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A ^{19}F NMR STUDY OF ELECTRONIC EFFECTS IN SOME ORGANO-ANTIMONY AND ORGANOBISMUTH COMPOUNDS CONTAINING METAL—HETEROATOM BONDS

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Summary

The ^{19}F NMR technique has been used to study the ground-state electronic effects of univalent organo-antimony and -bismuth substituents in compounds of the type $(C_6H_5)_nMSC_6H_4F$-3, $(C_6H_5)_nMSC_6H_4F$-4, $(C_6H_5)_4SbOC_6H_4F$-3, $(C_6H_5)_4SbOC_6H_4F$-4 and $(4\text{-}FC_6H_4)_2SbX$, where $(C_6H_5)_nM = (C_6H_5)_2Sb$, $(C_6H_5)_2Bi$ and $(C_6H_5)_4Sb$, X = C_6H_5S, CH_3COO, Cl, Br. It has been found that the electron-donating effect of the sulphur-containing groups increases in the order: $(C_6H_5)_2SbS < (C_6H_5)_2BiS < (C_6H_5)_4SbS$, the substituents $(C_6H_5)_4SbS$ and $(C_6H_5)_4SbO$ being the most electron-releasing among the $(C_6H_5)_nMS$ and $(C_6H_5)_nMO$ groups containing heavy non-transition metals. From the viewpoint of solvent susceptibility of their electronic effects the $(C_6H_5)_2SbS$, $(C_6H_5)_2BiS$ and $(C_6H_5)_4SbS$ groups resemble the $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ substituents, and differ from the C_6H_5HgS group, whereas the $(C_6H_5)_4SbO$ substituent differs in this respect from all other $(C_6H_5)_nMO$ groups. The low conjugating ability of the $(C_6H_5)_2SbS$ substituent and slight influence of steric hindrance upon its electronic effect have been explained by the operation of conformational factors. It has been established that the electronic interactions across the antimony—heteroatom bonds are mainly of inductive character and that the order of electron withdrawal for the ArSbX substituents can be reversed on transfer from an inert to coordinating solvent.

Introduction

In a previous paper [1] it has been shown that the ground-state electronic effect of the Ar_2Sb and Ar_2Bi substituents directly bonded to the aromatic ring is mainly inductive, its solvent susceptibility being in most cases close to zero. The present study was undertaken to obtain quantitative data concerning the ground-state electronic effects of organometallic substituents of the type $(C_6H_5)_nMO$ and $(C_6H_5)_nMS$ (M = Sb, Bi) and their dependence on solvent and steric hindrance. The other aim was to elucidate to what extent the nature of the ligand on the metal atom influences the electronic effect of the ArSbX group and its solvent susceptibility. Also these data were compared with the available information on the electronic effects of similar organometallic groups containing mercury, tin and lead [2], and with the electronic influences of the OH, CH_3O, SH and CH_3S substituents [3]. As in earlier investigations, the ^{19}F NMR technique was used. This is known to be a valuable and sensitive method of studying ground-state substituent effects and their dependence on solvent [3].

Results and discussion

For this investigation a number of substituted bis(*p*-fluorophenyl)stibines as well as organo-antimony and -bismuth derivatives of *m*- and *p*-fluorophenols and thiophenols of the type: $(4\text{-}FC_6H_4)_2SbX$ (X = Cl, Br, $OCOCH_3$, $SC_6H_4F\text{-}4$), $Ar_nMSC_6H_4F\text{-}3$ and $Ar_nMSC_6H_4F\text{-}4$ ($Ar_nM = (C_6H_5)_2Sb, (C_6H_5)_2Bi, (C_6H_5)_4Sb$, $(C_6H_5)_4SbOC_6H_4F\text{-}3$ and $(C_6H_5)_4SbOC_6H_4F\text{-}4$) have been prepared. The ^{19}F chemical shifts relative to internal fluorobenzene have been determined for the compounds indicated in benzene, chloroform and pyridine. Benzene was chosen as a relatively inert solvent from the viewpoint of specific metal solvation, chloroform as a weakly acidic solvent capable of forming hydrogen bonds, and pyridine as a strongly coordinating solvent. The data on fluorine chemical shifts in fluorophenols, fluorothiophenols and their derivatives are listed in Table 1.

From the results it can be seen that organometallic substituents of the Ar_2MS type exert a smaller overall electron-donating effect from the *p*-position

