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A ^{19}F NMR STUDY OF ELECTRONIC EFFECTS IN ORGANOMERCURY, -TIN AND -LEAD DERIVATIVES OF SOME FLUOROPHENOLS AND FLUOROTHIOPHENOLS

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SUMMARY

A number of organomercury, -tin and -lead derivatives of *m*- and *p*-fluoro-substituted phenols and thiophenols of the type R_nMOAr and R_nMSAr have been prepared. The ^{19}F chemical shifts relative to fluorobenzene have been measured in various solvents for all these compounds. On the basis of the data obtained, the electronic features of the substituents R_nMO and R_nMS have been studied and compared with those of OH, CH_3O, SH and CH_3S groups. The influence of various factors on the electronic effect of the organometallic substituent and on its solvent susceptibility is discussed. The coordinating abilities of the substituents $(C_2H_5)_3SnO$ and $(C_2H_5)_3$-SnS in solution have been compared with those of the OH and SH groups.

INTRODUCTION

In connection with our studies relating to the structure of organometallic derivatives of some tautomeric and potentially tautomeric systems[1-3], it has proved necessary to obtain quantitative evidence concerning the electronic effects of organomercury, -tin and -lead groups of the type R_nMOAr and R_nMSAr in the ground state as well as the effect of solvent. Information concerning this problem is meagre at present and includes an investigation of the electronic effect of the $(C_2H_5)_3SnOAr$ group by UV spectroscopy[4] and a study of the fluorine chemical shifts in the corresponding organometallic derivatives of pentafluorophenol and pentafluorothiophenol[5].

It should be pointed out, however, that in the first of these studies the results obtained may be strongly affected by the electron density distribution in the excited state, whereas in the latter study the electronic effect of the organometallic substituents may be substantially modified by the strong electron-withdrawing influence of the pentafluorophenyl group and by possible intramolecular coordination with the fluorine atom in the *ortho*-position[6].

Fluorine nuclear magnetic resonance is known to be a powerful method for investigating the electronic effects of various substituents in the ground state and their solvent susceptibility[7-9]. For this reason, and as an extension to our previous work[6], we have applied this method for resolving the above problems.

RESULTS AND DISCUSSION

For the purposes of this study a number of organomercury, organotin and organolead derivatives of *m*- and *p*-fluorophenols and fluorothiophenols have been prepared. The fluorine chemical shifts relative to internal fluorobenzene have been determined in chloroform, tetrahydrofuran and dimethyl sulphoxide for the compounds indicated, as well as for the corresponding fluorophenols, fluoroanisoles, fluorothiophenols and fluorothioanisoles. With respect to the specific solvation of the metal atom, chloroform was considered to be an inert solvent, DMSO a strongly coordinating solvent and THF a donor solvent of medium strength.

From Table 1 it may be seen that in all cases organometallic substituents of the type R_nMOAr are more electron-donating than OH and CH_3O groups, whereas the relative electronic effect of the sulphur analogues depends on the solvent. In chloroform, the electron-donating ability of these analogues is less than or comparable with that of SH and CH_3 groups, being somewhat greater in DMSO. With the substituents

TABLE 1

^{19}F CHEMICAL SHIFTS RELATIVE TO FLUOROBENZENE (in ppm)

Compound	*Solvent*		
	$CHCl_3$	*THF*	*DMSO*
$CH_3OC_6H_4F$-4	11.3	11.5	11.3
HOC_6H_4F-4	11.1	13.4	13.3
$(C_2H_5)_3SnOC_6H_4F$-4	14.0	15.5	16.7
$C_6H_5HgOC_6H_4F$-4	13.6	16.0	16.3
$(C_6H_5)_3SnOC_6H_4F$-4	13.1	14.2	16.5
$(C_6H_5)_3PbOC_6H_4F$-4	13.9	16.1	17.0
$CH_3OC_6H_4F$-3	−1.4	−1.1	−1.2
HOC_6H_4F-3	−1.4	−0.4	−0.4
$(C_2H_5)_3SnOC_6H_4F$-3	0.0	0.5	0.6
$C_6H_5HgOC_6H_4F$-3	−0.9	0.5	0.5
$(C_6H_5)_3SnOC_6H_4F$-3	−0.1	0.6	0.8
$(C_6H_5)_3PbOC_6H_4F$-3	0.2	0.8	0.6
$CH_3SC_6H_4F$-4	4.1	4.7	4.8
HSC_6H_4F-4	3.5	4.4	5.0
$(C_2H_5)_3SnSC_6H_4F$-4	4.1	4.3	5.4
$C_6H_5HgSC_6H_4F$-4	3.5	5.7	6.0
$(C_6H_5)_3SnSC_6H_4F$-4	3.2	3.2	5.1
$(C_6H_5)_3PbSC_6H_4F$-4	3.8	4.1	5.5
$CH_3SC_6H_4F$-3	−0.6	−0.4	−0.6
HSC_6H_4F-3	−0.9	−0.5	−0.6
$(C_2H_5)_3SnSC_6H_4F$-3	−1.1	−0.6	0.7
$C_6H_5HgSC_6H_4F$-3	−1.1	0.1	0.2
$(C_6H_5)_3SnSC_6H_4F$-3	−0.1	−0.2	0.9
$(C_6H_5)_3PbSC_6H_4F$-3	0.5	0.6	1.1
4-$FC_6H_4HgSC_6H_4F$-4	3.5	5.5	6.2
	−2.6[a]	−0.7[a]	0.2[a]
4-$O_2NC_6H_4HgSC_6H_4F$-4	3.2	5.5	6.2
4-$(CH_3)_2NC_6H_4HgSC_6H_4F$-4	4.1	5.7	6.0
$C_2H_5HgSC_6H_4F$-4	4.7	6.3	6.5

