

A ^{19}F NMR STUDY OF STERIC HINDRANCE AND INTRAMOLECULAR COORDINATION IN ORGANO-MERCURY, -TIN AND -LEAD DERIVATIVES OF 2,6-DIMETHYL-4-FLUOROTHIOPHENOL AND 2,6-DIBROMO-4-FLUOROTHIOPHENOL

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SUMMARY

Some organomercury, -tin and -lead derivatives of 2,6-dimethyl-4-fluorothiophenol and 2,6-dibromo-4-fluorothiophenol of the general type R_nMSAr have been prepared. The fluorine chemical shifts of the compounds relative to internal fluorobenzene and the ^{19}F SCS values for the corresponding substituents have been determined and discussed in terms of steric hindrance and intramolecular coordination, the behaviour of the organometallic substituents R_nMS in these respects being compared with that of the SH and CH_3S groups. The anomalously low steric requirements of R_nMS groups, as well as the differences in the strength of intramolecular coordination and its influence on the acceptor power of the metal atom, in the compounds of mercury, tin and lead have been demonstrated.

INTRODUCTION

Previous studies¹ concerning the ^{19}F NMR data for phenylmercury and triethyltin derivatives of 2,6-dibromo-4-fluorophenol have suggested the existence of intramolecular coordination between the organometallic group and the *ortho*-halogen substituent. In view of the differences in bond angles and electronegativities between divalent sulphur and oxygen, it seemed interesting to investigate to what extent the strength of the metal-halogen coordinate bond would be affected by the substitution of oxygen by sulphur. Further, in connection with fluorine NMR studies on intramolecular coordination in organometallic derivatives of phenols and thiophenols of the general type R_nMOAr and R_nMSAr , it was felt necessary to establish the manner in which the steric hindrance produced by inert substituents in the 2 and 6 positions of the benzene ring influences the electronic effect of the R_nMS substituents. Finally, it would be interesting to obtain additional information concerning the peculiarities in the behaviour of organomercury, -tin and -lead substituents of the above type, as well as of the SH and CH_3S groups with respect to steric hindrance and intramolecular coordination.

RESULTS AND DISCUSSION

In order to resolve the above problems, phenylmercury, triphenyltin and triphenyllead derivatives of 2,6-dimethyl-4-fluorothiophenol and 2,6-dibromo-4-fluorothiophenol have been prepared. The fluorine chemical shifts relative to internal fluorobenzene have been determined in chloroform and dimethylsulphoxide both for the compounds indicated and for the corresponding thiophenols and thioanisoles. From the data obtained the values of the ^{19}F substituent chemical shifts (SCS) were determined for the substituents investigated. These values characterize the influence of a substituent on the fluorine shielding in a given compound and in the case of the systems studied here, represent the fluorine chemical shifts relative to 3,5-dimethyl-fluorobenzene and 3,5-dibromofluorobenzene respectively. With derivatives of *p*-fluorothiophenol, used for comparison, the ^{19}F SCS values correspond to the fluorine chemical shifts relative to unsubstituted fluorobenzene. In the following discussion the changes in the fluorine SCS values for the organometallic groups R_nMS on introducing methyl and bromo substituents in the *o*-positions are compared with the corresponding changes for the methylmercapto and mercapto groups.

Comparison of the data presented in Table 1 for the ^{19}F SCS values of the given substituents in the derivatives of 2,6-dimethyl-4-fluorothiophenol and 2,6-di-

TABLE 1

^{19}F CHEMICAL SHIFTS RELATIVE TO INTERNAL FLUOROBENZENE AND ^{19}F SCS VALUES FOR THE SH, CH_3S AND R_nMS SUBSTITUENTS (in ppm)

