Use of the Metal-isotope Technique (Tin-116 and -124) to confirm Assignments in the Vibrational Spectra of Phenyltin Compounds

By **Nigel S. Dance** and **William R. McWihnnie,*** Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET
Robert C. Poller, Department of Chemistry, Queen Elizabeth College, London W8 7AH

Samples of isotopically pure (^{116}Sn and ^{124}Sn) tetraphenyltin, triphenyltin iodide, and triphenyltin acetate have been prepared and their i.r. spectra recorded. Shifts of bands corresponding to metal-sensitive vibrations of the order of 5 cm^{-1} have been observed. In this way the results of earlier empirical studies are shown to be broadly correct but some assignments need modification. It is noted that the term ‘ tin–phenyl stretch ’ has physical significance.

THE accumulated literature of organotin chemistry[1] inevitably contains many papers describing the infrared spectra of various classes of compound. The study, by vibrational spectroscopy, of phenyltin compounds has not been neglected with the result that, after the publication of a number of careful but empirical studies, assignments are generally accepted. Thus in the lower-frequency region the assignments of Poller[2] are accepted and shown to be applicable to a wide range of phenyltin compounds.[3] Modes involving movement of the tin atom have been variously designated ‘ tin–phenyl stretch or bend ’[2,3] or have been labelled as *X*-sensitive modes[4] following Whiffen.[5] The middle view that both descriptions are approximate[6] has also been advanced.

Isotopic studies, following Nakamoto,[7] on phenyltellurium dihalides[8] recently demonstrated that it is possible to base assignments for phenylmetal compounds on a firm experimental footing. In this short paper we attempt this for some phenyltin compounds.

EXPERIMENTAL

The compounds chosen for the study were $SnPh_4$, $SnPh_3I$, and $SnPh_3(O_2CMe)$. Tetraphenyltin is of known crystal structure.[9] Triphenyltin iodide is readily prepared and the $SnPh_3$ group is of approximate C_{3v} symmetry; also there was in our view some uncertainty in the assignment of ν(SnI). Finally, $SnPh_3(O_2CMe)$ was chosen since it is believed that the $SnPh_3$ group may be planar due to the tin atom becoming five-co-ordinate in the crystal *via* bridging carboxylate groups.[10] Thus the three compounds offer a variety of relatively high skeletal symmetries.

Economic constraints placed an upper limit on the use of the pure tin isotope of 20 mg per synthesis. Thus

---

[1] R. C. Poller, ‘ The Chemistry of Organotin Compounds,’ Logos Press, London, 1970.

[2] R. C. Poller, *Spectrochim. Acta*, 1966, **22**, 935.

[3] J. R. May, W. R. McWhinnie, and R. C. Poller, *Spectrochim. Acta*, 1971, **A27**, 969.

[4] A. L. Smith, *Spectrochim. Acta*, 1968, **A24**, 695.

[5] D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

[6] J. R. Durig, C. W. Sink, and J. B. Turner, *Spectrochim. Acta*, 1970, **A26**, 557.

[7] K. Nakamoto, *Angew. Chem. Internat. Edn.*, 1972, **11**, 666.

[8] N. S. Dance and W. R. McWhinnie, *J.C.S. Dalton*, 1975, 43.

[9] P. C. Chieh and J. Trotter, *J. Chem. Soc.* (*A*), 1970, 911.

[10] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1873.

various routes to tetraphenyltin starting from elemental tin (20 mg) were evaluated. The route chosen as the most satisfactory is outlined below. Isotopically pure tin (^{116}Sn or ^{124}Sn, 20 mg) was dissolved in concentrated hydrochloric acid and evaporated to dryness to afford tin(II) chloride dihydrate. A slurry of this material in diethyl ether was treated, dropwise, with an excess of phenyl-lithium in diethyl ether. A transitory red colour gave way to a white precipitate which was treated with bromobenzene (0.5 cm^3) and heated under reflux (30 min). The reaction mixture was hydrolysed with saturated ammonium chloride solution and extracted with hot benzene. Recrystallisation of the product from benzene afforded pure tetraphenyltin (15—20 mg). Tetraphenyltin could then be converted quantitatively into triphenyltin iodide by treatment with the stoicheiometric quantity of iodine in chloroform solution. Triphenyltin acetate was then obtained from $SnPh_3I$ in 80% yield by treatment with silver(I) acetate.

Infrared spectra were recorded in Polythene discs by taking replicate scans on a Perkin-Elmer 225 instrument and on a RIIC FS 720 interferometer. Peak positions were reproduced exactly in replicate scans on the interferometer and to within ± 0.5 cm^{-1} with the Perkin-Elmer 225. Since the observed shifts were of the order of 5 cm^{-1} they could be unambiguously identified.