TABLE 1

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

Compound	Solvent		
	C_6H_6	$CHCl_3$	C_5H_5N
$(C_6H_5)_2SbSC_6H_4F\text{-}3$	− 0.78	− 0.70	− 0.20
$(C_6H_5)_2BiSC_6H_4F\text{-}3$	− 0.18	− 0.26	− 0.49
$(C_6H_5)_4SbSC_6H_4F\text{-}3$	2.38	2.59	2.14
$CH_3SC_6H_4F\text{-}3$	− 0.46	− 0.60^a	− 0.53
$HSC_6H_4F\text{-}3$	− 0.80	− 0.90^a	− 0.75
$(C_6H_5)_2SbSC_6H_4F\text{-}4$	2.37	2.13	2.39
$(C_6H_5)_2BiSC_6H_4F\text{-}4$	3.17	2.69	3.94
$(C_6H_5)_4SbSC_6H_4F\text{-}4$	7.06	7.38	7.06
$CH_3SC_6H_4F\text{-}4$	4.40	4.10^a	4.75^b
$HSC_6H_4F\text{-}4$	3.96	3.50^a	4.57
$(4\text{-}FC_6H_4)_2SbSC_6H_4F\text{-}4$	1.80	1.58	3.11
	− 2.23^c	− 2.53^c	− 1.45^c
$(4\text{-}FC_6H_4)_2SbSC_6H_5$	− 2.13	− 2.38	− 1.47
$4\text{-}FC_6H_4Sb(SC_6H_4F\text{-}4)_2$	1.06	0.89	2.47
	− 3.37^d	− 3.71^d	− 2.16^d
$4\text{-}FC_6H_4Sb(SC_6H_5)_2$	− 2.89	− 3.27	− 2.09
$(C_6H_5)_4SbOC_6H_4F\text{-}3$	1.32	1.79	1.04
$CH_3OC_6H_4F\text{-}3$	− 1.33	− 1.40^a	− 1.47

TABLE 1 (continued)

Compound	Solvent		
	C_6H_6	$CHCl_3$	C_5H_5N
HOC_6H_4F-3	− 1.10	− 1.40[a]	− 0.85
$(C_6H_5)_4SbOC_6H_4F$-4	16.80	17.20	16.50
$CH_3OC_6H_4F$-4	11.58	11.30[a]	11.50
HOC_6H_4F-4	11.60	11.10	13.48

[a] From ref. 2. [b] From ref. 10. [c] For the $(4\text{-}FC_6H_4)_2Sb$ group. [d] For the $4\text{-}FC_6H_4Sb$ group.

relative to those of the HS and CH_3S groups. At the same time, the $(C_6H_5)_2BiS$ group is more electron-releasing than the $(C_6H_5)_2SbS$ group both from the *m*- and *p*-positions, which apparently indicates a greater polarity of the Bi—S bond relative to that of the Sb—S bond. Further, the data in Table 1 reveal that the fluorine shielding increases dramatically in going from the $(C_6H_5)_2SbS$ to the $(C_6H_5)_4$ SbS substituent. The considerably greater electron-donating ability of the organometallic substituent containing pentavalent antimony compared to that containing trivalent antimony is evidently due to the greater polarity of the metal—sulphur bond in the former case. This is in good agreement with the available literature data [4, 5].

A comparison of the present results with the data obtained previously [2] shows that the substituents $(C_6H_5)_4SbS$ and $(C_6H_5)_4SbO$ are the most electron-donating among the univalent organometallic groups of the types Ar_nMS and Ar_nMO containing heavy non-transition metals. The introduction of *p*-fluoro substituents into the $(C_6H_5)_2SbS$ group decreases the polarity of the Sb—S bond in benzene and chloroform. However, the introduction of fluorine in the thiophenol moiety hardly changes the electron density on the antimony atom, as evidenced by the comparison of the fluorine chemical shifts in the fluorophenyl groups on the metal atom for the compounds $(4\text{-}FC_6H_4)_2SbSC_6H_5$ and $(4\text{-}FC_6H_4)_2SbSC_6H_4F$-4. An appreciable effect is observed in chloroform and benzene only in the case of the simultaneous introduction of two fluoro substituents in the thiophenol moieties of the compound $4\text{-}FC_6H_4Sb(SC_6H_5)_2$.

Considering the solvent influences on the electric effects of organometallic substituents, it is appropriate to discuss the behaviour of the derivatives of *p*-fluorothiophenol and *p*-fluorophenol. For these derivatives the solvent effects should be more pronounced due to the competetive conjugation with the aromatic ring of the sulphur or oxygen lone-pair electrons and those of the fluorine. The solvent susceptibility of the electronic effect of the $(C_6H_5)_2SbS$ group, which can be taken, as a first approximation, as the change in fluorine chemical shift in $(C_6H_5)_2SbSC_6H_4F$-4 on transfer from an inert to a proton-donating or coordinating solvent, is close to zero. The behaviour of the $(C_6H_5)_2BiS$ group in this respect is different and similar to that of the SH substituent, the fluorine shielding decreasing on transfer from benzene to chloroform and increasing on transfer to pyridine in both cases.

The observed difference in the solvent susceptibilities of the electronic effect for the $(C_6H_5)_2SbS$ and $(C_6H_5)_2BiS$ substituents is probably associated with the different Lewis acidities of the corresponding metals, which can be explained by their position in the periodic table. Thus it is known [6] that there are two factors determining the variation of the acidity of heavy metal atoms in the same group with increasing nuclear charge. On the one hand, the decrease in the attraction between the metal nucleus and lone-pair electrons of the donor atom, which arises from the increased shielding of the nucleus by the inner electron shells, should reduce the acidity of the metal. On the other hand, the energy difference between the *p* and *d* orbitals decreases with increasing atomic number, which should lead to a decrease in energy expenditure required for the rehybridization of the metal orbitals accompanying the formation of solvated species. From the greater acidity of bismuth relative to antimony, shown by the present results, it may be concluded that the latter factor is predominant in determining the acidity of these metals.