Compound	Solvent			
	CHCl_3		DMSO	
	$\delta(\text{F})$	SCS	$\delta(\text{F})$	SCS
$\text{CH}_3\text{SC}_6\text{H}_4\text{F-4}$	4.1	4.1	4.8	4.8
$\text{HSC}_6\text{H}_4\text{F-4}$	3.5	3.5	4.5 ^a	4.5 ^a
$\text{C}_6\text{H}_5\text{HgSC}_6\text{H}_4\text{F-4}$	3.5	3.5	6.0	6.0
$4\text{-FC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	3.5	3.5	6.2	6.2
$(\text{C}_6\text{H}_5)_3\text{SnSC}_6\text{H}_4\text{F-4}$	3.2	3.2	5.1	5.1
$(\text{C}_6\text{H}_5)_3\text{PbSC}_6\text{H}_4\text{F-4}$	3.8	3.8	5.5	5.5
$\text{CH}_3\text{SC}_6\text{H}_2(\text{CH}_3)_2\text{-2,6-F-4}$	1.3	-1.1	1.2	-0.9
$\text{HSC}_6\text{H}_2(\text{CH}_3)_2\text{-2,6-F-4}$	5.4	3.0	5.7	3.6
$\text{C}_6\text{H}_5\text{HgSC}_6\text{H}_2(\text{CH}_3)_2\text{-2,6-F-4}$	4.0	1.6	5.6	3.5
$4\text{-FC}_6\text{H}_4\text{HgSC}_6\text{H}_2(\text{CH}_3)_2\text{-2,6-F-4}$	3.7	1.3	5.3	3.2
$(\text{C}_6\text{H}_5)_3\text{SnSC}_6\text{H}_2(\text{CH}_3)_2\text{-2,6-F-4}$	4.0	1.6	4.3	2.2
$(\text{C}_6\text{H}_5)_3\text{PbSC}_6\text{H}_2(\text{CH}_3)_2\text{-2,6-F-4}$	4.3	1.9	5.1	3.0
$\text{CH}_3\text{SC}_6\text{H}_2\text{Br}_2\text{-2,6-F-4}$	-3.6	0.8	-4.0	0.8
$\text{HSC}_6\text{H}_2\text{Br}_2\text{-2,6-F-4}$	1.8	6.2	1.6 ^a	6.0 ^a
$\text{C}_6\text{H}_5\text{HgSC}_6\text{H}_2\text{Br}_2\text{-2,6-F-4}$	0.8	5.2	2.1	6.9
$4\text{-FC}_6\text{H}_4\text{HgSC}_6\text{H}_2\text{Br}_2\text{-2,6-F-4}$	0.8	5.2	2.3	7.1
$(\text{C}_6\text{H}_5)_3\text{SnSC}_6\text{H}_2\text{Br}_2\text{-2,6-F-4}$	-0.2	4.2	2.7	7.5
$(\text{C}_6\text{H}_5)_3\text{PbSC}_6\text{H}_2\text{Br}_2\text{-2,6-F-4}$	0.7	5.1	2.7	7.5

^a In pyridine.

bromo-4-fluorothiophenol with data for the compounds not substituted in the 2 and 6 positions indicates the following regularities. Thus, introduction of methyl and bromo substituents in the 2 and 6 positions with respect to the CH_3S group lowers the SCS of the latter, this effect being more pronounced with 2,6-dimethyl-4-fluorothioanisole for which the results obtained are in good agreement with the literature data². These observations indicate that the CH_3S group is twisted out of the plane of the aromatic ring due to steric hindrance. The latter inhibits $3p_\pi-2p_\pi$ conjugation between the lone-pair electrons of the sulphur atom and the ring, leading to the lowering in the electron-donating ability of the above substituent². The greater steric effect of *ortho*-methyl groups in comparison with *ortho*-bromo substituents may be similar to the steric influence of two *ortho*-iodo substituents upon the electronic effect of the CH_3O group which is smaller than that of two methyl groups³.

In the present instance the smaller steric effect of the bromo substituents may be due to the fact that in the actual conformation the angle of twist of the CH_3S group out of the plane of the ring is less in 2,6-dibromo-4-fluorothioanisole than in 2,6-dimethyl-4-fluorothioanisole. Inspection of molecular models shows that, despite the equality of the van der Waals' radii of the bromine atom and the methyl group⁴, the approximate values of the dihedral angle between the C-S bond and the plane of the ring are 85° and 70° for 2,6-dimethyl-4-fluorothioanisole and 2,6-dibromo-4-fluorothioanisole respectively, provided that the bromo and methyl substituents are co-planar with the aromatic ring.

In addition, the deformability of the electron cloud and the ease of twist of the C-X bond out of the plane of the ring appear to increase on passing from the methyl group to the bromo substituent, as is indicated by a concomitant increase in the polarizability and a decrease in the force constant of the C-X bond⁵. Finally, the observed result may be partly associated with the fact that the bromo substituents compensate to some extent the decrease in the electron-donating ability of the CH_3S group. This may be a result of the stereoelectronic effect⁶ involving electrostatic repulsion between the unshared electron pairs of the sulphur and halogen atoms. A final assessment of the cause of the observed differences in the influence of *ortho*-methyl groups and bromo substituents on the SCS value of the CH_3S group must await X-ray diffraction data for the compounds considered or their analogues.

The SCS value for the SH group is affected differently by the introduction of methyl groups and bromo substituents in the *ortho*-positions, being somewhat decreased in the former case and considerably increased in the latter. The decrease in the SCS value for the SH group produced by the *ortho*-methyl substituents may arise from its partial twisting out of the plane of the benzene ring. According to the literature⁷⁻⁸, two *ortho*-methyl groups are incapable of twisting an OH group out of the plane of the aromatic ring. Nevertheless, in view of the smaller C-S-H angle relative to the C-O-H angle and the greater S-H bond length in comparison with that of the O-H bond, the above explanation seems to be reasonable. Actually, examination of molecular models shows that in 2,6-dimethyl-4-fluorothiophenol the SH group may be slightly twisted out of the plane of the ring by the influence of the methyl substituents.

