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A ^{19}F NMR INVESTIGATION OF THE TRANSMISSION OF ELECTRONIC EFFECTS THROUGH TIN–AROMATIC CARBON BONDS

D. N. KRAVTSOV, B. A. KVASOV, T. S. KHAZANOVA and E. I. FEDIN
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
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SUMMARY

A number of triaryl(4-fluorophenyl)tin compounds have been prepared. The fluorine chemical shifts relative to fluorobenzene as an internal standard have been measured for all these compounds in chloroform, and a linear relationship between these values and the $\Sigma\sigma^{\circ}$ values for the substituted phenyl groups attached to the tin atom has been demonstrated. The results obtained suggest that the transmission of electronic effects from one aromatic ring to another in compounds of the type Ar_4Sn occurs mainly by an inductive mechanism. In conjunction with the data on similar systems containing other bridging atoms, the results obtained provide a quantitative measure of the relative ability of tin–aromatic carbon bonds to transmit electronic effects.

INTRODUCTION

In a previous paper[1] we have reported a ^{19}F NMR spectroscopic study of electronic effects in the systems $4\text{-}FC_6H_4Sn(CH_3)_2X$ and $4\text{-}FC_6H_4Sn(CH_3)_2Ar$ which has enabled quantitative data to be obtained on the ability of the $Sn(CH_3)_2$ bridging group to relay electronic effects. On the basis of this investigation it has been concluded that in order to obtain a more exact and quantitative evaluation of the ability of tin–aromatic carbon bonds to transmit such effects a study should be made of model systems in which the relative contributions from various types of electronic interactions which may operate in tin–substituent bonds would remain approximately constant in a given series of compounds even though the electronic properties of the substituents attached to the metal atom may vary considerably. Compounds of the general type $Ar_3SnC_6H_4F\text{-}4$ appear to be the most suitable from this point of view, because the electronic interactions in the tin–aromatic carbon bond are apparently mainly inductive and because simultaneous variation of the nature of the three aryl groups attached to the tin atom would be expected to produce a considerable range of fluorine chemical shifts associated with the *p*-fluorophenyl group. In conjunction with data on similar systems containing carbon or lead bridging atoms, this would provide more reliable quantitative evidence for the relative ability of the tin–aromatic carbon bonds to transmit electronic effects.

RESULTS AND DISCUSSION

A number of compounds of the type $Ar_3SnC_6H_4F$-4, where Ar=4-$(CH_3)_2NC_6H_4$, 4-$CH_3OC_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, C_6H_5, 4-FC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 3-$CF_3C_6H_4$, 3,4-$Cl_2C_6H_3$, 3,5-$Cl_2C_6H_3$ or 3,4,5-$Cl_3C_6H_2$, have been prepared in the present work and the fluorine chemical shifts relative to fluorobenzene as an internal standard have been determined in chloroform for them all. This solvent was used because it had been shown previously[1] that in most cases changing the solvent from cyclohexane to chloroform does not significantly influence the electronic effect of the $Sn(CH_3)_2Ar$ substituents and because all the compounds studied were reasonably soluble in this solvent. The data on the fluorine chemical shifts observed for the compounds studied are presented in Table 1.

TABLE 1

^{19}F CHEMICAL SHIFTS FOR TRIARYL-(4-FLUOROPHENYL)TIN COMPOUNDS IN CHLOROFORM RELATIVE TO INTERNAL FLUOROBENZENE (in ppm)

Compound	δ_F
4-$FC_6H_4Sn(C_6H_4N(CH_3)_2-4)_3$	−0.16
4-$FC_6H_4Sn(C_6H_4OCH_3$-4$)_3$	−1.13
4-$FC_6H_4Sn(C_6H_4CH_3$-4$)_3$	−1.13
4-$FC_6H_4Sn(C_6H_4CH_3$-3$)_3$	−1.15
4-$FC_6H_4Sn(C_6H_5)_3$	−1.52
4-$FC_6H_4Sn(C_6H_4F$-4$)_3$	−2.31
4-$FC_6H_4Sn(C_6H_4Cl$-4$)_3$	−2.63
4-$FC_6H_4Sn(C_6H_4Cl$-3$)_3$	−3.07
4-FC $H_4Sn(C_6H_4CF_3$-3$)_3$	−3.43
4-$FC_6H_4Sn(C_6H_3Cl_2$-3,4$)_3$	−3.91
4-$FC_6H_4Sn(C_6H_3Cl_3$-3,5$)_3$	−4.53
4-$FC_6H_4Sn(C_6H_2Cl_3$-3,4,5$)_3$	−5.25