[a] Chemical shifts for the 4-FC_6H_4Hg group.

R_nMO and R_nMS, in chloroform, for a given organic group on the metal atom the overall electron-releasing ability of the substituents increases with the nature of the metal in the order: Sn < Hg < Pb. Substituents with ethyl groups on the metal are more electron-donating than those with phenyl groups, the electronic effect of the organometallic groups being more strongly affected by the nature of the hydrocarbon radicals than by that of the metal atom.

In the case of arylmercury *p*-fluorothiophenoxides we have succeeded in demonstrating the influence of the substituent in the ring on the electronic effect of the organometallic group, whose electron-donating ability increases in the order: $4\text{-}O_2NC_6H_4HgS < C_6H_5HgS < 4\text{-}(CH_3)_2NC_6H_4HgS$. Again, by using arylmercury thiophenoxides and *p*-fluorothiophenoxides we have investigated the transmission of electronic effects in both possible directions through the –HgS– bridging group, and from Table 2 it may be seen that changes in electron density, produced by introduction of the *p*-dimethylamino group, are transmitted through the –HgS– bridge with the same ease in both directions, the ability of the above group to relay electronic effects being comparable, as a first approximation, to that of the $-CH_2S-$ bridging group. Unfortunately, a similar investigation of *p*-nitro substituted compounds could not be carried out due to the low solubility of the corresponding arylmercury thiophenoxides in chloroform.

TABLE 2

^{19}F CHEMICAL SHIFTS IN CHLOROFORM RELATIVE TO FLUOROBENZENE (in ppm)

Compound	*δ(F)*	*Compound*	*δ(F)*
$C_6H_5HgSC_6H_4F\text{-}4$	3.5	$4\text{-}(CH_3)_2NC_6H_4HgSC_6H_4F\text{-}4$	4.1
$4\text{-}FC_6H_4HgSC_6H_5$	−2.4	$4\text{-}FC_6H_4HgSC_6H_4N(CH_3)_2\text{-}4$	−1.8
$4\text{-}FC_6H_4CH_2SC_6H_5$	2.3	$4\text{-}FC_6H_4CH_2SC_6H_4N(CH_3)_2\text{-}4$	2.9

TABLE 3

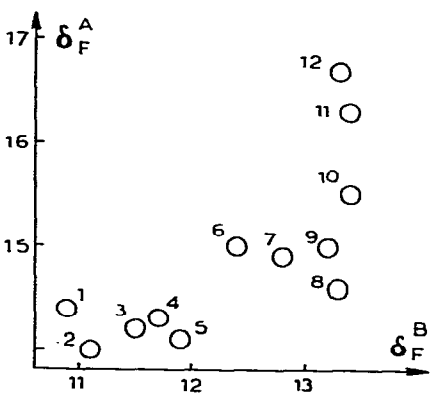
^{19}F CHEMICAL SHIFTS RELATIVE TO FLUOROBENZENE (in ppm)