The marked increase in the SCS value for the SH group upon the introduction of *ortho*-bromo substituents possibly arises from a considerable transfer of electron density from the halogen lone-pair electrons into the antibonding orbital of the S-H

bond through internal hydrogen bonding¹⁰. At the same time the frequency of the SH group in the IR spectrum does not change significantly when *ortho*-bromo substituents are introduced. Thus, $\nu(\text{SH})$ for a solution of 2,6-dibromo-4-fluorothiophenol in CCl_4 is 2576 cm^{-1} , being 2574 cm^{-1} for *p*-fluorothiophenol and 2585 cm^{-1} for thiophenol, according to the literature data¹¹. However, it should be borne in mind that electron-withdrawing substituents shift the SH band to higher frequencies^{11,12} and that the *ortho*-bromo substituent is an electron acceptor¹³. Furthermore, it should be remembered that the band of the SH group is not appreciably displaced on hydrogen bond formation¹⁴. Thus, the absence of a shift of the SH group band to lower frequencies in 2,6-dibromo-4-fluorothiophenol relative to *p*-fluorothiophenol probably arises from the fact that the weak influence of the internal hydrogen bond is virtually counterbalanced by the electron-attracting effect of the bromo substituents.

In contrast, the PMR data clearly indicate the presence of intramolecular hydrogen bonding in 2,6-dibromo-4-fluorothiophenol. In CCl_4 solution $\delta(\text{SH})$ for this compound is 4.72 ppm relative to TMS, in comparison with a value of 3.25 ppm for *p*-fluorothiophenol. Using the relationship between $\delta(\text{SH})$ for substituted thiophenols with the Hammett σ constants¹⁵ and using a value of 0.55 for σ_0 for the bromo substituent¹³, the chemical shift of the SH group proton in 2,6-dibromo-4-fluorothiophenol (calculated on an additive basis) should amount to only 3.57 ppm, thus giving a difference between the experimental and calculated values of greater than 1 ppm and indicating the presence of an internal hydrogen bond.

The nature of the halogen atom appears to have an appreciable influence on the strength of the internal hydrogen bond in 2,6-dihalogenothiophenols. Thus, for 2,6-dichloro-4-fluorothiophenol in chloroform solution the increase in the ^{19}F SCS value for the SH group relative to *p*-fluorothiophenol is only 0.5 ppm. Evidently, the strength of the internal hydrogen bond is influenced both by the size of the halogen atom and by its ionization potential¹⁶. At the same time, in interpreting the above result it should be remembered that it is possible that the stereoelectronic interaction between the lone-pair electrons of the sulphur and halogen atoms may play some role in the influence of *ortho*-halogen substituents upon the ^{19}F SCS for the SH group.

Introduction of methyl groups in the 2 and 6 positions relative to the organometallic substituent R_nMS leads, as expected, to a decrease in the SCS value for this substituent. This suggests that the organometallic substituent is twisted out of the plane of the aromatic ring due to non-bonded interactions between the metal atom and the methyl group. The close similarity between the changes in the SCS values for different R_nMS groups indicates that their steric requirements are approximately equal. Surprisingly though, the changes in the SCS values are substantially smaller for organometallic substituents than for the CH_3S group. Inspection of molecular models shows that the steric requirements of the R_nMS substituents should not be less than those of the methylmercapto group so that the extent to which the substituent is twisted out of the plane of the aromatic ring should be comparable in both cases.

One possible cause for the above anomalous observation may be the greater ease of M-S bond stretching deformation in comparison with that of the C-S bond. Although no data on the stretching force constants of the bonds Hg-S, Sn-S and Pb-S appear in the literature, comparison of the corresponding data¹⁷ for C-Cl, Sn-Cl and Pb-Cl bonds shows that the ease of deformation of the element-halogen

bond is considerably increased on passing from carbon to metals. In this connection, it might be supposed that in organometallic derivatives of 2,6-dimethyl-4-fluorothiophenol stretching of the metal-sulphur bond occurs through severe non-bonded interactions between the organometallic group and the *ortho*-methyl substituent. This would result in the polarization of the metal-sulphur bond and the appearance of an additional negative charge on the sulphur atom relative to an uncrowded molecule. This additional negative charge would in turn increase the fluorine shielding and thereby partially compensate for the decrease in the SCS value for the organometallic group produced by the steric restraint on its co-planarity with the aromatic ring.

However, comparison of the fluorine chemical shifts of the 4-FC₆H₄HgS group in corresponding organomercury derivatives of *p*-fluorothiophenol and 2,6-dimethyl-4-fluorothiophenol (Table 2) shows that the shielding of fluorine in the benzene ring attached to the mercury atom does not change appreciably on going from the former compound to the latter. This indicates the absence of any significant additional polarization of the Hg-S bond which might increase the partial negative charge on the sulphur atom and the partial positive charge on the metal atom. Hence, if stretching of the metal-sulphur bond due to steric hindrance does occur it is not accompanied by any appreciable additional polarization of the bond. At the same time, the above stretching can partially reduce steric hindrance and decrease the degree of twisting of the organometallic substituent out of the plane of the ring.