The results obtained clearly show that the fluorine chemical shift associated with the *p*-fluorophenyl group depends substantially upon the nature of the aryl substituent attached to the metal atom, the overall range of ^{19}F chemical shifts in the system studied being approximately equal to 5 ppm. From Fig. 1 and Table 2 it can be seen that a good linear relationship exists between the values of the fluorine chemical shift in the series of compounds studied and the $\Sigma\sigma^\circ$ values for the substituted phenyl group[2] attached to the metal atom. The existence of such a linear relationship between δ_F and $\Sigma\sigma^\circ$ indicates that transmission of substituent effects from one aromatic ring to another through the tin atom proceeds mainly by an inductive mechanism. The lack of any mesomeric interaction between a *para*-substituent on the aromatic group attached to the tin atom and the fluorine in the *p*-fluorophenyl group is especially clearly demonstrated by the fact that introduction of *p*-methoxy and *p*-methyl groups has a similar effect on the fluorine chemical shift despite the fact that these two groups exert a considerably different effect on the fluorine shielding as far as competitive conjugation between these groups and the fluorine on the benzene ring is concerned[3]. At the same time, it should be remembered that due to the specific

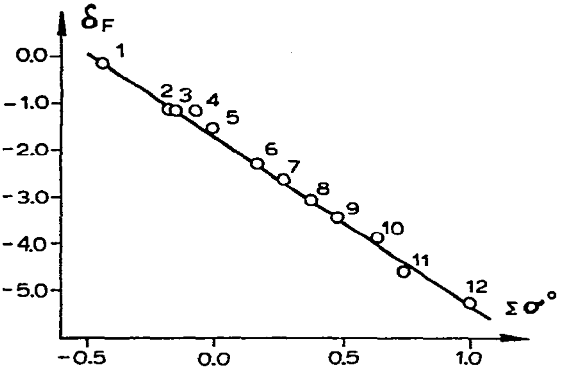

Fig. 1. Plot of the ^{19}F chemical shifts for 4-$FC_6H_4SnAr_3$ in chloroform *versus* the $\Sigma\sigma^{\circ}$ values for the substituted phenyl groups attached to the metal atom: 1, 4-$(CH_3)_2NC_6H_4$; 2, 4-$CH_3OC_6H_4$; 3, 4-$CH_3C_6H_4$; 4, 3-$CH_3C_6H_4$; 5, C_6H_5; 6, 4-FC_6H_4; 7, 4-ClC_6H_4; 8, 3-ClC_6H_4; 9, 3-$CF_3C_6H_4$; 10, 3,4-$Cl_2C_6H_3$; 11, 3,5-$Cl_2C_6H_3$; 12, 3,4,5-$Cl_3C_6H_2$.

TABLE 2

PARAMETERS OF CORRELATION EQUATIONS[a] ($Y = a + bX$)

System	*X*	*Y*	*n*	*a*	*b*
	$\Sigma\sigma^{\circ}$	δ_F	12	−1.65	−3.65
4-$FC_6H_4SnAr_3$	*S*	S_a	S_b	*r*	*CL*
	0.122	0.0407	0.0861	0.997	99.9
System	*X*	*Y*	*n*	*a*	*b*
4-$FC_6H_4SnAr_3$ (I)	δ_F(I)	δ_F(II)	6	−0.122	0.269
4-$FC_6H_4Sn(CH_3)_2Ar$ (II)	*S*	S_a	S_b	*r*	*CL*
	0.0355	0.0298	0.009	0.996	99.9

[a] n = Number of compounds in the system; r = correlation coefficient; S = standard error of the estimate; S_a = standard error of the coefficient a; S_b = standard error of the coefficient b; CL = confidence level for significance of correlation.

geometry of the *d*-orbitals it is not possible to completely exclude the possibility of some d_{π}–p_{π} interaction between the vacant tin orbitals and each separate aromatic ring[4–5].

The rather narrow confidence limits for the slope of the correlation line, which is equal to -3.65 ± 0.19 with a 95% significance level, is of considerable interest. In conjunction with data on similar systems containing other bridging atoms this allows the quantitative characterization of the relative ability of tin–aromatic carbon bonds to transmit electronic effects with a relative error of only ±5%. Thus, the results obtained can be used to compare the transmission ability of tin–aromatic carbon bonds with those of lead–aromatic carbon and aliphatic carbon–aromatic carbon bonds by employing the model systems $Ar_3PbC_6H_4F$-4 and $Ar_3CC_6H_4F$-4. In this connection it should be noted that the influence of substituted phenyl groups attached to the tin atom upon the fluorine shielding appears to be approximately additive. This is revealed by a comparison of the systems $Ar_3SnC_6H_4F$-4 and $Ar(CH_3)_2SnC_6H_4F$–4. Plotting the fluorine chemical shifts for compounds of the latter system[1] against those of the former gives a good linear relationship (Fig. 2, Table 2), the 95% confidence limits for the slope of the straight line obtained being

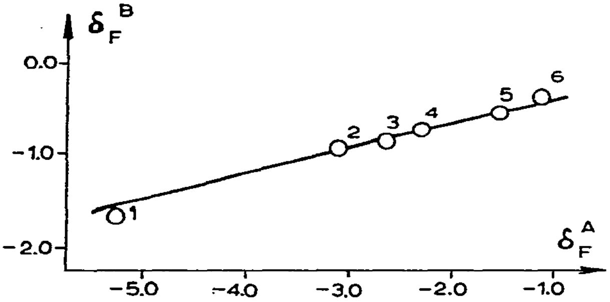

Fig. 2. Plot of the ^{19}F chemical shifts for 4-$FC_6H_4Sn(CH_3)_2Ar$ in chloroform (δ_F^A) *versus* those for 4-$FC_6H_4SnAr_3$ in the same solvent (δ_F^B): 1, 3,4,5-$Cl_3C_6H_2$; 2, 3-ClC_6H_4; 3, 4-ClC_6H_4; 4, 4-FC_6H_4; 5, C_6H_5; 6, 4-$CH_3OC_6H_4$.

