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MÖSSBAUER STUDIES OF SOME HETEROARYL- AND SUBSTITUTED ARYL-TIN COMPOUNDS

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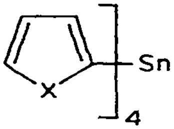
Summary

Mössbauer data are reported for tetra-(2-furyl)tin, tetra-(2-thienyl)tin and a range of tetraaryltin compounds. It is concluded that the significant decrease in isomer shifts in the heteroaryl derivatives compared to these in tetraphenyltin is due to the marked σ-electron-withdrawing capacity of the heteroaryl groups which result from the inductive effect of the heteroatoms.

Introduction

Recently we have been interested in assessing the electronic effects of heteroaryl substituents (e.g. 2-furyl, 2-thienyl) on reactions occurring at phosphorus. Such five membered heteroaromatic substituents are of considerable interest in that they are able to act either as electron-donating or electron-withdrawing groups. When the π-electron system of the heterocycle interacts with an adjacent atom, then the ring system is electron-donating, but when such π-interactions do not occur, then the ring systems behave as electron-withdrawing groups, due to the electronegativity of the heteroatoms. From the results of studies of the reactivity of a wide range of compounds [1], we have concluded that when directly attached to phosphorus, the 2-furyl and 2-thienyl groups behave as significantly electron-withdrawing substituents. There would seem to be little tendency for these "π-excessive" heterocyclic systems to be involved in $p_\pi \rightarrow d_\pi$ interaction with the Group V element.

We have now extended our study of substituent effects to organotin compounds, and in this paper report a study of the Mössbauer spectra of the tetraheteroaryltin compounds (I, X = O or S), together with a comparison of the Mössbauer data for some substituted aryltin compounds.



(I)

Experimental

Tetra-(2-furyl)tin and tetra-(2-thienyl)tin were prepared by the reactions of the appropriate 2-heteroaryl organolithium reagent with tin(IV) chloride in ether, as described previously [2]. Samples of tetra(*o*-tolyl)tin, tetra(*m*-tolyl)-tin, tetra(*p*-tolyl)tin, tetra(*p*-chlorophenyl)tin, and tetra(*o*-phenoxyphenyl)tin were kindly supplied by Dr. E.J. Bulten, of TNO Utrecht, The Netherlands.

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer, the symmetrical triangular velocity drive waveform being derived from the multichannel analyser driven in the time mode by an external crystal controlled oscillator, 512 channels were used throughout. A 15 mCi $Ca^{119}SnO_3$ source was used at room temperature, and the samples were packed in perspex discs and cooled to 80 K using a continuous flow cryostat with helium exchange gas. The spectrometer was calibrated using the magnetic splitting of an enriched ^{57}Fe absorber foil. The data were folded to determine the zero velocity position, and the folded data fitted with Lorentzian functions by a least squares fitting program [3].

The non-linearity of the spectrometer was determined, by a free fit of the Fe data, to be less than ±0.06%. The quoted experimental error of ±0.02 mm s^{-1} in the measured values of the isomer shift takes into account errors associated with non-linearities, calibration, zero velocity determination and computer fitting.

Results and discussion

Table 1 shows the ^{119m}Sn Mössbauer data for the tetraheteroaryltin compounds, together with that recorded for tetraphenyltin and some substituted aryltin compounds under the same conditions.

Figure 1 shows the Mössbauer spectrum of tetra(*o*-tolyl)tin which is typical of the series; the solid line represents the computer fit to the data.

Each of the compounds studied gave a single line absorption. The isomer shifts of the heteroaryltin compounds I (X = O or S) are seen to be significantly different from those of tetraphenyltin and the substituted tetraaryltin compounds, and indicate a reduction in the *s*-electron density at the tin atom in the heteroaryl derivatives. This decrease in electron density in the heteroaryl derivatives compared to the aryl systems could be attributed to one, or a combination of, the following:

TABLE 1

MÖSSBAUER DATA FOR TETRA(HETERO)ARYLTIN COMPOUNDS, Ar_4Sn

Ar	Isomer shift [a] $\delta \pm 0.02$ mm s^{-1}
2-Furyl	1.06
2-Thienyl	1.10
Phenyl	1.26
o-$CH_3C_6H_4$	1.27
m-$CH_3C_6H_4$	1.25
p-$CH_3C_6H_4$	1.28
p-ClC_6H_4	1.25
o-$C_6H_5OC_6H_4$	1.20

[a] Relative to $CaSnO_3$.

(i) the σ-inductive effect of the heteroaryl groups due to the electronegative heteroatom;

(ii) an increase in the atomic core shielding effect due to an increase in p, d, or f-electron density near to the nucleus as a result of e.g. $p_\pi \rightarrow d_\pi$ interactions with the heteroatoms; and

(iii) an increase in the coordination number of the tin atom as a result of inter- or intra-molecular interactions with the heteroatoms.