TABLE 2

¹⁹F CHEMICAL SHIFTS OF THE 4-FC₆H₄HgS GROUP RELATIVE TO INTERNAL FLUOROBENZENE (in ppm)

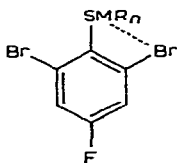
Compound	Solvent	
	CHCl ₃	DMSO
4-FC ₆ H ₄ HgSC ₆ H ₄ F-4	-2.6	0.2
4-FC ₆ H ₄ HgSC ₆ H ₂ (CH ₃) ₂ -2,6-F-4	-2.5	0.1
4-FC ₆ H ₄ HgSC ₆ H ₂ Br ₂ -2,6-F-4	-1.0	0.0

Another possible explanation for the anomalous results reported here involves the greater compressibility of the mercury electron cloud relative to that of hydrogen, as indicated by the high value of the atomic refractivity of mercury in organomercury compounds¹⁸. As a result of the greater polarizability of the electron cloud of the mercury atom in comparison with that of the methyl group, the dihedral angle between the Hg-S bond and the plane of the aromatic ring in the phenylmercury derivative of 2,6-dimethyl-4-fluorothiophenol may be less than that found in molecular models, in which a value of 2.1 Å has been used for the hard-sphere van der Waals' radius of mercury¹⁹. This, in turn, should lead to a smaller change in the SCS value for the RHgS substituent due to steric hindrance in comparison with the expected value.

The above considerations are also valid for the other organometallic substituents of the type R_nMS investigated in this study which also have anomalously low steric requirements as shown by the method employed. It should be pointed out that

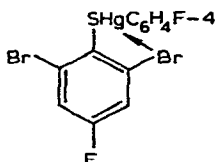
the sole analogy found in the literature refers to the unusually low steric requirements of mercury substituents in the case of cyclohexylmercury compounds²⁰, which lead to the absence of conformational preference in the equilibrium of axial and equatorial conformers of the corresponding mercurial compounds. Evidently, final elucidation of the causes which determine the anomalously low steric requirements of the R_nMS groups, as indicated by the ^{19}F NMR data, will be possible only after an X-ray examination of the compounds investigated or their analogues.

Introduction of bromo substituents *ortho* to the organometallic group R_nMS leads to an increase in the corresponding SCS value. Consequently, bromo substituents, whose size is close to that of the methyl group⁴, interact with the organometallic substituent differently from methyl groups, suggesting intramolecular coordination:

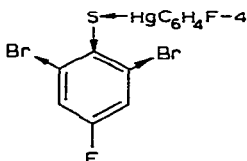


The partial transfer of electron density from the halogen lone pair electrons into the vacant orbitals of the metal atom results in an increase in the electron-releasing ability and the SCS value of the organometallic substituent. The increase outweighs the decrease in the SCS value for the corresponding substituent which arises from the partial steric inhibition of mesomeric electron-donation to the ring due to the virtual twist of the substituent out of the plane of the ring. As indicated earlier¹, this effect is probably associated with the different sensitivities of *m*- and *p*-fluorine chemical shifts to equal changes in electron density on a substituent conjugated with the aromatic ring.

The presence of intramolecular coordination in the compounds investigated is also supported by a comparison of the ^{19}F chemical shifts in the $4-FC_6H_4HgS$ group for the corresponding derivatives of *p*-fluorothiophenol and 2,6-dibromo-4-fluorothiophenol (Table 2). Introduction of bromo substituents *ortho* to the organometallic group increases the fluorine shielding, whereas according to the literature¹³ the *ortho*-bromo substituent possesses a considerable overall electron-withdrawing effect. The increase in the fluorine shielding in the $4-FC_6H_4HgS$ group can be explained only in terms of a transfer of electron density into the vacant orbitals of mercury due to intramolecular coordination with halogen, *i.e.*,



more than compensating for electron withdrawal from the mercury atom which results from the electron-attracting influence of two *ortho*-bromo substituents:



If the steric requirements for the R_nMS groups and the changes in the corresponding SCS values upon introduction of *ortho*-bromo substituents are assumed to be approximately equal, it may be concluded that the strength of intramolecular coordination increases in the order: $(C_6H_5)_3SnS < (C_6H_5)_3PbS < C_6H_5HgS$. This sequence appears to be related to the differences in the bond distances, the sizes of vacant orbitals and especially to the preferred geometry for the coordinated state of triorganotin and -lead groups on the one hand and of organomercury groups on the other²¹.

It is interesting to note that the increase in the ^{19}F SCS value for the R_nMS substituents on introduction of *ortho*-bromo substituents is comparable with that for the R_nMO groups in derivatives of 2,6-dibromo-4-fluorophenol¹, whereas the corresponding increase in the SCS value for the SH group is considerably greater than that for hydroxyl. Apparently, the observed difference is due to the presence of vacant low energy orbitals in the case of metals and their absence in the case of hydrogen. As a result the partial transfer of electron density from halogen lone-pair electrons into the vacant orbitals of the metal atom due to intramolecular coordination polarizes the metal-sulphur bond to a smaller extent than the similar transfer of electron density into the antibonding orbital of the S-H bond, which occurs upon formation of internal hydrogen bonds, polarizes the latter.

