sh))	300 p (300 w) 292 (303 m)	δ (CX) ν_{19}
295 p (300 vw) 304, 298	(299 vw) ~300 (sh) (304 (sh))	250 p (248 vw) 259 (252 m)	253 (245 vw)	δ (CX) ν_{30}
156	153	131	132	δ (CX) ν_{20}
61	57	63	63	C-C torsion

^a Raman data are shown first; infrared data are shown in brackets. Data on the first line refer to solutions while those on the second line refer to solid materials.

of isolated group vibrations. The local symmetries of the $YC_6H_5CH_2Z$ moiety ($Z =$ rest of the molecule) and of the C_nMX_m skeleton ($M =$ metal, $X =$ halogen, $n = 2, 3, m = 1, 2$) are considered separately.

The $YC_6H_5CH_2Z$ moiety has been studied in a previous paper², the bands originating from vibrations of the $YC_6H_5CH_2Z$ moiety being easily assigned (Table 1).

The C_3SnCl and C_2SnCl_2 skeletons belong to the point group C_{3v} and C_{2v} respectively. A complication in the interpretation of the vibrational spectra is the possibility that a change in the skeletal symmetry occurs through autocomplexation and/or solvent interaction. Studies of the tin-chlorine stretching vibration may be used to resolve this question, however, for $\nu(Sn-Cl)$ is known to be very sensitive to association. Thus autocomplexation (with chlorine atom bridges) and solvent interaction affecting the hybridisational state of the tin atom have both been reported⁶ as causing a marked decrease in the $\nu(Sn-Cl)$ frequency. The $\nu(Sn-Cl)$ frequency data obtained in this study (Table 2) indicate that in this case free molecules exist

TABLE 2

FUNDAMENTAL FREQUENCIES OF THE C_nSnCl_{4-n} SKELETON^a

	C_6H_{12}	C_6H_6	$(CH_3)_2Co$	Solid (in nujol)
<i>a. $\nu(Sn-Cl)$</i>				
$(C_6H_5CH_2)_3SnCl$	345 p (340 vs)	343 p (334 vs)	~ 310 (~ 310 m)	295 (295 vs) ^b
$(FC_6H_4CH_2)_3SnCl$	331 p (339 vs)	330 p (336 vs)	~ 300 (~ 300 m)	304 (291 vs) 298 (313 (sh)) (302 (sh))
$(ClC_6H_4CH_2)_3SnCl$	345 p (341 vs)	338 p (333 vs)	~ 300 (300 m)	293 (298 vs)
$(C_6H_5CH_2)_2SnCl_2$		352 p (348 vs)	~ 340 (335 m)	341 (336 vs) 323 (320 vs)
$(FC_6H_4CH_2)_2SnCl_2$		351 p (349 vs)	329 (337 vs) (325 (sh))	(332 vs) 324 (327 vs) (318 (sh))
$(ClC_6H_4CH_2)_2SnCl_2$		354 p (348 vs)	~ 325 (328 s)	329 (324 vs)
<i>b. $\nu(Sn-C)$</i>				
$(C_6H_5CH_2)_3SnCl$	582 (577 w) 563 p	583 (576 w) 566 p	584 565 p	582 (582 vw) 563 (558 vw)
$(FC_6H_4CH_2)_3SnCl$	~ 575 (578 vw) 557 p (553 vw)	~ 575 563 p (~ 565 m) ^b	576 561 p (558 w)	572 (570 w) 559 (560 w)
$(ClC_6H_4CH_2)_3SnCl$		572 (~ 570 (sh)) 556 p (556 w)	574 558 p	574 (571 w) 545 (545 w)
$(C_6H_5CH_2)_2SnCl_2$		(581 w) 570 p (563 w)	~ 590 572 p	~ 583 (580 s) 568 (566 w)
$(FC_6H_4CH_2)_2SnCl_2$		(570 w) (560 w)	~ 580 (573 m) 567 p (~ 565 (sh))	(571 s) 564 (560 (sh))
$(ClC_6H_4CH_2)_2SnCl_2$		(572 vw) (563 vw)	564 p	(567 s) 562 (558 (sh))

^a Raman data are shown first; infrared data are shown in brackets. ^b Unresolved multiplet.

in cyclohexane and benzene solutions, from which it follows that the vibrational spectra of these solutions can be analyzed from the basis of the proposed symmetry.

Some controversy still exists, however, about the vibrational bands in the 450–500 cm^{-1} region³. On one hand, the frequency shifts observed in this region on *para*-substitution are consistent with those observed for the 16b vibration. On the other hand, the Raman bands show the characteristic pattern for $\nu(\text{Sn}-\text{C})$ vibrations (sym. vibration: strong, polarized; asym. vibration: weak, depolarized). To resolve this problem it is proposed to study in the near future the vibrational spectra of some *meta*- and *ortho*-substituted benzytlin compounds.

The influence of *para*-substitution on the skeletal Sn–Cl stretching vibration is apparently negligible, which is not unexpected when it is considered that a distance of six bonds exists between the substituent and the tin atom. In contrast, *para*-substitution causes a slight decrease in the frequency of the Sn–C stretching vibration (Table 2b). This may be due to the electron-withdrawing effect of the halogen substituents, causing a lowering of the $p_{\pi}-d_{\pi}$ overlap between the π -electron cloud of the phenyl ring and the appropriate d -orbital of the tin atom and resulting in a weakening of the Sn–C bond.

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