The increase in electron-accepting properties of the aromatic radicals on the antimony atom enhances the coordinating ability of the metal considerably, since on transfer from benzene to pyridine the fluorine shielding in the thiophenol moiety of the compound $(4\text{-}FC_6H_4)_2SbSC_6H_4F\text{-}4$ increases by approximately one ppm. It is also noteworthy that the increase in electron density on the antimony atom upon specific solvation is transmitted to the fluorine atoms of all three aromatic rings with approximately the same efficiency. This apparently arises because the transmission of solvation effects to the fluorine atoms of the $(4\text{-}FC_6H_4)_2Sb$ group proceeds only inductively [1], whereas the transmission of these effects to the fluorine atom of the $SC_6H_4F\text{-}4$ moiety is enhanced in addition by the conjugation of the sulphur lone-pair electrons with the aromatic ring. A similar situation has been met previously in the case of $4\text{-}FC_6H_4HgSC_6H_4F\text{-}4$ [2]. Finally, the decrease in fluorine shielding in $(C_6H_5)_2BiSC_6H_4F\text{-}4$ on going from benzene to chloroform may be connected with hydrogen bonding between chloroform and the sulphur atom, which corresponds to the greater polarity of the Bi—S bond relative to that of the Sb—S bond.

From the data obtained in the present work and the greater electronegativity of oxygen relative to that of sulphur [7] it may be expected that the polarity of the metal—heteroatom bonds and the partial positive charge on the metal atom will increase in the substituent order: $(C_6H_5)_2SbS < (C_6H_5)_4SbS < (C_6H_5)_4SbO$. This should have led to an increase in coordinating ability of antimony in the same sequence, due to the greater attraction of the donor lone-pair electrons and reduced energy of the vacant *d* orbitals, facilitating sp^3d hybridization upon solvation [8]. However, the data in Table 1 indicate that the substituents $(C_6H_5)_4SbS$ and $(C_6H_5)_4SbO$ possess practically no solvent susceptibility of electronic effect. This is probably connected with the steric hindrance produced by the four phenyl groups, which inhibit the approach of solvent molecules to the metal atom. It should be noted that the above factor cannot be responsible for the lack of coordinating ability of antimony in the $(C_6H_5)_2SbS$ group, since the inspection of molecular models shows that in $(C_6H_5)_2SbSC_6H_4F\text{-}4$ the approach of solvent molecules to the metal atom is not hindered by the ligands. In general, it should be concluded that from the viewpoint of solvent susceptibility of their electronic effects the $(C_6H_5)_2SbS$, $(C_6H_5)_4SbS$ and $(C_6H_5)_2BiS$ groups are similar to the $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ substituents, but different from the C_6H_5HgS group [2]. At the same time, the $(C_6H_5)_4SbO$ substituent

TABLE 2

INDUCTIVE AND RESONANCE PARAMETERS OF SUBSTITUENTS

Substituent	σ_I			σ_R^0		
	C_6H_6	$CHCl_3$	C_5H_5N	C_6H_6	$CHCl_3$	C_5H_5N
$(C_6H_5)_2SbS$	0.19	0.18	0.11	−0.11	−0.10	−0.09
$(C_6H_5)_2BiS$	0.11	0.12	0.02	−0.11	−0.10	−0.15
$(C_6H_5)_4SbS$	−0.25	−0.28	−0.22	−0.16	−0.16	−0.17
CH_3S	0.15	0.17	0.16	−0.17	−0.16	−0.14
HS	0.20	0.23	0.19	−0.16	−0.15	−0.14
$(C_6H_5)_4SbO$	−0.10	−0.17	−0.06	−0.53	−0.52	−0.53
CH_3O	0.27	0.28	0.29	−0.43	−0.43	−0.44
HO	0.24	0.29	0.20	−0.43	−0.42	−0.48

contrasts sharply in this respect with the $(C_6H_5)_3SnO$, $(C_6H_5)_3PbO$ and C_6H_5HgO groups [2].

In order to obtain quantitative characteristics of the electronic effect of the substituents studied, the values of σ_I and σ_R^0 were calculated from the fluorine chemical shifts by using the Taft equations [9, 10]. These values are given in Table 2 together with the corresponding data for the HO, HS, CH_3O and CH_3S groups, partly determined in the present investigation and partly taken from the literature [2, 9, 10]. Inspection of Table 2 shows that substitution of the $(C_6H_5)_2Sb$ group for hydrogen in the HS substituent reduces the electron-accepting inductive effect of the latter. The mesomeric electron-donating effect of the $(C_6H_5)_2SbS$ group turns out to be considerably smaller than those of the HS and CH_3S substituents. On the basis of the inductive effects of the $(C_6H_5)_2SbS$, CH_3S and HS groups, it might have been expected that the conjugating abilities of these substituents should have been comparable. The opposite situation actually observed can be explained by the possible operation of the following factors. First, with the $(C_6H_5)_2SbS$ substituent, the d_π—p_π conjugation between the sulphur lone-pair electrons and metal vacant orbitals is theoretically possible, and this may impede the p_π—p_π conjugation of sulphur electrons with the aromatic ring. Secondly, the conformational effects, which will be discussed below, may play a substantial role.