It appeared interesting to determine the manner in which steric interactions and intramolecular coordination of the SH group and organometallic substituents with *ortho*-groups affect the solvent susceptibility of their electronic effect, the change in the ^{19}F chemical shift and the SCS value for the corresponding substituent on transfer from $CHCl_3$ to DMSO being taken as approximate measures of these effects. Comparison of the data in Table 1 shows that the solvent susceptibility of the electronic effect of the SH group decreases considerably upon introduction of methyl groups in the 2 and 6 positions. This indicates that methyl substituents impede the solvation of this group, which is paralleled by the reduced ability of hydroxyl in 2,6-dimethylphenol to form hydrogen bonds with solvents⁸.

The solvent susceptibility of the electronic effect of organometallic groups is also reduced when *ortho*-methyl substituents are introduced, but to a lesser extent. This result may be due to steric inhibition of metal solvation arising from the interaction of the organic radicals on the metal atom with the *ortho*-methyl substituents in the solvated species. However, it has been found that such an interaction is not the main cause of the decreased solvent susceptibility of electronic effect observed for organometallic substituents. Indeed, as indicated by the data on the fluorine chemical shift in the $4-FC_6H_4HgS$ group for the corresponding derivatives of *p*-fluorothiophenol and 2,6-dimethyl-4-fluorothiophenol (Table 2), the solvent susceptibilities of the electronic effect of the $ArSHg$ groups and the coordinating ability of the metal atom in these compounds are approximately equal.

For the former compound, changes in the chemical shift on transfer from $CHCl_3$

to DMSO are practically the same for the fluorine nuclei in both aromatic rings. This may be related to the fact that the polarization of the C–Hg bond due to solvent–metal interactions is transmitted to the fluorine atom of the 4-FC₆H₄Hg group solely by an inductive mechanism²², whereas polarization of the Hg–S bond due to solvation also enhances the ability of the sulphur lone-pair electrons to conjugate with the aromatic ring. In view of these observations, it may be concluded that, at least in the case of organomercury substituents, the decrease in the solvent susceptibility of the electronic effect of the R_nMS groups upon the introduction of *ortho*-methyl substituents is due to less efficient transmission of solvation effects to the fluorine nucleus through steric inhibition of conjugation between the sulphur lone-pair electrons and the ring, rather than from steric hindrance to metal atom solvation.

Introduction of *ortho*-bromo substituents leads to a decrease in the solvent susceptibilities of the electronic effects of the SH group and organomercury substituents, but enhances those of the organotin and -lead groups. An especially pronounced reduction in the solvent susceptibility of electronic effect is observed for the SH group, the corresponding SCS value decreasing even on transfer from chloroform to pyridine. Consequently, if hydrogen bonding between the SH group and pyridine still occurs the extent of electron charge transfer during such bonding²³ is apparently the same as for internal hydrogen bonding due to the *ortho*-bromo substituent.

It should be pointed out that with organomercury groups the decrease in solvent susceptibility of the electronic effect actually results from a reduction in the coordinating ability of the metal atom. This is shown by the fact that the change in the ¹⁹F chemical shift in the 4-FC₆H₄HgS group on passing from chloroform to DMSO (Table 2) is smaller for the organomercury derivative of 2,6-dibromo-4-fluorothiophenol than for that of *p*-fluorothiophenol.

The observed difference in the behaviour of the solvent susceptibilities of the electronic effect of the organometallic groups R_nMS upon the introduction of *ortho*-bromo substituents may be a consequence of the dual nature of the influence of *ortho*-halogen atoms on the coordinating ability of the metal, as well as of differences in the strengths of intramolecular coordination with mercury on the one hand, and with tin and lead on the other. The coordinating ability of the metal atom should be enhanced²⁴ by the electron-attracting effect of *ortho*-bromo substituents¹³ and lowered by intramolecular coordination²⁵. The solvent susceptibility of the electronic effect of the organometallic groups in the derivatives of 2,6-dibromo-4-fluorothiophenol increases in the sequence C₆H₅HgS < (C₆H₅)₃PbS < (C₆H₅)₃SnS, which is the reverse of that indicated above for the strength of intramolecular coordination. This suggests that in organomercury derivatives the influence of intramolecular coordination upon the coordinating ability of the metal atom outweighs the electron-withdrawing effect of the halogen substituents, whereas for the organotin and -lead substituents the opposite occurs. This difference may be due to various factors depending on whether intramolecular coordination is absent or present in the solvated species formed.

In the former case, provided that the electron-attracting effect of the halogen substituents is transmitted to the mercury, tin and lead atoms with the same facility, the net result will be mainly determined by the fact that the SCS values for ArHgS groups in chloroform are already increased to a greater extent than the corresponding values for the (C₆H₅)₃SnS and (C₆H₅)₃PbS substituents, due to stronger intramole-

cular coordination in the organomercury derivatives. As a result, on transfer from chloroform to DMSO, *i.e.* on going from an intramolecularly coordinated state to a state with no intramolecular coordination, the changes in the SCS values for the ArHgS groups would be relatively smaller than if passage occurred between a hypothetical state with no intramolecular coordination in the inert solvent to the solvated state with intermolecular coordination.