RESULTS AND DISCUSSION

Relevant shift data are given in the Table.

Tetraphenyltin.—The results give a satisfactory confirmation of earlier assignments[3] of ν_{asym}(SnPh). The two bands that undergo a shift reasonably correspond to the $(B + E)$ components of the antisymmetric stretching mode in S_4 symmetry.[9] The weak band at 221 cm^{-1} was assigned as ν_{sym}(SnPh)[3] which should be inactive in the i.r. No motion of the tin atom is involved in the symmetric breathing mode, hence the absence of a shift is consistent with (but does not confirm) the earlier assignment. No measurable shifts for deformation modes are expected.[7]

Spectra of isotopically pure (^{116}Sn or ^{124}Sn) phenyltin compounds below 400 cm^{-1} [625 cm^{-1} for $SnPh_3(O_2CMe)$]

$^{116}SnPh_4$	$^{124}SnPh_4$	Assignment
396w	396w	w_1
389w	389w	w
*270*s	*265*s	ν_{asym}(SnPh)
265 (sh)	*259* (sh)	
221w	221w	ν_{sym}(SnPh)
209m	209m	δ(SnPh) (or phenyl u)
192m	192m	
151w	151w	
$^{116}SnPh_3I$	$^{124}SnPh_3I$	
*271*s	*266*s	ν_{asym}(SnPh)
262 (sh)	262 (sh)	
*242*m	*238*m	ν_{sym}(SnPh)
235m	235m	phenyl u
*159*w	*154*w	ν(SnI)
$^{116}SnPh_3(O_2CMe)$	$^{124}SnPh_3(O_2CMe)$	
322w	322w	δ(OCO)
284 (sh)	*280* (sh)	ν_{asym}(SnPh)
*274*s	*269*s	
265 (sh)	*260* (sh)	
211m	211m	phenyl u
205w	205w	
450m	450m	phenyl y
*612*w	608w	ν(SnO)

Triphenyltin Iodide.—Some modifications to earlier assignments are needed. Poller[2] assigned bands in the solution spectrum of $SnPh_3I$ at 265—272 cm^{-1} as ν_{asym}(SnPh) and at 241 and 239 cm^{-1} as ν_{sym}(SnPh). The great similarity between solution and solid-state spectra indicates that no major structural change occurs on crystallisation. Since the structure is reasonably expected to be trigonal pyramidal with a skeletal (SnC_3I) symmetry C_{3v}, both ν_{asym}(SnPh) and ν_{sym}(SnPh) should undergo isotopic shifts. Thus the data show that the bands at 271 (^{116}Sn) or 266 cm^{-1} (^{124}Sn) are due to ν_{asym}(SnPh), and those at 242 (^{116}Sn) or 238 cm^{-1} (^{124}Sn) are due to ν_{sym}(SnPh). The modes at 262 and 235 cm^{-1} did not undergo measurable shifts. Also a weak band at 159 cm^{-1} (^{116}Sn) underwent a shift to 154 cm^{-1} (^{124}Sn) which identifies it as the tin–iodine stretching frequency. This does not agree with a previous assignment of 170 cm^{-1} from a Raman study.[11] The band at 170 cm^{-1} is probably the phenyl x mode which can be strong in the Raman and weak or absent in the i.r.

Triphenyltin Acetate.—The i.r.-active tin–phenyl stretch was clearly located at *ca.* 272 cm^{-1}; however, it is a composite band which indicates that a skeletal symmetry of D_{3h} for SnC_3 is an inadequate basis for interpretation of the spectrum. This is perhaps not surprising in this case where we anticipate a polymeric structure, and it is hence dangerous to conclude on this evidence that the SnC_3 group may be non-planar. Other assignments suggested do follow closely those suggested for triphenyltin benzoate,[3] and we are able to be more positive in the assignment of a tin–oxygen stretch at *ca.* 610 cm^{-1}.

This brief investigation has placed much previous work on a sounder experimental footing. Whiffen[5] pointed out that, for a monosubstituted benzene (PhX), three modes (q, r, and t) involve stretching of the Ph–X bond. Further, the work of Becher and Hofler[12] on the monohalogenobenzenes indicated that the fraction of Ph–X stretching in the t mode increases very significantly with the mass of the halogen atom. In view of the fact that no modes other than those indicated in the Table show metal sensitivity, we are of the view that the description 'tin–phenyl stretch' does have some physical basis when applied to the metal-sensitive low-frequency vibrations.

One of us (N. S. D.) thanks the S.R.C. for a studentship.

[6/935 *Received*, 17*th May*, 1976]

---

[11] H. Kriegsmann and H. Geissler, *Z. anorg. Chem.*, 1963, **323**, 170.

[12] H. J. Becher and F. Hofler, *Spectrochim. Acta*, 1969, **A25**, 1703.