Solvent	*Compound*			
	$HOC_6H_4F\text{-}4$	$(C_2H_5)_3Sn\text{-}OC_6H_4F\text{-}4$	$HSC_6H_4F\text{-}4$	$(C_2H_5)_3Sn\text{-}SC_6H_4F\text{-}4$
Cyclohexane	10.9	14.4	3.5	4.4
Carbon tetrachloride	11.5	14.2	3.5	4.0
Benzene	11.7	14.3	4.0	4.1
Chloroform	11.1	14.0	3.5	4.1
Nitromethane	11.9	14.1	4.2	4.3
Acetonitrile	12.4	15.0	4.1	4.4
Dimethoxyethane	13.3	14.6	4.0	4.5
Ethyl acetate	13.2	15.0	4.4	4.2
Dioxane	12.8	14.9	4.4	4.4
Tetrahydrofuran	13.4	15.5	4.4	4.3
Pyridine	13.4	16.3	4.5	4.4
Dimethyl sulphoxide	13.3	16.7	5.0	5.4

As mentioned above, the fluorine chemical shift in the organometallic derivatives under consideration is substantially solvent dependent. In this respect these compounds differ from fluoroanisoles and fluorothioanisoles, but are similar to fluorophenols and fluorothiophenols. As with other substituents[8], the chemical shift of the fluorine is more sensitive to solute/solvent interactions in the *p*-position than in the *m*-position. In the case of the organometallic derivatives of fluorophenols and fluorothiophenols the observed solvent dependence of the fluorine chemical shifts appears to be primarily due to specific solvation of the metal atom[10-11].

The change in the fluorine chemical shift in the corresponding compound on replacing chloroform by DMSO as a solvent can be taken as a measure of the solvent susceptibility of the electronic effect for the substituent investigated. At the same time it should be remembered that this is a somewhat arbitrary measure. Thus, the more detailed data (Table 3 and Fig. 1–2) for *p*-fluorophenol, *p*-fluorothiophenol and their triethyltin derivatives over a wide range of solvents indicates a lack of correlation between the fluorine chemical shifts in the corresponding pairs of compounds. This provides good evidence for the specificity of solvation of organotin substituents in comparison with that for the OH and SH groups.

Correlations of the above type appear to hold only when the nature of the acceptor centre, in particular that of the metal atom in organometallic substituents, is the same for both series of compounds. Such was the case, for example, with the similar correlations involving (*m*- and *p*-fluorophenyl)mercury derivatives[11]. The fluorine chemical shifts in triethyltin derivatives show no linear dependence with those in *p*-fluorophenol and *p*-fluorothiophenol apparently because, in general, there is no correlation between the Lewis and Brønsted acidities[12]. Nevertheless, bearing in mind that DMSO is one of the most powerful donor solvents and chloroform does not coordinate appreciably with the metal atom[11], it may be assumed that the measure of the solvent susceptibility of electronic effect proposed above is quite reasonable as a first approximation.



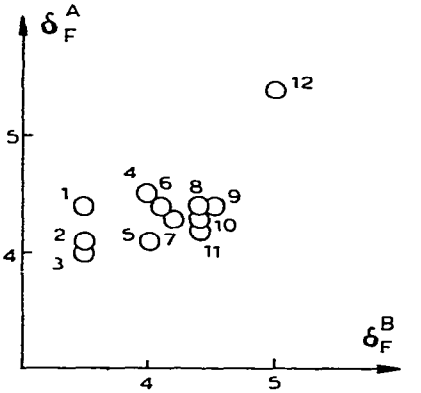


Fig. 1. Plot of the ^{19}F chemical shift in triethyltin *p*-fluorophenoxide (δ_F^A) against that in *p*-fluorophenol (δ_F^B): 1, cyclohexane; 2, chloroform; 3, carbon tetrachloride; 4, benzene; 5, nitromethane; 6, acetonitrile; 7, dioxane; 8, dimethoxyethane; 9, ethyl acetate; 10, tetrahydrofuran; 11, pyridine; 12, dimethyl sulphoxide.

Fig. 2. Plot of the ^{19}F chemical shift in triethyltin *p*-fluorothiophenoxide (δ_F^A) against that in *p*-fluorothiophenol (δ_F^B): 1, cyclohexane; 2, chloroform; 3, carbon tetrachloride; 4, dimethoxyethane; 5, benzene; 6, acetonitrile; 7, nitromethane; 8, dioxane; 9, pyridine; 10, tetrahydrofuran; 11, ethyl acetate; 12, dimethyl sulphoxide.

The data of Table 3 indicate that chloroform can exert some influence on the electronic effect of hydroxyl and the corresponding organometallic substituents, as a result of hydrogen bond formation with the oxygen lone-pair electrons, although this influence is weak in comparison with that of coordinating solvents. From these results it is evident that, when considering the solvent susceptibilities of electronic effects for such organometallic substituents, it would be more appropriate to compare the changes in the ^{19}F chemical shifts on transfer from an inert solvent, for example, cyclohexane or carbon tetrachloride, to a solvating medium. Unfortunately, this procedure is not always possible due to the low solubility of many organometallic phenoxides in the solvents indicated.