If intramolecular coordination is retained in the solvated species, the difference in the behaviour of the coordinating abilities of the organometallic groups upon the introduction of *ortho*-halogen substituents may be determined by other factors. Thus, apart from the difference in the extent of charge transfer due to intramolecular coordination, the main factor governing the change in the coordinating ability of the organometallic group may be the differences in the degree of community of the metal atom orbitals²⁶ used by such pairs of ligands as sulphur-solvent and solvent-bromo substituent in the solvated species of the organometallic derivatives discussed. Where retention of intramolecular coordination occurs, the tetrahedral configuration of the sp^3 -hybridized mercury orbitals should persist (Fig. 1) in the solvated species of the organomercury derivatives of 2,6-dibromo-4-fluorothiophenol. For this orbital configuration the degree of community of the metal orbitals²⁶ used by the corresponding ligands can be shown to be 100% for the ligand pairs sulphur-solvent and solvent-bromine respectively. As a result, the increase in the electron-attracting power of the orbital used in the metal-solvent coordinate bond, which results from electron withdrawal by the halogen substituents through the mercury-sulphur bond, is compensated by an equivalent transfer of electron density into the vacant mercury orbital due to intramolecular coordination with the bromo substituent.

The reverse should be observed with organotin and -lead derivatives of 2,6-dibromo-4-fluorothiophenol. Thus, in the solvated species of the triphenyltin derivative the octahedral configuration of the $5sp^3d^2$ -hybridized tin orbitals (Fig. 2) is probably present if retention of intramolecular coordination occurs. For this orbital configuration the degree of community of the metal orbitals used respectively by the ligand pairs sulphur-solvent and solvent-bromine will be different. Corresponding calculations²⁶ show that for the former pair it amounts to 100% but is only 25% for

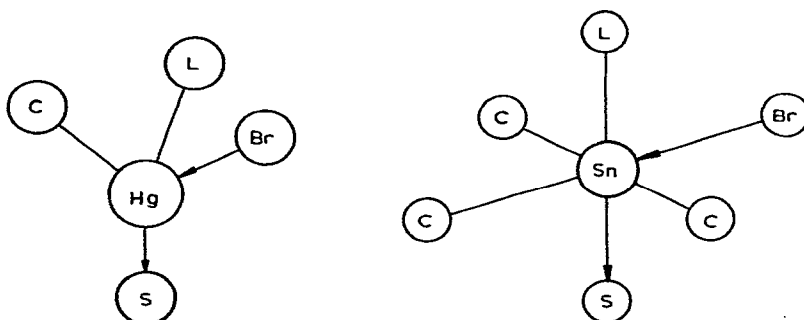


Fig. 1. The suggested configuration of ligands around the metal atom in the solvated species of the phenylmercury derivative of 2,6-dibromo-4-fluorothiophenol (L = the solvent molecule).

Fig. 2. The suggested configuration of ligands around the metal atom in the solvated species of the triphenyltin derivative of 2,6-dibromo-4-fluorothiophenol (L = the solvent molecule).

the latter. Consequently, the increase in the electron-accepting power of the tin orbital which is responsible for the metal-solvent coordinate bond, which results from electron withdrawal through the tin-sulphur bond, cannot be counterbalanced by an equivalent transfer of electron density into the vacant metal orbital through coordination with the *ortho*-halogen substituent.

In general, if the extent of charge transfer due to intramolecular coordination and of electron withdrawal due to the electron-attracting effect of the *ortho*-substituents are not equal this has no influence on the difference considered above between tetrahedrally and octahedrally coordinated metal atoms. If the purely electrostatic interaction²⁶ between the *ortho*-substituent and the solvent donor atom in the solvated species is ignored, it is possible to suggest that where intramolecular coordination of the univalent organotin and -lead groups occurs in the compounds investigated the electron-accepting ability of the metal orbital involved in the metal-solvent coordinate bond will decrease on condition that the extent of charge transfer into the vacant metal orbital upon intramolecular coordination is more than four times greater than the extent of electron withdrawal from the metal atom. In contrast, with the organomercury groups, a decrease in the electron-accepting power of the metal orbital responsible for bonding to the solvent molecule will occur if the above ratio is greater than unity.

It is hoped that further studies will shed more light on the problems which have arisen during the course of the present investigation. In particular, examination of organometallic derivatives of 3,5-dihalo-4-fluorothiophenols should enable the establishment of the extent to which the solvent susceptibility of electronic effect of the R_nMS groups changes upon introduction of electron-withdrawing substituents into the thiophenol moiety when intramolecular coordination is absent. Similarly, use of tris(*p*-fluorophenyl)tin and -lead derivatives of *ortho*-halothiophenols should enable the manner in which the electron density on these metals is influenced by the introduction of *ortho*-halogen substituents to be studied.