0.269±0.026. The somewhat smaller value of the slope compared to the expected value of 0.33 may be related to the influence of the nature of the organic radicals upon the efficiency of the tin atom to transmit electronic effects, as well as to some deviation from an additive relationship.

In conclusion, it is hoped that further work, which is presently underway, will enable quantitative estimations to be made of the extent to which the nature of the bridging atom affects the transmission of electronic effects in lead and carbon analogues of the organotin compounds investigated in this present study.

EXPERIMENTAL

General

The ^{19}F NMR spectra were recorded at 34° on a Hitachi–Perkin–Elmer R-20 spectrometer operating at 56.4 MHz. All measurements were performed on solutions of concentration not greater than 0.2 $mol \cdot l^{-1}$. The use of the substitution method for the determination of fluorine chemical shifts has been described elsewhere[6]. The experimental error in the estimation of the fluorine chemical shifts was not greater than ±0.1 ppm. Chloroform was purified by a conventional method and distilled over phosphorus pentoxide, its purity being checked by means of its ^{1}H NMR spectrum.

The organotin compounds studied in the present communication were synthesized by the action of the corresponding organo-magnesium or -lithium compounds upon 4-fluorophenyltin trichloride as reported in the literature[7]. The preparation of tetra(4-fluorophenyl)tin and triphenyl(4-fluorophenyl)tin has been

TABLE 3

ANALYTICAL DATA AND MELTING POINTS OF TRIARYL(4-FLUOROPHENYL)TIN COMPOUNDS

Compound	*Yield*	*M.p.*	*Analysis* *found (calcd.)* (%)	
	(%)	(°)	*C*	*H*
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{CH}_3\text{-4})_3$	75	170	66.53 (66.53)	5.36 (5.13)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{CH}_3\text{-3})_3$	69	75	66.47 (66.53)	5.35 (5.13)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{OCH}_3\text{-4})_3$	37	74	61.02 (61.41)	4.94 (4.91)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{Cl-4})_3$	70	169	52.50 (52.50)	2.89 (2.95)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{Cl-3})_3$	66	84	52.56 (52.50)	2.82 (2.95)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_3\text{Cl}_2\text{-3,4})_3$	58	148	43.87 (44.22)	2.07 (2.01)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_3\text{Cl}_2\text{-3,5})_3$	54	142	44.16 (44.22)	2.39 (2.01)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_2\text{Cl}_3\text{-3,4,5})_3$	50	145	38.07 (38.17)	1.30 (1.33)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{CF}_3\text{-3})_3$	66	84	49.66 (49.96)	2.63 (2.49)
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{-4})_3$	73	144	62.79 (62.73)	6.13 (5.97)

described in the literature previously$^{7-8}$. Some typical examples of the preparation of the triaryl(4-fluorophenyl)tin compounds are given below. Analytical results and melting points of compounds not reported in the literature are presented in Table 3.

Tris(4-methylphenyl) (4-fluorophenyl)tin

To a solution of *p*-tolylmagnesium bromide obtained from 5.85 g (35 mmol) of 4-bromotoluene and 0.85 g of magnesium turnings in 30 ml of dry ether was added 3.2 g (10 mmol) of (4-fluorophenyl)tin trichloride with stirring^7. After refluxing for 2 h, the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl. The ether layer was separated, washed with an aqueous solution of KF and water, dried over $CaCl_2$ and the solvent removed under reduced pressure. 2.5 g (75%) of a crystalline substance were obtained and purified by recrystallization from pentane.

Tris(4-dimethylaminophenyl) (4-fluorophenyl)tin

To a solution of 4-dimethylaminophenyllithium (prepared from 6.0 g (30 mmol) of 4-bromodimethylaniline and 0.22 g of lithium in 20 ml of dry ether) under nitrogen was added 3.2 g (10 mmol) of (4-fluorophenyl)tin trichloride with stirring. After refluxing for 1 h, the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl. The ether layer was separated, washed with an aqueous solution of KF and water, dried over Na_2SO_4 and the solvent removed. 4.2 g (73%) of a crystalline substance were obtained and recrystallized from ethanol. The other triaryl(4-fluorophenyl)tin compounds were prepared in a similar fashion and recrystallized from hexane or ethanol.

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