The introduction of the $(C_6H_5)_2Bi$ group instead of hydrogen reduces the electron-accepting inductive effect of the HS substituent in all solvents to a greater extent than does the introduction of the $(C_6H_5)_2Sb$ group, due to the greater polarity of the Bi—S bond compared to that of the Sb—S bond. The conjugative electron-donating effect of the $(C_6H_5)_2BiS$ substituent turns out to be smaller than that of the HS group in all solvents except pyridine. The reduced conjugating ability of this substituent in benzene and chloroform can be determined by the same factors, as in the case of the $(C_6H_5)_2SbS$ group, which are counterbalanced in pyridine by the effect of the metal solvation.

The data of Table 2 reveal that substitution of the $(C_6H_5)_4Sb$ group for hydrogen in the HS and HO substituents produces a great change in the electronic effects of these groups. In contrast to the HS, CH_3S, HO and CH_3O groups, the values of σ_I become negative, indicating the electron-donating inductive effect of the $(C_6H_5)_4SbS$ and $(C_6H_5)_4SbO$ substituents, while the conjugating

TABLE 3

^{19}F SCS VALUES FOR SUBSTITUENTS IN CHLOROFORM (IN ppm)

Compound	Substituent	SCS
$(C_6H_5)_2SbSC_6H_4F$-4	$(C_6H_5)_2SbS$	2.13
$CH_3SC_6H_4F$-4	CH_3S	4.10[a]
HSC_6H_4F-4	HS	3.50[a]
$(C_6H_5)_2SbSC_6H_2(CH_3)_2$-2,6-F-4	$(C_6H_5)_2SbS$	0.12
$CH_3SC_6H_2(CH_3)_2$-2,6-F-4	CH_3S	−1.10[a]
$HSC_6H_2(CH_3)_2$-2,6-F-4	HS	3.00[a]

[a] Taken from ref. 12.

ability also increases in the latter case, being close to that of the HS and CH_3S groups in the former. The difference between the mesomeric behaviour of the above substituents and that of the $(C_6H_5)_2SbS$ group can be explained by the greater polarity of the $(C_6H_5)_4Sb—X$ bonds relative to that of the $(C_6H_5)_2Sb—X$ bonds. This cancels or outweighs the influence of the conformational factors to be discussed later.

In order to obtain evidence concerning the influence of steric hindrance produced by inert substituents in the positions 2 and 6 of the benzene ring upon the electronic effect of the $(C_6H_5)_nMS$ groups, we have studied the $(C_6H_5)_2Sb$ derivative of 2,6-dimethyl-4-fluorothiophenol. Unfortunately, we failed to prepare the corresponding $(C_6H_5)_2Bi$ and $(C_6H_5)_4Sb$ derivatives due to their instability. The ^{19}F SCS values for the $(C_6H_5)_2SbS$, HS and CH_3S groups in the above compound, its analogue without *o*-methyl substituents and the corresponding fluorothiophenols and fluorothioanisoles in chloroform are listed in Table 3. Inspection of the results reveals the following regularities.

The introduction of two methyl groups in the positions 2 and 6 to the $(C_6H_5)_2SbS$ substituent leads to a decrease in the ^{19}F SCS value for this group which is observed in $(C_6H_5)_2SbSC_6H_4F$-4. This enables us to suppose that the $(C_6H_5)_2Sb$ group is twisted away from the plane of the thiophenol ring, due to nonbonded interactions between the metal atom and the CH_3 groups, which reduces the conjugation of the lone-pair sulphur electrons with the aromatic ring. The change in the ^{19}F SCS for the $(C_6H_5)_2SbS$ substituent on introducing *o*-methyl groups is close to the corresponding changes in the ^{19}F SCS values for the C_6H_5HgS, $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ groups, somewhat greater than that for the HS substituent, and practically twice as low as the change in the ^{19}F SCS value for the CH_3S group [11, 12]. The data obtained appear to indicate that the phenomenological steric requirements of the C_6H_5Hg, $(C_6H_5)_3Sn$, $(C_6H_5)_3Pb$ and $(C_6H_5)_2Sb$ groups involved in nonbonded interactions with *o*-methyl substituents are approximately equal, being at the same time smaller than those of the CH_3 group. The equality of the steric requirements of these organometallic groups is associated with the fact that in the organometallic derivatives of 2,6-dimethylthiophenols the steric interactions are mainly determined by contacts between the metal atom and CH_3 groups [13] in which the aryl radicals on the metal do not participate.