EXPERIMENTAL

General comments

The ¹⁹F NMR spectra were recorded at 34° on a Hitachi-Perkin-Elmer R-20 spectrometer operating at 56.4 MHz. All measurements were performed on dilute solutions of concentration not greater than 0.2 *M*. The use of the substitution method for the determination of fluorine chemical shifts has been described elsewhere¹. The data on the ¹⁹F chemical shifts in the organometallic derivatives of *p*-fluorothiophenol were taken from the previous communication²⁷. The solvents used were purified and dried by conventional methods.

Organometallic derivatives of 2,6-dimethyl-4-fluorothiophenol and 2,6-dibromo-4-fluorothiophenol were prepared by the reaction of organometallic hydroxides with the corresponding thiophenols, or by the interaction of sodium thiophenoxides with organometallic halides. Some typical examples of the preparation of these derivatives are given below. The melting points and analytical data for the organometallic derivatives of thiophenols not reported previously are presented in Table 3. The synthesis of organometallic derivatives of *p*-fluorothiophenol has been described in a previous communication²⁷.

TABLE 3

ANALYTICAL DATA AND MELTING POINTS FOR ORGANOMETALLIC DERIVATIVES OF 2,6-DIMETHYL-4-FLUOROTHIOPHENOL AND 2,6-DIBROMO-4-FLUOROTHIOPHENOL

Compound	M.p. (°C)	Analysis (%)			
		Found		Calcd.	
		C	H	C	H
C ₆ H ₃ HgSC ₆ H ₂ (CH ₃) ₂ -2,6-F-4	194-195	38.75	3.02	38.88	3.00
4-FC ₆ H ₄ HgSC ₆ H ₂ (CH ₃) ₂ -2,6-F-4	195-196	37.20	2.69	37.33	2.66
(C ₆ H ₅) ₃ SnSC ₆ H ₂ (CH ₃) ₂ -2,6-F-4	97-99	61.46	4.63	61.78	4.55
(C ₆ H ₅) ₃ PbSC ₆ H ₂ (CH ₃) ₂ -2,6-F-4	102-104	52.56	3.94	52.61	3.87
C ₆ H ₅ HgSC ₆ H ₂ Br ₂ -2,6-F-4	203-204	25.38	1.27	25.62	1.24
4-FC ₆ H ₄ HgSC ₆ H ₂ Br ₂ -2,6-F-4	214-216	25.29	1.34	24.82	1.03
(C ₆ H ₅) ₃ SnSC ₆ H ₂ Br ₂ -2,6-F-4	133-134	45.50	2.81	45.35	2.67
(C ₆ H ₅) ₃ PbSC ₆ H ₂ Br ₂ -2,6-F-4	124-125	40.17	2.59	39.83	2.35

Although the ¹⁹F NMR spectrum of 2,6-dimethyl-4-fluorothioanisole has been studied by Goodman and Taft², data on the preparation of this compound and of the corresponding thiophenol seem to be lacking in the literature. We have prepared 2,6-dimethyl-4-fluorothiophenol by the action of elemental sulphur on (2,6-dimethyl-4-fluorophenyl)magnesium bromide. 2,6-Dibromo-4-fluorothiophenol was synthesized from 2,6-dibromo-4-fluoroaniline by the modified procedure of Kopylova and Hasanova²⁸. The corresponding thioanisoles were obtained by methylation of the thiophenols with (CH₃)₂SO₄. 3,5-Dimethylfluorobenzene and 3,5-dibromofluorobenzene were prepared by the reported procedures^{29,30}

2,6-Dimethyl-4-fluorothiophenol

To the Grignard reagent, prepared from 10.2 g (0.05 mole) of 2,6-dimethyl-4-fluorobromobenzene²⁹ and 1.5 g of magnesium in 50 ml of dry ether, was added with stirring 1.3 g of sulphur powder in small portions. After heating on a water bath for 20 min, the reaction mixture was decomposed by the addition of 100 ml of 5% hydrochloric acid. The resulting oil was extracted with benzene, the benzene solution washed with water and dried over Na₂SO₄. On removal of the solvent the resulting product was distilled under reduced pressure, yielding 3.8 g (48%) of a colourless oil with b.p. 94-95°/13 mm, *n*_D²⁰ = 1.5485. (Found: C, 61.61; H, 5.83; S, 20.45. C₈H₉FS calcd.: C, 61.58; H, 5.76; S, 20.51%.)

2,6-Dimethyl-4-fluorothioanisole

5.0 g (40 mmole) of dimethyl sulphate was added dropwise to a solution of 2.2 g (15 mmole) of 2,6-dimethyl-4-fluorothiophenol and 1.5 g of NaOH in 20 ml of water with vigorous stirring. The oil formed was extracted with benzene, the benzene solution washed with 5% NaOH and water and dried over Na₂SO₄. On removal of the solvent, distillation of the residue in vacuum gave 1.5 g (70%) of a colourless oil with b.p. 91-93°/20 mm, *n*_D²⁰ = 1.5361. (Found: C, 63.33; H, 6.63; S, 19.16. C₉H₁₁FS calcd.: C, 63.52; H, 6.47; S, 18.82%.)