The solvent influence on the fluorine shielding is the most pronounced in the case of the organometallic derivatives of *p*-fluorophenol. In these compounds the solvent susceptibility of electronic effect of the organometallic substituents with phenyl groups on the metal atom is somewhat higher for tin and lead than for mercury, whereas for similar derivatives of *p*-fluorothiophenol the opposite is the case. In going from oxygen-containing substituents to their sulphur analogues, the solvent susceptibility of electronic effect of organotin and -lead groups decreases significantly, whilst that of organomercury substituents does not change appreciably. In this connection it is notable that for the derivatives of *p*-fluorothiophenol the changes in electronic effect of organotin and organolead substituents on transfer from chloroform to THF are considerably smaller than on transfer to DMSO, whereas for organomercury groups they are comparable.

The observed differences in the solvent susceptibilities of electronic effect of the organomercury, -tin and -lead substituents probably arises from the fact that in the compounds studied the approach of solvent molecules to the mercury atom is not sterically hindered, whereas in the case of tin and lead it may be inhibited by the aryl groups attached to the metal. Another possible reason for the difference observed may be associated with the fact that the change from *sp*- to sp^2-hybridization for the mercury atom on solvation requires less energy than the change from sp^3- to sp^3d-hybridization for tin and lead. In the former case re-hybridization involves an additional orbital with energy equal to that of the *p*-orbital already participating in hybridization, while in the latter re-hybridization involves a *d*-orbital whose energy is different from that of any orbital previously hybridized. For the reasons discussed above, solvent interaction with organotin and -lead groups of the type R_3MS seems to be possible only in those cases where the solvent molecules possess a large coordinating ability.

The data of Table 1 also indicate that the solvent susceptibility of the electronic effect of the organometallic groups decreases, as a rule, with increasing electron-donating ability of the organic radicals attached to the metal atom. On the other hand, coordinating solvents exert a levelling effect with respect to the influence of the substituents on the metal upon the electronic effect of the organometallic groups. It is notable that for (*p*-fluorophenyl)mercury *p*-fluorothiophenoxide the changes in the fluorine chemical shifts on passing from chloroform to DMSO are approximately equal for both aromatic rings. Apparently, this can be attributed to the fact that an increase in the electron density on mercury due to specific solvation is transmitted to the fluorine atom of the (*p*-fluorophenyl)mercury group largely by an inductive mechanism[11], whereas polarization of the mercury–sulphur bond also enhances the ability of the

sulphur lone-pair electrons to conjugate with the aromatic ring.

On the basis of the data on the fluorine chemical shifts in the compounds investigated, and the Taft correlations[7-8], the values of σ_I and σ_R^0 for the various organometallic groups have been calculated and compared with those for OH, CH_3O, SH and CH_3S substituents (Table 4). Examination of the results obtained shows that

TABLE 4

INDUCTIVE AND RESONANCE PARAMETERS OF SUBSTITUENTS

Substituent	σ_I			σ_R^0		
	$CHCl_3$	*THF*	*DMSO*	*$CHCl_3$*	*THF*	*DMSO*
HO	0.29	0.14	0.14	−0.42	−0.47	−0.47
CH_3O	0.28	0.24	0.26	−0.43	−0.43	−0.42
C_6H_5HgO	0.22	0.01	0.01	−0.50	−0.52	−0.53
$(C_2H_5)_3SnO$	0.08	0.00	0.00	−0.48	−0.51	−0.54
$(C_6H_5)_3SnO$	0.10	0.00	−0.03	−0.45	−0.46	−0.53
$(C_6H_5)_3PbO$	0.06	−0.03	0.00	−0.46	−0.52	−0.55
HS	0.23	0.16	0.17	−0.15	−0.17	−0.19
CH_3S	0.17	0.14	0.17	−0.16	−0.17	−0.18
C_6H_5HgS	0.23	0.06	0.06	−0.15	−0.19	−0.20
$(C_2H_5)_3SnS$	0.23	0.17	0.00	−0.17	−0.17	−0.17
$(C_6H_5)_3SnS$	0.10	0.11	−0.03	−0.14	−0.11	−0.14
$(C_6H_5)_3PbS$	0.00	0.00	−0.07	−0.11	−0.12	−0.15