In connection with some new information on this point, it should be pointed out that the small changes in the ^{19}F SCS values for the $(C_6H_5)_nMS$ groups upon introduction of *o*-methyl substituents may arise from conformational effects, rather than from small steric requirements of the $(C_6H_5)_nM$ groups, as has been suggested previously [12]. Thus, it has been found [14] that in triphenyltin 2-methylthiophenoxide, in the crystalline state, the angle between the C—S—Sn plane and that of the thiophenol aromatic ring is 80°. Assuming that the angle of rotation around the C—S bond is determined mainly by the intramolecular factors, rather than by the crystal packing effects, it may be supposed that already in the preferred conformation of the organometallic derivatives of *p*-fluorothiophenol, in solution, the angle between the C—S—M plane and that of the thiophenol ring is closer to 90° than to 0° due to nonbonded repulsive interactions between the metal and *o*-hydrogen atoms. This factor should inhibit conjugation of the lone-pair sulphur electrons with the ring even in the absence of two *o*-methyl substituents and may be responsible for the reduced conjugating ability of the $(C_6H_5)_3SbS$ group and slight influence of *o*-methyl substituents upon the electronic effect of the $(C_6H_5)_nMS$ groups.

The greater change in the electronic effect of the CH_3S group upon introducing *o*-methyl substituents, as evidenced by the ^{19}F NMR data, suggests that in the predominant conformation of *p*-fluorothioanisole the angle between the C—S—C plane and that of the aromatic ring is closer to 0° than the corresponding angle in the organometallic derivatives of *p*-fluorothiophenol, the conformations corresponding to the coplanarity of the above planes being sufficiently populated. It may be supposed that the differences in the conformational behaviour of the CH_3S and $(C_6H_5)_nMS$ groups, which seem to exist despite the similarity in the values of the effective Van der Waals radii of the CH_3 group [15, 16] and heavy metal atoms [13, 15, 17], are due to the anisotropy of the Van der Waals radius of the CH_3 group and synchronous rotation of the CH_3 and CH_3S groups.

Thus, the minimal Van der Waals radius of the CH_3 group, which corresponds to the contacts in the direction of the bisector of the H—C—H angle, is 1.7 Å and different from the effective Van der Waals radius (2.0 Å) of the CH_3 group [18]. As a result, with the synchronous rotation of the CH_3S group around the S—C_{Ar} bond and of the CH_3 group around the C—S bond, the nonbonded repulsive interactions between the *o*-hydrogen atom and the CH_3 group in the eclipsed conformation may occur in the direction of the minimal Van der Waals radius of the latter. In this case the steric hindrance in the eclipsed conformation of *p*-fluorothioanisole will be smaller and the population of this conformation greater than in the case of contacts involving the maximal or effective Van der Waals radius of the CH_3 group, which correspond to the asynchronous rotation of the CH_3 and CH_3S groups. In contrast, for the $(C_6H_5)_nMS$ substituents such a possibility is ruled out, since Van der Waals radii of atoms appear to be isotropic in the directions perpendicular to the valence bonds of the corresponding atom [15]. The final solution to this problem can be obtained only after an electronographic investigation of thioanisoles and organometallic thiophenoxides of the type R_nMSAr in the vapour phase.

The last part of the present study was concerned with the influence of the ligands on the metal atom upon the electronic effect and solvent susceptibility of the elctronic effect for the ArSbX groups, and involved investigation of the

TABLE 4

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

Compound	Solvent		
	C_6H_6	$CHCl_3$	C_5H_5N
$(4\text{-}FC_6H_4)_2SbCl$	−3.15	−3.77	−0.48
$(4\text{-}FC_6H_4)_2SbBr$	−3.17	−3.68	−0.64
$(4\text{-}FC_6H_4)_2SbOCOCH_3$	−2.82	−3.34	−1.01
$(4\text{-}FC_6H_4)_2SbSC_6H_5$	−2.13	−2.38	−1.47

$(4\text{-}FC_6H_4)_2SbX$ compounds. The data on the fluorine chemical shifts in the corresponding systems are given in Table 4. A consideration of the results reveals the following regularities. The solvent susceptibility of electronic effect for the ArSbX substituents, in which the antimony atom is directly bonded to a heteroatom, is rather large and much greater than that of the Ar_2Sb groups [1]. The fluorine shielding diminishes on transfer from benzene to chloroform and increases in going from benzene to pyridine. In the former case this probably arises from hydrogen bond formation between the solvent and the anionic part of the molecule, whereas in the latter the specific solvation of the antimony atom apparently takes place. This interpretation is supported by considerably smaller changes in the fluorine shielding for $(4\text{-}FC_6H_4)_3Sb$ on transfer from chloroform to pyridine [1], despite the similarity in molecular geometry between this compound and substituted bis(*p*-fluorophenyl)stibines. According to the changes in the fluorine shielding on passing from benzene to pyridine, the coordinating ability of antimony changes in parallel with the electron-accepting ability of the ligand on the metal atom.

As can be seen from Table 4, introduction of the $4\text{-}FC_6H_4SbX$ substituents into the aromatic ring deshields the fluorine nucleus, the electron-withdrawing properties of such groups being rather pronounced. On the basis of the fluorine chemical shifts in chloroform and benzene, it can be concluded that the electron-withdrawing effect of the ArSbX groups in these solvents increases in the order: $C_6H_5S < CH_3COO < Br < Cl$. It is interesting to note that in pyridine a reversed order of electron-accepting ability of the ArSbX substituents is observed: $Cl < Br < CH_3COO < C_6H_5S$, which evidently results from specific solvation of the metal atom. The observed behaviour of the electronic effect of the ArSbX groups seems to be a specific feature of organoantimony substituents, since the reversal of the order of electron-withdrawal on transfer from an inert to a coordinating solvent has not been observed for mercury and organotin substituents [19, 20].

