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A COMPARATIVE ^{19}F NMR STUDY OF ELECTRONIC EFFECTS IN SOME FLUOROARYL COMPOUNDS OF ANTIMONY AND BISMUTH AND IN THEIR CARBON AND NITROGEN ANALOGUES

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SUMMARY

A number of *m*- and *p*-fluorophenyl compounds of type $Ar_2QC_6H_4F$ (Q = Sb, Bi, N and CH; Ar = C_6H_5, C_6H_4F) have been prepared. The ^{19}F chemical shifts relative to fluorobenzene have been measured in cyclohexane, chloroform and pyridine for all these compounds. On the basis of the data obtained, the electronic nature of the Ar_2Sb and Ar_2Bi substituents has been studied and compared with that of the corresponding $(C_6H_5)_2N$ and $(C_6H_5)_2CH$ groups. The electronic effect of the Ar_2Sb and Ar_2Bi substituents has been shown to be mainly inductive, its solvent susceptibility being in most cases close to zero relative to both electron- and proton-donating solvents.

INTRODUCTION

Little information exists at present in the literature regarding the electronic effects of substituents containing non-transition metals. In particular, no systematic and quantitative studies have been made regarding the electronic effects of the organometallic substituents R_2Sb and R_2Bi (where R is a hydrocarbon radical). Apparently, this omission is connected with the considerable difficulties involved in the determination of the polar constants for such substituents by conventional chemical methods, owing to the rather high reactivity of the metal–carbon bonds as well as to the scarcity of corresponding model systems.

It would appear, however, that the investigation of the electronic effects of these substituents would be of considerable interest from the point of view of comparing them with the electronic influences of similar Group V analogues and with those of univalent organo-mercury, -tin and -lead substituents. The ^{19}F NMR technique appears to be most useful for such studies since recently this method has allowed systematic and quantitative studies to be made of the electronic features of substituents containing some non-transition metals[1–4].

RESULTS AND DISCUSSION

In order to obtain quantitative information regarding the various electronic effects and the influence of solvents for organo-antimony and -bismuth substituents of the R_2M type directly bonded to the aromatic ring, we have investigated a number of fluorophenyl derivatives of antimony and bismuth containing fluorine in the *meta* or *para* position with respect to the Ar_2M substituent, as well as some nitrogen and carbon analogues, *i.e.* $(3\text{-}FC_6H_4)_3M$ and $(4\text{-}FC_6H_4)_3M$ where M=Sb, Bi and $(C_6H_5)_2Q(3\text{-}FC_6H_4)$ and $(C_6H_5)_2Q(4\text{-}FC_6H_4)$ where Q=Sb, Bi, N, CH.

The fluorine chemical shifts relative to internal fluorobenzene have been determined in solvents of different solvating properties for the above compounds, the solvents chosen being cyclohexane, chloroform and pyridine. Cyclohexane was chosen as a non-interacting solvent, chloroform as a weakly acidic solvent capable of forming hydrogen bonds and pyridine as a strongly coordinating solvent.

TABLE 1

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

Compound	*Solvent*		
	C_6H_{12}	$CHCl_3$	C_5H_5N
$(4\text{-}FC_6H_4)_3Sb$	−1.17	−1.13	−1.09
$(3\text{-}FC_6H_4)_3Sb$	−1.63	−1.47	−1.27
$(C_6H_5)_2Sb(4\text{-}FC_6H_4)$	−0.41	−0.58	−0.55
$(C_6H_5)_2Sb(3\text{-}FC_6H_4)$	−0.80	−0.74	−0.88
$(4\text{-}FC_6H_4)_3Bi$	−0.48	−0.32	0.16
$(3\text{-}FC_6H_4)_3Bi$	−1.76	−1.52	−1.05
$(C_6H_5)_2Bi(4\text{-}FC_6H_4)$	0.26	0.11	0.47
$(C_6H_5)_2Bi(3\text{-}FC_6H_4)$	−1.01	−0.95	−0.75
$(C_6H_5)_2N(4\text{-}C_6H_4)$	6.88	6.60	6.47
$(C_6H_5)_2N(3\text{-}FC_6H_4)$	−0.94	−0.81	−1.06
$(C_6H_5)_2CH(4\text{-}FC_6H_4)$	3.91	3.75	3.75
$(C_6H_5)_2CH(3\text{-}FC_6H_4)$	0.07	0.09	0.01
$(CH_3)_2N(4\text{-}FC_6H_4)$	16.62	15.88	16.60