substitution of hydrogen in OH and SH groups by an organometallic subsitutuent R_nM has the greatest effect, in most cases, on the inductive effect of the above groups. Substitution of an organometallic group R_nM for hydrogen in OH and SH substituents results in a considerably greater decrease of the electron-withdrawing inductive effect in coordinating solvents. The changes in σ_R^0 indicate that the above replacement in hydroxyl leads to an increase in the ability of the unshared electrons of the oxygen atom to conjugate with the aromatic ring. This may be taken to suggest that the donor-acceptor interactions of the p_π–p_π or p_π–d_π type are absent in the metal–oxygen bond. Another possible explanation is that conjugation of the oxygen lone-pair electrons with the ring is favoured more strongly by the greater polarity of the metal–oxygen σ-bond, in comparison with that of the H–O bond, than it is inhibited by the above donor/acceptor interaction. Only in the case of triphenyltin and -lead derivatives of fluorothiophenols do the changes induced upon introduction of the organometallic substituents into the mercapto group apparently indicate possible p_π–d_π conjugation. However, comparison of the changes in σ_R^0 for the hydroxy, mercapto and organometallic substituents on transfer from chloroform to THF and DMSO does not definitely confirm the presence of p_π–p_π or p_π–d_π conjugation in the compounds investigated. Thus, it appears that such conjugation is considerably counterbalanced by the inductive electron-donating effect of the R_nM groups.

In connection with the studies on the solvent susceptibility of the electronic

effects of the organometallic groups R_nMO and R_nMS, it seemed of interest to compare their ability to coordinate to donor sites of solute molecules with that of OH and SH groups. Such a comparison was possible in the case of triethyltin derivatives of *p*-fluorophenol and *p*-fluorothiophenol, as these compounds are liquids and the fluorine chemical shift in the *p*-position is more sensitive to solvent/substituent interactions than in the *m*-position.

It is well known that phenols undergo extensive association in inert solvents due to hydrogen bond formation[13-16], trimers being the most probable associates[16]. In contrast, thiophenols are much less able to associate[17]. Similarly, trialkyltin alkoxides are not associated in solutions of inert solvents[18].

We first investigated the concentration dependence of the fluorine chemical shifts in *p*-fluorophenol, *p*-fluorothiophenol and their triethyltin derivatives over the concentration range from dilute solutions in carbon tetrachloride to pure liquids. From Fig. 3 it may be seen that for all these compounds, with the exception of *p*-fluorophenol, as well as for *p*-fluoroanisole and *p*-fluorothioanisole increasing the concentration results in a corresponding increase in the fluorine shielding relative to fluorobenzene in CCl_4. This is due to simultaneous changes in the bulk magnetic susceptibility, diamagnetic anisotropy and the nature of van der Waals interactions on transfer from a solution in carbon tetrachloride to the pure substance. It is important to note that, as far as the concentration dependence of the fluorine chemical shift is concerned, organotin derivatives behave in a similar manner to *p*-fluoroanisole and *p*-fluorothioanisole.

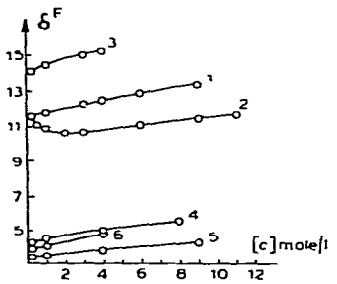


Fig. 3. Concentration dependence of the ^{19}F chemical shifts in CCl_4 solution relative to fluorobenzene in the same solvent: 1, $CH_3OC_6H_4F$-4; 2, HOC_6H_4F-4; 3, $(C_2H_5)_3SnOC_6H_4F$-4; 4, $CH_3SC_6H_4F$-4; 5, HSC_6H_4F-4; 6, $(C_2H_5)_3SnSC_6H_4F$-4.

The concentration dependence of the ^{19}F chemical shift in *p*-fluorophenol differs markedly from that in other compounds. A change in concentration from 0.01 to 2.0 *M* displaces the fluorine resonance to lower field. Only upon further increase in concentration does the fluorine shielding begin to increase. As a result, the overall change in the fluorine chemical shift relative to fluorobenzene in CCl_4 on passing from the carbon tetrachloride solution to the pure substance is close to zero. This behaviour can only be attributed to two competing but opposite factors. These may involve the general tendency to a high-field shift, characteristic of other compounds investigated, and an additional cause leading to fluorine deshielding.