That (iii) is the possible cause of the observed effects is effectively ruled by the results of recent X-ray structural studies [4] of I (X = S) which showed that

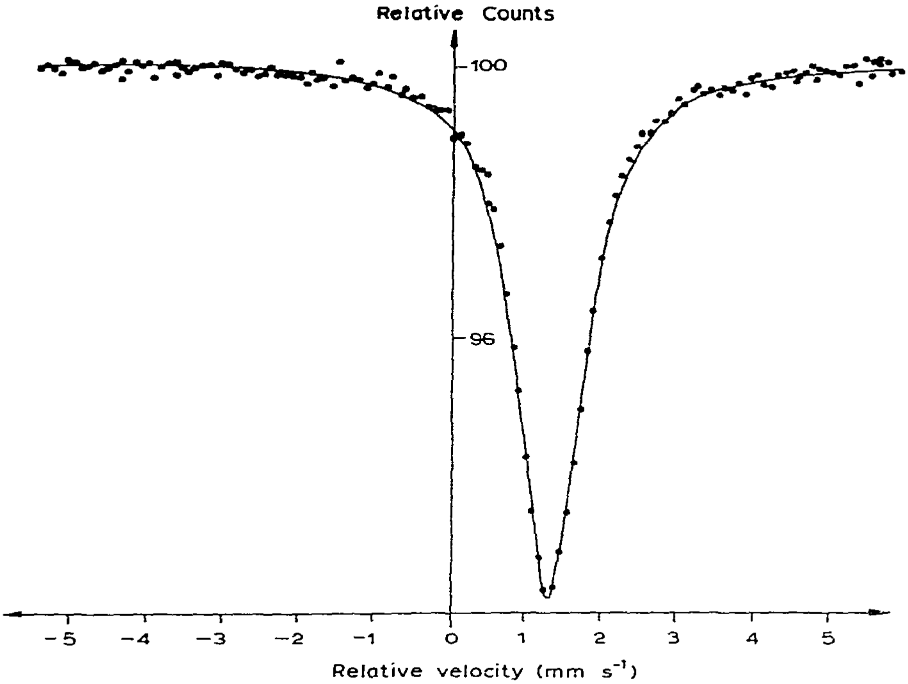


Fig. 1. Mössbauer spectrum of tetra(o-tolyl)tin (50 mg) recorded at 80 K.

the coordination about tin is tetrahedral, and that the nearest tin—sulphur distance is outside the sum of the Van der Waals radii.

Studies of the ^{117}Sn and ^{119}Sn satellites in the ^{1}H NMR spectra of tetraheteroaryltin compounds have been interpreted as indicating that there is little or no $p_\pi \rightarrow d_\pi$ interaction between the "π-excessive" ring system and the tin atom [5]. The same conclusion was reached following ^{13}C NMR studies on a range of phenyl, furyl, and thienyl organometallic compounds [6].

If these conclusions are valid, then the decrease in the Mössbauer isomer shifts for tetra-2-furyl- and tetra-2-thienyl-tin must be caused by (i) above, i.e., a decrease in the *s*-electron density at the tin nucleus as a result of the inductive effect of the heteroatom.

The isomer shift data for the substituted phenyltin compounds (Table 1) and also comparable data in the literature for other compounds of this type, show that both the nature and position of the substituent group have little effect on the *s*-electron density at the tin atom. This is probably because, in most cases, the inductive effect of the substituent is largely insulated from the tin by the intervening carbon atoms. In the case of the heteroaryltin compounds I, the heteroatom is only one atom removed from the metal.

The Mössbauer data for tetrakis(*o*-phenoxyphenyl)tin are also of some interest. The isomer shift is slightly lower than for the other tetraaryltin compounds studied, in keeping with the inductive effect of the *o*-oxygen atom, two atoms removed from tin. However, there is no evidence for an intramolecular coordination from the *o*-oxygen atom to the tin similar to those believed to be involved in related phosphorus [7], arsenic [8] and iridium [9] compounds. Such an interaction would have been expected to cause at the very least a broadening of the Mössbauer lines, if not the appearance of quadrupole splitting. In the spectrum of the above compound, the line width was of the same order as for the other tetraaryltin compounds.

References

1 See, e.g., D.W. Allen, B.G. Hutley and M.T.J. Mellor, J. Chem. Soc. Perkin II, (1974) 1690; (1977) 789; (1977) 1705.

2 G. Barbieri and F. Taddei, J. Chem. Soc. (B), (1971) 1903.

3 G. Lang and B.W. Dale, Nucl. Instrum. Methods, 116 (1974) 567.

4 A. Karipides, A.T. Reed, D.A. Haller and F. Hayes, Acta Crystal., B33 (1977) 950; D.W. Allen and I.W. Nowell, unpublished results.

5 G. Barbieri and F. Taddei, J. Chem. Soc. Perkin II, (1972) 1323.

6 D. Doddrell, K.G. Lewis, C.E. Mulquiney, W. Adcock, W. Kitching and M. Bullpit, Austr. J. Chem., 27 (1974) 417.

7 W.E. McEwen, Wen-I. Shiau, Younn-Ing Yeh, D.N. Schulz, R.U. Pagilagan, J.B. Levy, C. Symmes Jr., G.O. Nelson and I. Granoth, J. Amer. Chem. Soc., 97 (1975) 1787.

8 W.E. McEwen, J.E. Fountaine, D.N. Schulz and Wen-I. Shiau, J. Org. Chem., 41 (1976) 1684.

9 E.M. Miller and B.L. Shaw, J. Chem. Soc. Dalton, (1974) 480.