Inspection of the data obtained (Table 1) shows that in most cases the fluorine chemical shift in antimony and bismuth compounds is hardly affected on going from cyclohexane to pyridine. A perceptible increase in fluorine shielding is observed only for symmetric fluorophenyl derivatives of bismuth. Similar slight changes in fluorine shielding on transfer from the former to the latter solvent are also found for the corresponding nitrogen and carbon compounds. These changes probably arise from differences in the nature of the Van der Waals' interactions between the solute and solvent molecules[5]. On this basis, it may be concluded that as a general rule in aryl derivatives of antimony and bismuth (as for those of tin and lead[4] but in contrast to the arylmercury compounds[3]) the metal atom is incapable of coordinating to the molecules of strongly solvating solvents, despite the fact that it has vacant orbitals. As a result, as far as the solvent susceptibility of the substituent electronic effect is concerned, the antimony and bismuth compounds studied in this work are as inert as the corresponding nitrogen and carbon analogues.

Apparently, the inertness of the metal atoms towards specific solvation effects is probably connected with the type of hybridization of the antimony and bismuth orbitals in the compounds concerned. Thus, the p^3-state is known[6] to be characteristic of higher elements in Group VB of the Periodic Table especially in compounds of the R_3M type. For this reason, coordination of the metal atom with a solvent molecule should lead to a change in hybridization from p^3 to sp^3d, a change which could require a considerable expenditure of energy due to the energy difference between the different orbitals involved in the hybridization. This interpretation is supported by the somewhat greater change in fluorine shielding when the bismuth compounds are transferred from cyclohexane to pyridine, where the energy difference between the p and d orbitals may be expected to be smaller than in the corresponding analogues.

Another likely explanation for the poor coordination between the respective metal atoms and molecules of strongly solvating solvents is that a purely electrostatic repulsion occurs between the metal lone-pair electrons and those of the solvent donor atom. In the present case, however, and in contrast to the aryl compounds of tin and lead[4], steric hindrance apparently does not play an important role in determining the inertness of the metal atom. This conclusion is supported by the inspection of molecular models which show that for pyramidal molecules of the $(C_6H_5)_3Bi$ type[7] the aryl groups do not hinder the approach of solvent molecules to the metal atom.

From Table 1 it can be seen that a change in solvent from cyclohexane to chloroform has apparently little influence on the fluorine chemical shifts in all the compounds investigated. This suggests that the lone-pair electrons of nitrogen, antimony and bismuth are quite inert as far as hydrogen bond formation with the latter solvent is concerned. The very low proton-accepting power of the lone-pair electrons in the compounds Ar_3N, Ar_3Sb and Ar_3Bi is especially clearly demonstrated when the changes in fluorine chemical shift for the relevant fluoroaryl compounds and *p*-fluoro-*N*,*N*-dimethylaniline on going from cyclohexane to anisole and phenol are compared. From Table 2 it may be seen that the fluorine shielding in all these compounds remains virtually unchanged on transfer to anisole, which is consistent with the poor proton-donating ability of this solvent. In contrast, changing the solvent from cyclohexane to phenol drastically reduces the fluorine shielding in *p*-fluoro-*N*,*N*-dimethylaniline through hydrogen-bond formation between the phenolic hydroxyl and the lone-pair electrons of the dimethylamino group[8], but has little effect on the fluorine chemical shifts of the other compounds. This suggests that, despite the existence of weak complexes of triphenylamine, trialkylantimony, tri-

TABLE 2

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

Compound	*Solvent*		
	C_6H_{12}	$C_6H_5OCH_3$	C_6H_5OH
$(C_6H_5)_2Sb(4\text{-}FC_6H_4)$	−0.41	−0.54	−0.69
$(C_6H_5)_2Bi(4\text{-}FC_6H_4)$	0.26	0.25	0.04
$(C_6H_5)_2N(4\text{-}FC_6H_4)$	6.88	6.50	6.36
$(C_6H_5)_2CH(4\text{-}FC_6H_4)$	3.91	3.72	3.66
$(CH_3)_2N(4\text{-}FC_6H_4)$	16.62	16.46	9.29

phenylantimony and triphenylbismuth with phenol and acetic acid[9–11], the proton-accepting ability of the lone-pair electrons in the triaryl derivatives of nitrogen, antimony and bismuth is much lower than in compounds of the dimethylaniline type. Thus, as far as the inertness of the electronic effect of the corresponding substituents to the influence of proton-donating solvents is concerned, these compounds may be considered to be analogous to triarylmethanes which have no lone-pair electrons.