Bearing in mind the data on phenol association[15-16], we may assume that fluorine deshielding during the initial increase in concentration arises from the formation of associates with intermolecular hydrogen bonds. After an appropriate con-

centration is reached, all the molecules of *p*-fluorophenol are in an associated form. This stops further deshielding of fluorine, and as a result other factors begin to operate and fluorine shielding increases. This interpretation is supported by the fact that the minimum in the plot of fluorine chemical shift against concentration in *p*-fluorophenol occurs in the region 2.0 *M*, whereas according to the data in the literature[15], self-association of phenol in CCl_4 solution is complete at approximately 1.5 *M* concentration. Thus, it may be concluded that the six-membered cycle involving intermolecular hydrogen bonds, which is formed as a result of the self-association of *p*-fluorophenol[16], apparently withdraws electrons from the aromatic ring.

This effect is further illustrated by comparing the changes in the electronic effects of some substituents on passing from dilute solutions in CCl_4 to pure substances (Table 5). If fluorobenzene is used as an internal standard in both cases the specific interactions are demonstrated more clearly. The observed changes in the fluorine chemical shifts relative to internal fluorobenzene in the same medium show that the electron-donating ability of hydroxyl decreases considerably on transfer from the inert solvent to the pure substance, while the electronic effect of other substituents does not change appreciably. For CH_3O and CH_3S groups this is due to specific association being impossible in the corresponding compounds. Furthermore, if slight association does take place in the case of *p*-fluorothiophenol[19], it still does not significantly affect the electronic effect of the SH group. The same conclusion also holds for $(C_2H_5)_3SnO$ and $(C_2H_5)_3SnS$ groups, their electronic effects being practically unchanged by transfer to the pure substances. Thus, these results provide further evidence that the ability of the $(C_2H_5)_3SnO$ group to self-associate is much less than that of the OH group. On the other hand, the $(C_2H_5)_3SnS$ substituent is similar in its behaviour to the SH group.

TABLE 5

CHANGES IN ^{19}F CHEMICAL SHIFTS RELATIVE TO INTERNAL FLUOROBENZENE ON TRANSFER FROM CCl_4 SOLUTIONS TO PURE SOLUTES (in ppm)

Compound	$\Delta\delta(F)$	*Compound*	$\Delta\delta(F)$
$CH_3OC_6H_4F$-4	0.0	$CH_3SC_6H_4F$-4	0.3
HOC_6H_4F-4	−1.5	HSC_6H_4F-4	0.4
$(C_2H_5)_3SnOC_6H_4F$-4	−0.2	$(C_2H_5)_3SnSC_6H_4F$-4	0.2

It seemed of interest to examine as well whether the above regularities hold when the donor site is located in an unlike molecule. For this reason the changes in the fluorine chemical shifts relative to fluorobenzene in the same medium were determined for a number of *p*-substituted fluorobenzenes containing substituents with lone-pair electrons on transfer from cyclohexane solutions to solutions in phenol, anisole, triethyltin phenoxide and their sulphur analogues. Inspection of the data presented in Table 6 shows that in the case of *p*-fluoroanisole and *p*-fluoro-*N*,*N*-dimethylaniline transfer to solution in anisole, thioanisole and organotin derivatives produces only a slight change in the fluorine chemical shifts, which is comparable

with the experimental error. In contrast, the fluorine resonance in these compounds experiences a considerable low-field shift on going from cyclohexane solution to solutions in phenol, whereas the influence of thiophenol on the fluorine shielding is similar to that of thioanisole.

TABLE 6

^{19}F CHEMICAL SHIFTS RELATIVE TO FLUOROBENZENE (in ppm)

Compound	*Solvent*			
	C_6H_{12}	$CH_3OC_6H_5$	HOC_6H_5	$(C_2H_5)_3SnOC_6H_5$
$CH_3OC_6H_4F$-4	11.7	11.5	10.2	11.6
$(CH_3)_2NC_6H_4F$-4	16.6	16.4	9.2	16.5
4-FC_6H_4CHO	−9.5	−9.6	−12.6	−10.2
4-$FC_6H_4COCH_3$	−6.1	−6.7	−9.8	−7.3
4-$FC_6H_4COOCH_3$	−6.0	−6.4	−8.6	−6.9
4-$FC_6H_4NO_2$	−9.1	−9.7	−11.6	−9.9
	C_6H_{12}	$CH_3SC_6H_5$	HSC_6H_5	$(C_2H_5)_3SnSC_6H_5$
$CH_3OC_6H_4F$-4	11.7	11.5	11.4	11.6
$(CH_3)_2NC_6H_4F$-4	16.6	16.5	16.2	16.5

According to the literature data[20-22], the phenol hydroxyl can form intermolecular hydrogen bonds with the aromatic π-electron system, as well as with various substituents having unshared electron pairs, but not with halogen in the aromatic ring. Therefore, in solutions of fluorobenzene and its *p*-substituted derivatives in phenol hydrogen-bonded associates may exist which involve the phenolic hydroxyl on the one hand and π-electrons of the ring and lone-pair electrons of the substituent on the other. In our case the formation of hydrogen bonds between the OH group of phenol and CH_3O and $(CH_3)_2N$ substituents deshields fluorine on transfer to phenolic solutions, while slight changes in the ^{19}F chemical shifts on transfer to solutions in thiophenol and organotin derivatives indicate no (or negligible) coordination of the SH group and organotin substituents with the above groupings.