2,6-Dibromo-4-fluorothiophenol

A solution of 10.5 g (0.15 mole) of NaNO_2 in 20 ml of H_2O was added dropwise with stirring and cooling to $0-5^\circ$ to a suspension of 26.9 g (0.1 mole) of 2,6-dibromo-4-fluoroaniline³⁰ in a mixture of 40 ml of concentrated hydrochloric acid and 40 ml of water. After addition of the NaNO_2 solution was complete, the reaction mixture was stirred for 4 h at the same temperature. The filtered diazo-solution was added with stirring at 5° to a solution of 9.3 g H_3BO_3 in 30 ml of 40% hydrofluoric acid. The resulting precipitate of diazonium tetrafluoroborate was filtered, washed with a small amount of ice-cold water, methanol and ether respectively, and dried in vacuum; 24.0 g (62%) of 2,6-dibromo-4-fluorobenzenediazonium tetrafluoroborate was obtained. A suspension of 23.3 g (0.06 mole) of the diazonium salt in 20 ml of water was added in small portions to a stirred solution of 9.6 g (0.06 mole) of potassium xanthogenate in 70 ml of water heated to $50-60^\circ$. After the addition of the diazonium salt, the reaction mixture was heated at 100° for 0.5 h. After cooling, the reddish-brown precipitate which separated was filtered, washed with water and dissolved in 180 ml of ethanol. To the resulting solution 56 g of KOH was added and the mixture refluxed on a steam-bath for 7 h. The solvent was removed under reduced pressure and the residue treated with water. The insoluble solid was filtered, the filtrate acidified with diluted hydrochloric acid, and the product formed was steam distilled. 11.0 g (59%) of a colourless solid was obtained with m.p. $58-59^\circ$ after crystallization from light petroleum. (Found: C, 25.26; H, 1.00; F, 6.28; S, 11.25. $\text{C}_6\text{H}_3\text{Br}_2\text{FS}$ calcd.: C, 25.17; H, 1.04; F, 6.64; S, 11.20%.)

It was found that solutions of 2,6-dibromo-4-fluorothiophenol in DMSO readily produce a crystalline solid insoluble in aqueous NaOH, which might be the corresponding disulphide. Indeed, the disulphide obtained by oxidation of the thiophenol with iodine in alkaline solution turned out to be identical with the above compound, their mixture showing no depression of melting point. 2,2',6,6'-Tetrabromo-4,4'-difluorodiphenyldisulphide exists as pale yellow crystals with m.p. $229-230^\circ$ after crystallization from aqueous dimethylformamide. (Found: C, 25.31; H, 0.59; S, 11.22. $\text{C}_{12}\text{H}_4\text{Br}_4\text{F}_2\text{S}_2$ calcd.: C, 25.26; H, 0.70; S, 11.22%.)

2,6-Dibromo-4-fluorothioanisole

To a solution of 2.86 g (10 mmole) of 2,6-dibromo-4-fluorothiophenol and 0.6 g KOH in 10 ml of water at 60° was added with stirring 1.26 g (10 mmole) of dimethyl sulphate. The oil formed solidified on cooling. The resulting solid was washed with 5% NaOH, water and dried to yield 2.5 g (84%) of colourless crystals with m.p. 48° . Crystallization from light petroleum raised the melting point to 53° . (Found: C, 28.51; H, 1.75; S, 10.61. $\text{C}_7\text{H}_5\text{Br}_2\text{FS}$ calcd.: C, 28.00; H, 1.66; S, 10.66%.)

2,6-Dichloro-4-fluorothiophenol

This compound was prepared from 2,6-dichloro-4-fluoroaniline³⁰ with an overall yield of 25% in the same way as its bromo analogue. Colourless crystals were obtained with m.p. 32° after crystallization from light petroleum. (Found: C, 36.60; H, 1.66. $\text{C}_6\text{H}_2\text{Cl}_2\text{FS}$ calcd.: C, 36.54; H, 1.52%.)

Phenylmercury 2,6-dimethyl-4-fluorothiophenoxide

To a hot solution of 1.47 g (5 mmole) of phenylmercury hydroxide³¹ in 30 ml

of ethanol was added a solution of 0.78 g (5 mmole) of 2,6-dimethyl-4-fluorothiophenol in 5 ml of the same solvent. The reaction mixture was evaporated under reduced pressure and the residue recrystallized from cyclohexane, affording 1.8 g (88%) of colourless crystals.

Triphenyltin 2,6-dibromo-4-fluorothiophenoxide

A hot solution of 2.15 g (5 mmole) of triphenyltin bromide³² in 20 ml of ethanol was added to a solution of 1.43 g (5 mmole) of 2,6-dibromo-4-fluorothiophenol and 0.3 g KOH in 20 ml of the same solvent. The reaction mixture was evaporated in vacuum and the residue treated with water. The insoluble solid was filtered, washed with water and dried. Crystallization from ethanol gave 2.8 g (91%) of a white microcrystalline powder.

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