The causes of the relative inertness of the lone-pair electrons in the aryl compounds of antimony, bismuth and nitrogen, however, seem to be somewhat different. In triarylamines, the low donor-ability of the nitrogen lone-pair electrons is caused by a strong delocalization of the electron density due to conjugation between the electron pair and the three aromatic rings. In contrast, in aryl compounds of antimony and bismuth the poor donor-ability of the metal lone-pair electrons is due to their being located in the virtually inaccessible *s*-orbital[6]. Thus, the results obtained indicate that the solvent susceptibility of electronic effect in Ar_2Sb and Ar_2Bi groups (which may be determined to a first approximation as the change in the fluorine chemical shift in the corresponding compound on transfer from an inert to a coordinating or proton-donating solvent) is in most cases close to zero despite the presence of lone-pair electrons and vacant orbitals in the metal atom.

In addition the data obtained indicate that the introduction of Ar_2Sb and Ar_2Bi groups into aromatic rings leads, as a rule, to a decrease in the fluorine shielding in the *meta* and *para* positions, organometallic substituents with fluoroaryl groups attached to the metal atom being more electron-withdrawing than those with phenyl groups. The $(C_6H_5)_2Bi$ substituent is an exception, however, in that a slight increase in the fluorine shielding at the *para* position is observed on introduction of this group. Introduction of the corresponding nitrogen-containing substituents results in a considerable enhancement of the fluorine shielding in the *para* position, but to a deshielding of fluorine in the *meta* position.

To obtain quantitative estimates of the electronic effects of the substituents studied, the σ_I and σ_R^0 values have been calculated from the Taft correlation equations[12–13] using the various measured fluorine chemical shifts. The relevant data are presented in Table 3. Inspection of the σ_I and σ_R^0 values reveals that the ground-state electronic effect of the Ar_2Sb abd Ar_2Bi substituents is mainly inductive in character. Thus, in this respect the above substituents are similar to the corresponding univalent organo-mercury[3], -tin and -lead[4] groups. The electron-withdrawing inductive effect of the organoantimony and bismuth groups is very similar to that of

TABLE 3

INDUCTIVE AND RESONANCE PARAMETERS OF VARIOUS SUBSTITUENTS

Substituent	σ_I			σ_R^0		
	C_6H_{12}	$CHCl_3$	C_5H_5N	C_6H_{12}	$CHCl_3$	C_5H_5N
$(C_6H_5)_2Sb$	0.19	0.20	0.21	−0.01	−0.01	−0.01
$(C_6H_5)_2Bi$	0.23	0.22	0.19	−0.04	−0.04	−0.04
$(C_6H_5)_2N$	0.21	0.19	0.23	−0.26	−0.25	−0.25
$(C_6H_5)_2CH$	0.08	0.07	0.08	−0.13	−0.12	−0.13

the $(C_6H_5)_2N$ substituent, being markedly different from the weaker inductive influence of the $(C_6H_5)_2CH$ group.

The similarity between the σ_I values for the substituents $(C_6H_5)_2N$, $(C_6H_5)_2Sb$ and $(C_6H_5)_2Bi$, which occurs despite the considerable decrease in electronegativity on going from nitrogen to antimony and bismuth[14], is of considerable interest. As an explanation it may be tentatively suggested that the decrease in the electron-accepting ability of the Ar_2M group associated with the metal–carbon bond, which occurs in going from nitrogen to bismuth, is compensated for by a simultaneous reduction in the electron-donating through-space interaction[15-16] between the electronic system of the hetero atom and the π-electrons of the aromatic ring. Interactions of such type are less important for antimony and bismuth than for nitrogen due to the greater length of the carbon–metal bonds, as well as the greater size and diffuseness of the orbitals for the larger metal atoms.