Although similar data for other *p*-substituted fluorobenzenes are somewhat less conclusive, they nevertheless demonstrate clearly the fact that the $(C_2H_5)_3SnO$ group is less capable of association with the nitro group and carbonyl-containing substituents than hydroxyl. At the same time it should be pointed out that the changes in the fluorine chemical shifts for carbonyl-containing compounds are considerably greater on transfer to solutions in triethyltin phenoxide than on transfer to anisole solutions. These results appear to indicate some interaction of the organotin group with the carbonyl-containing substituents.

In summary, it may be said that both in the case of association with unlike molecules and of self-association the ability of the $(C_2H_5)_3SnO$ group to coordinate in solution with substituents in the aromatic ring is low in comparison to that of the OH group.

EXPERIMENTAL

General comments

The ^{19}F NMR spectra were recorded at 34° using Hitachi H-60 and Hitachi–Perkin–Elmer R-20 spectrometers operating at 56.4 MHz. Chemical shift measurements were taken on dilute solutions of concentration not greater than 0.2 *M*. For *p*-fluorophenol in inert solvents, solutions with concentrations in the order of 0.02 *M* were used. The spectra of solutions in phenol and the spectrum of neat *p*-fluorophenol were recorded using supercooled samples. The substitution method[6] was used for determination of the ^{19}F chemical shifts in the compounds investigated relative to internal fluorobenzene. The experimental error in the fluorine chemical shifts did not exceed ± 0.1 ppm.

The solvents used were purified by standard methods. Fluorophenols, fluoroanisoles, their sulphur analogues and other derivatives of fluorobenzene were prepared by known procedures and their physical properties checked against the reported values[7–8]. Organometallic derivatives of fluorophenols were obtained by the reaction of organometallic hydroxides and triethyltin methoxide with the corresponding compounds. Analogous derivatives of fluorothiophenols were prepared by the interaction of organometallic hydroxides and triethyltin methoxide with thiophenols, as well as by the exchange reactions of organometallic acetates and bromides with sodium fluorothiophenoxides. The preparation of (*p*-fluorophenyl)mercury

TABLE 7

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF ORGANOMETALLIC DERIVATIVES OF FLUOROPHENOLS AND FLUOROTHIOPHENOLS

Compound	*M.p.* (°C) *or b.p.* (°C/*mm*)	*Analysis* (%)			
		Found		*Calcd.*	
		C	*H*	*C*	*H*
$C_6H_5HgOC_6H_4F$-3	96–98	36.96	2.47	37.06	2.33
$(C_2H_5)_3SnOC_6H_4F$-3	130/3	45.40	5.83	45.47	6.04
$(C_6H_5)_3SnOC_6H_4F$-3	65–67	62.80	3.91	62.51	4.15
$(C_6H_5)_3SnOC_6H_4F$-4	69–71	62.13	4.12	62.51	4.15
$(C_6H_5)_3PbOC_6H_4F$-3	69–70	52.89	3.59	52.44	3.48
$(C_6H_5)_3PbOC_6H_4F$-4	75–76	52.40	3.66	52.44	3.48
$C_6H_5HgSC_6H_4F$-3	96–97	35.31	2.10	35.60	2.24
$C_2H_5HgSC_6H_4F$-4	50–51	26.66	2.22	26.93	2.54
$C_6H_5HgSC_6H_4F$-4	92–93	35.87	2.02	35.60	2.24
4-$FC_6H_4HgSC_6H_4F$-4	136–137	34.20	2.03	34.08	1.90
4-$O_2NC_6H_4HgSC_6H_4F$-4	252–253	32.13	1.60	32.04	1.79
4-$FC_6H_4HgSC_6H_4NO_2$-4	244–246	32.17	1.75	32.04	1.79
4-$(CH_3)_2NC_6H_4HgSC_6H_4F$-4	113–114	38.01	2.79	37.54	3.15
4-$FC_6H_4HgSC_6H_4N(CH_3)_2$	162–164	37.54	3.18	37.54	3.15
$(C_2H_5)_3SnSC_6H_4F$-3	120/1	43.00	5.55	43.29	5.75
$(C_6H_5)_3SnSC_6H_4F$-3	81–82	59.91	3.82	60.41	4.01
$(C_6H_5)_3SnSC_6H_4F$-4	115–116	60.25	3.99	60.41	4.01
$(C_6H_5)_3PbSC_6H_4F$-3	83–84	51.06	3.34	50.96	3.39
$(C_6H_5)_3PbSC_6H_4F$-4	117–118	50.55	3.48	50.96	3.39