If the assumption is made that the interaction across the Sb—X bonds proceeds, as in the case of the Sb—Ar bond [1], mainly in inductive fashion, then it may be expected that the influence of the ligands on the metal atom upon the electronic effect of the ArSbX group will be determined by their inductive parameter σ_I. In this connection the fluorine chemical shifts in compounds of the type $(4\text{-}FC_6H_4)_2SbX$ were plotted against the σ_I values for the ligands on the metal atom, taken from the papers of Taft and Charton [9, 21]. A good straight line was obtained (Fig. 1, Table 5). The existence of a good

TABLE 5

PARAMETERS OF THE CORRELATION EQUATION $\sigma_F = \rho\sigma_I + C$ FOR THE COMPOUNDS $(4\text{-}FC_6H_4)_2SbX$ IN CHLOROFORM[a, b]

n	*ρ*	*C*	S_ρ
5	−8.13	−0.02	0.33
S_C	*S*	*r*	*CL*
0.14	0.35	0.99	99.9

[a] The value of σ_F for X = C_6H_5 was calculated from the data for $(4\text{-}FC_6H_4)_3Sb$ and $(C_6H_5)_2SbC_6H_4F\text{-}4$ [1] by using an additive scheme. [b] *n* = number of points; *r* = correlation coefficient; *S* = standard error of the estimate; S_ρ = standard error of the coefficient *ρ*, S_C = standard error of the coefficient *C*; *CL* = confidence level for significance of correlation.

linear correlation between the fluorine chemical shifts for the compounds $(4\text{-}FC_6H_4)_2SbX$ in chloroform and inductive parameters of the ligands indicates that the interactions across the Sb—X bonds are in fact mainly of inductive character. This observation lends further support to the conclusion that the reduced conjugating ability of the $(C_6H_5)_2SbS$ substituent arises from conformational effects associated with the twist of the C—S—Sb plane from coplanarity with the thiophenol ring, rather than from d_π—p_π bonding between antimony and sulphur.

Experimental

General

The ^{19}F NMR spectra were recorded at 34° using a Hitachi—Perkin—Elmer R-20 spectrometer operating at 56.4 MHz. All the measurements were made for diluted solutions at concentrations not greater than 0.2 *M*. The determination of the fluorine chemical shifts by the substitution method has been described elsewhere [22]. The experimental standard error of the fluorine chemical shifts was not greater than ± 0.1 ppm. The solvents were purified by conventional procedures. Benzene was distilled over sodium before use, chloroform over phosphorus pentoxide and pyridine was distilled over potassium hydroxide and dried over molecular sieves (4 Å). The purity of the solvents was checked by PMR.

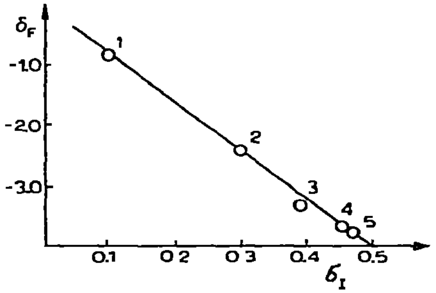

Fig. 1. Plot of the ^{19}F chemical shifts for the compounds $(4\text{-}FC_6H_4)_2SbX$ in chloroform versus the σ_I values of the group on the metal atom: 1, C_6H_5; 2, SC_6H_5; 3, $OCOCH_3$; 4, Br; 5, Cl.

Diphenyl(arylthio)bismuthines and diaryl(arylthio)stibines were prepared by the interaction of diphenylhalobismuthines and diaryl(acetoxy)stibines with substituted sodium thiophenoxides. *p*-Fluorophenyl(diarylthio)stibines were synthesized by the reaction of *p*-fluorostibinoxide with the corresponding thiophenols. Tetraphenylantimony fluorophenoxides and fluorothiophenoxides were obtained by the treatment of tetraphenylantimony methoxide with fluorophenols and fluorothiophenols. Attempts to prepare diphenyl(fluorophenoxy)-stibines and -bismuthines, as well as the $(C_6H_5)_2Bi$ and $(C_6H_5)_4Sb$ derivatives of 2,6-dimethyl-4-fluorothiophenol, failed. The known di(*p*-fluorophenyl)halostibines [23] were obtained by the treatment of di(*p*-fluorophenyl)-acetoxystibine with the corresponding acids.

The purity of most of the compounds investigated was checked by TLC on alumina. The physical properties and analytical data for the compounds not reported in the literature are given in Table 6. Typical examples of the synthesis of the compounds studied in the present communication are presented below.

Diphenyl(m-fluorophenylthio)bismuthine

To a solution of 0.6 g (4 mmol) of sodium *m*-fluorothiophenoxide in 20 ml of absolute ethanol was added 1.7 g (4 mmol) of diphenylbromobismuthine [24]. The reaction mixture was heated to reflux. The precipitate of diphenylbromostibine dissolved and a yellow solution resulted. The solvent was removed under reduced pressure, the residue washed with water and dried. 2.3 g (99%) of a solid was obtained which formed yellow needles after recrystallization from petroleum ether.

Di(p-fluorophenyl)(phenylthio)stibine

To a hot solution of 1.8 g (5 mmol) of di(*p*-fluorophenyl)acetoxystibine in 20 ml of absolute ethanol was added a solution of 0.65 g (5 mmol) of sodium thiophenoxide in 20 ml of the same solvent. The reaction mixture was heated to reflux and the solvent removed under vacuum. The oily residue was washed with water, dissolved in ether and the ethereal solution dried over Na_2SO_4. After evaporation of the solvent 1.9 g (90%) of a yellow oil was obtained, which was purified by chromatography in a thick layer of alumina, using a mixture of petroleum ether and acetone (6/1) as eluent.

Di(p-fluorophenylthio)(p-fluorophenyl)stibine

To a suspension of 1.7 g (5 mmol) of *p*-fluorophenylstibinoxide [23] in 20 ml of ethanol was added 1.3 g (10 mmol) of *p*-fluorothiophenol. The reaction mixture was heated to reflux, which resulted in almost complete dissolution of the precipitate. The solution formed was filtered and the solvent removed under reduced pressure, yielding 1.9 g (84%) of the residue, which gave a pale-yellow solid after recrystallization from methanol.

Di(p-fluorophenyl)acetoxystibine

A solution of 55 g (0.5 mol) of freshly distilled *p*-fluoroaniline in a mixture of 150 ml of concentrated hydrochloric acid and 350 ml of water was cooled to 0° and diazotized with a solution of 35 g (0.51 mol) of $NaNO_2$ in 50 ml of water. To the resulting diazosolution a solution of 115 g (0.5 mol) of $SbCl_3$

TABLE 6

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF ORGANO-ANTIMONY AND -BISMUTH COMPOUNDS

Compound	Yield (%)	M.p.[a] (°C)	R_f[b]	Analysis found (calcd.) (%)	
				C	H
$(C_6H_5)_2BiSC_6H_4F$-3	99	79-80	0.4	43.98 (44.09)	3.05 (2.88)
$(C_6H_5)_2BiSC_6H_4F$-4	99	89-90	0.4	43.84 (44.09)	2.95 (2.88)
$(C_6H_5)_2SbSC_6H_4F$-3	79	oil	0.6	53 96 (53.63)	3.56 (3.50)
$(C_6H_5)_2SbSC_6H_4F$-4	80	48-49	0.6	53.37 (53.63)	3.58 (3.50)
$(4\text{-}FC_6H_4)_2SbSC_6H_5$	90	oil	0.7	51.54 (51.33)	3.11 (3.11)
$(4\text{-}FC_6H_4)_2SbSC_6H_4F$-4	64	oil	0.6	48.99 (49.24)	2.51 (2.71)
4-$FC_6H_4Sb(SC_6H_5)_2$	78	107-108	0.5	49.24 (49.68)	2.70 (3.23)
4-$FC_6H_4Sb(SC_6H_4F\text{-}4)_2$	84	120-121	0.7	45.89 (45.89)	2.53 (2.57)
$(C_6H_5)_2SbSC_6H_2(CH_3)_2$-2,6-F-4	100	78-79	0.7	55.24 (55.72)	3.95 (4.21)
$(C_6H_5)_4SbSC_6H_4F$-3	80	134-135	0.7	64.28 (64.66)	4.21 (4.34)
$(C_6H_5)_4SbSC_6H_4F$-4	84	130-131	0.7	64.61 (64.66)	4.13 (4.34)
$(C_6H_5)_4SbOC_6H_4F$-3	82	139-141	0.1	66.16 (66.58)	4.35 (4.47)
$(C_6H_5)_4SbOC_6H_4F$-4	88	159-160	0.6	66.29 (66.58)	4.36 (4.47)
$(4\text{-}FC_6H_4)_2SbOCOCH_3$	4	120-121	—	44.72 (45.33)	2.99 (2.99)
$(4\text{-}FC_6H_4)_2SbBr$	66	50-52	—	36.58 (36.78)	1.94 (2.06)

[a] The compounds melt with decomposition. [b] A mixture of petroleum ether and acetone (6/1) was used as eluent.

in 75 ml of concentrated hydrochloric acid was added, with cooling and vigorous stirring. The pale yellow precipitate formed was filtered, washed with 2% hydrochloric acid, ethanol, ether and dried to give 100 g (60%) of the double diazonium salt.

25 g of zinc dust was placed in a four-necked flask equipped with a stirrer, reflux condenser and thermometer. After addition of 300 ml of hot ethyl acetate, 100 g of the double diazonium salt was added in small portions with vigorous stirring. The solvent began to boil and a vigorous decomposition of the salt occurred. After the evolution of nitrogen had ceased, the reaction mixture was filtered and the filtrate evaporated under vacuum without heating. The residue was washed with 50 ml of 5 *N* hydrochloric acid and then with 25 ml of the same acid. The residue was dissolved in a five-fold volume of ethanol, and the resulting solution cooled with ice and the precipitate formed was filtered.