thiophenoxide has been described elsewhere[23]. Analytical results and physical properties of compounds not reported previously[6,24] are presented in Table 7. The preparation of some organometallic derivatives which illustrate the experimental procedures used in obtaining the compounds studied in the present investigation are described below.

Triethyltin m-fluorophenoxide

m-Fluorophenol (1.12 g, 10 mmole) was added to 2.37 g (10 mmole) of triethyltin methoxide[25]. After evaporating the methanol under reduced pressure, the residue was vacuum distilled yielding 2.8 g (88%) of a colourless oil with n_D^{20} 1.5261.

Triphenyllead m-fluorophenoxide

To a hot solution of 2.27 g (5 mmole) of triphenyllead hydroxide[26] in 100 ml of ethanol was added 0.56 g (5 mmole) of *m*-fluorophenol. The reaction mixture was evaporated under reduced pressure, and the residue was recrystallized from heptane to give 2.0 g (74%) of a colourless microcrystalline powder.

Phenylmercury m-fluorophenoxide

m-Fluorophenol (0.56 g, 5 mmole) was added to a hot solution of 1.47 g (5 mmole) of phenylmercury hydroxide[27] in 20 ml of methanol. The solvent was removed in vacuum, and the residue recrystallized from a benzene/heptane mixture (1/1) affording 1.6 g (82%) of a colourless microcrystalline powder.

Triphenyltin p-fluorothiophenoxide

To a hot solution of 1.83 g (5 mmole) of triphenyltin hydroxide[28] in 30 ml of methanol was added 0.64 g (5 mmole) of *p*-fluorothiophenol. A white precipitate formed immediately. The reaction mixture was evaporated under reduced pressure and the residue recrystallized from ethanol, yielding 1.8 g (74%) of colourless crystals.

(p-Fluorophenyl)mercury p-fluorothiophenoxide

A solution of 0.20 g of NaOH and 0.64 g (5 mmole) of *p*-fluorothiophenol in 10 ml of ethanol was added to a hot solution of 1.72 g (5 mmole) of *p*-fluorophenylmercury acetate[11] in 50 ml of ethanol. After cooling to room temperature the reaction mixture was diluted with 300 ml of water, the resulting precipitate filtered, washed with water and dried; 1.7 g (80%) of a white precipitate was obtained, which was recrystallized from ethanol.

Ethylmercury p-fluorothiophenoxide

To a boiling solution of 1.0 g (4 mmole) of ethylmercury bromide[29] in 50 ml of ethanol was added a solution of 0.13 g NaOH and 0.43 g (4 mmole) of *p*-fluorothiophenol in 10 ml of the same solvent. After cooling the reaction mixture, 300 ml of water was added. The precipitate formed was filtered, washed with water and dried to give 0.8 g (70%) of the product. Crystallization from ethanol afforded colourless crystals.

Phenyl p-fluorobenzyl sulphide

p-Fluorobenzyl chloride[30] (7.2 g, 50 mmole) was added to a stirred solution of

1.15 g sodium and 5.5 g (50 mmole) of thiophenol in 30 ml of ethanol. After stirring for 2 h, the reaction mixture was diluted with 150 ml of water, the resulting precipitate filtered, washed with water and dried. Recrystallization from ethanol gave 4.4 g (39%) of colourless crystals with m.p. 56–57°. (Found: C, 71.64; H, 5.11; F, 8.89. $C_{13}H_{11}FS$ calcd.: C, 71.55; 5.04; F, 8.71%.)

p-Fluorobenzyl p-(dimethylamino)phenyl sulphide

This compound was prepared in a similar manner to that described above by the interaction of *p*-fluorobenzyl chloride with *p*-(dimethylamino)thiophenol[31] to give a 42% yield of product. Colourless crystals with m.p. 70–71° were obtained after recrystallization from petroleum ether. (Found: C, 68.97; H, 6.38; F, 7.03. $C_{15}H_{16}FNS$ calcd.: C, 68.96; H, 6.13; F, 7.27%.)

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