The filtrate was poured into a mixture of 5% ammonia and crushed ice, with stirring. The precipitate formed was washed repeatedly with water and then treated with ether. After filtration the ethereal solution was evaporated, affording di(*p*-fluorophenyl)stibinoxide as a red oil. This was treated with acetic acid to give 6.9 g (4%) of a white crystalline solid, m.p. 120-121°, after recrystallization from acetic acid.

Di(p-fluorophenyl)bromostibine

2.0 g (6 mmol) of di(*p*-fluorophenyl)acetoxystibine was dissolved in 10 ml of hot acetic and then rapidly cooled to room temperature. An excess of 48% hydrobromic acid was added to the resulting solution, leading to the separation of a pale brown oil which crystallized on standing. The resulting solid was filtered with suction and dried in vacuum over NaOH and P_2O_5, affording 1.6 g (66%) of crystals. Attempts to find a solvent for recrystallization failed.

Tetraphenylantimony p-fluorophenoxide

A mixture of 1.1 g (2.5 mmol) of tetraphenylantimony methoxide [25] and 0.28 g (2.5 mmol) of *p*-fluorophenol in 25 ml of dry benzene was refluxed for 2 h. The solvent was removed under vacuum to give 1.2 g (88%) of a solid which formed colourless crystals after recrystallization from octane.

Tetraphenylantimony p-fluorothiophenoxide

A mixture of 1.1 g (2.5 mmol) of tetraphenylantimony methoxide and 0.32 g (2.5 mmol) of *p*-fluorothiophenol in 25 ml of dry benzene was refluxed for 2 h. After evaporation of the solvent, 1.3 g (84%) of a colourless solid was obtained which was recrystallized from octane.

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References

1 A.N. Nesmeyanov, D.N. Kravtsov, B.A. Kvasov, S.I. Pombnk and E.I. Fedin, J. Organometal. Chem., 47 (1973) 367.
2 A.N. Nesmeyanov, D.N. Kravtsov, B.A. Kvasov, E.M. Rokhlina, V.M. Pachevskaya, L.S. Golovchenko and E.I. Fedin, J. Organometal. Chem., 38 (1972) 307.
3 P.R. Wells, S. Ehrenson and R.W. Taft, Progr. Phys. Org. Chem., 6 (1968) 147.
4 G.E. Coates, M.L.H. Green and K. Wade, Organometallic Compounds, Vol. I, Methuen, London, 1967, p. 522.
5 R.G. Goel, Can. J. Chem., 47 (1969) 4607.
6 D.P.N. Satchell and P.S. Satchell, Chem. Rev., 69 (1969) 251.
7 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Interscience, New York, 1962, p. 92.
8 H.H. Jaffé, J. Phys. Chem., 58 (1954) 185.
9 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Andersen and G.T. Davies, J. Amer. Chem. Soc., 85 (1963) 709.
10 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K K. Andersen and G.T. Davies, J. Amer. Chem. Soc., 85 (1963) 3146.
11 L. Goodman and R.W. Taft, J. Amer. Chem. Soc., 87 (1965) 4385.
12 D.N. Kravtsov, B.A. Kvasov, L.S. Golovchenko, E.M. Rokhlina and E.I. Fedin, J. Organometal. Chem., 39 (1972) 107.

13 N.G. Bokii, Yu.T. Struchkov, D.N. Kravtsov and E.M. Rokhlina, Zh. Strukt. Khim., 14 (1973) 291.
14 N.G. Bokii, Yu.T. Struchkov, D.N. Kravtsov and E.M. Rokhlina, Zh. Strukt. Khim., in press.
15 A. Bondi, J. Chem. Phys., 68 (1964) 441.
16 R.L. Avoyan, Yu.T. Struchkov and V.G. Dashevskii, Zh. Strukt. Khim., 7 (1966) 289.
17 N.W. Aicock, Advan. Inorg. Chem. Radiochem., 15 (1972) 2.
18 M. Charton, J. Amer. Chem. Soc., 91 (1969) 615.
19 D.N. Kravtsov, B.A. Kvasov, L.S. Golovchenko and E.I. Fedin, J. Organometal. Chem., 36 (1972) 227.
20 D.N. Kravtsov, B.A. Kvasov, T.S. Khazanova and E.I. Fedin, J. Organometal. Chem., 61 (1973) 219.
21 M. Charton, J. Org. Chem., 29 (1964) 1222.
22 A.N. Nesmeyanov, D.N. Kravtsov, E.I. Fedin, B.A. Kvasov, V.M. Pachevskaya and L.S. Golovchenko, Dokl. Akad. Nauk SSSR, 183 (1968) 1098.
23 A.B. Bruker, Zh. Obshch. Khim., 27 (1957) 2223.
24 H. Gilman and H.I. Yablunky, J. Amer. Chem. Soc., 63 (1941) 207.
25 G.O. Doak, G.G. Long and L.D. Freedman, J. Organometal. Chem., 12 (1968) 443.