The small σ_R^0 values for the Ar_2Sb and Ar_2Bi groups and their negative signs indicate the absence of any perceptible electron-withdrawing effect due to $d_\pi - p_\pi$ conjugation between the π-electrons of the aromatic ring and the vacant orbitals of the metal atom. On the other hand, the electron-releasing effect associated with $p_\pi - p_\pi$ conjugation between the metal lone-pair electrons and the aromatic ring is also virtually zero. In this respect antimony- and bismuth-containing organometallic substituents are very different from $(C_6H_5)_2N$ and $(C_6H_5)_2CH$ groups which exert a considerable electron-releasing conjugative effect. As far as the above nitrogen-containing substituent is concerned, the electron-donating effect in the *para* position arises from conjugation between the nitrogen lone-pair electrons and the π-electronic system of the aromatic ring, whereas in the case of the $(C_6H_5)_2CH$ group this effect is apparently connected with σ,π-conjugation between the C–H (and probably C–C bonds) and the ring. The observed absence of conjugation between the metal lone-pair electrons and the aromatic ring seems to be due to the practically 100% *s* character[6] of these electrons, while the absence of conjugation between the aryl-carbon–metal bonds and the π-electrons of the ring may be associated with the greater size and diffuseness of the metal orbitals, which interferes substantially with their overlap with the electron orbitals of the aromatic ring.

In conclusion it should be mentioned that it is hoped that a further study of the above problem, which is at present under way, will indicate how the nature of substituents on the metal atom influences the electronic effect and its solvent susceptibility as far as antimony- and bismuth-containing groups are concerned and will enable a comparison to be made between the ability of antimony and bismuth to transmit electronic effects with those of nitrogen- and carbon-containing bridging groups.

EXPERIMENTAL

General comments

The ^{19}F NMR spectra were recorded at 34° using a Hitachi–Perkin–Elmer R-20 spectrometer operating at 56.4 MHz. Chemical shift measurements were made on dilute solutions of concentration not greater than 0.2 *M*. The determination of the ^{19}F chemical shifts by the substitution method has been described elsewhere[17]. The experimental error in the fluorine chemical shifts did not exceed ±0.1 ppm. The spectra of solutions in phenol were recorded using supercooled samples.

TABLE 4

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF FLUOROARYL COMPOUNDS

Compound	*Yield* (%)	R_F[a]	*M.p.* (°C)	*Analysis found (calcd.) (%)* C	H
$(C_6H_5)_2Sb(4\text{-}FC_6H_4)$	69	0.76	46–47	58.29 (58.27)	3.78 (3.77)
$(C_6H_5)_2Sb(3\text{-}FC_6H_4)$	72	0.71	30–32	58.51 (58.27)	3.77 (3.77)
$(C_6H_5)_2Bi(4\text{-}FC_6H_4)$	47	0.75	53–54	47.49 (47.16)	3.20 (3.05)
$(C_6H_5)_2Bi(3\text{-}FC_6H_4)$	78	0.76	56–57	47.16 (47.16)	3.16 (3.05)
$(C_6H_5)_2CH(4\text{-}FC_6H_4)$	50	0.74	40–42	87.00 (87.02)	5.86 (5.72)
$(C_6H_5)_2CH(3\text{-}FC_6H_4)$	40	0.78	39–40	86.94 (87.02)	5.73 (5.72)
$(C_6H_5)_2N(3\text{-}FC_6H_4)$	50	0.79	102–103	82.25 (82.13)	5.37 (5.33)

[a] In a mixture of petroleum ether and acetone (10/1).

The solvents were purified by conventional methods. Cyclohexane was distilled over sodium and chloroform over phosphorus pentoxide. Pyridine was distilled over potassium hydroxide and dried over molecular sieves.

The symmetrical fluoroaryl compounds of antimony and bismuth described in the literature[18–19] were obtained by the action of *m*- and *p*-fluorophenylmagnesium bromides upon antimony and bismuth trichlorides, whereas the unsymmetrical compounds were prepared by the reaction of the above organomagnesium compounds with diphenylchloroantimony and diphenylchlorobismuth. (*p*-Fluorophenyl)diphenylamine reported in the literature[20] and the corresponding *meta* isomer were obtained using the procedure proposed for the former compound. *m*- and (*p*-Fluorophenyl)diphenylmethanes were prepared by the method used in the preparation of triphenylmethane[21]. Methylation of *p*-fluoroaniline with dimethylsulphate afforded *p*-fluoro-*N*,*N*-dimethylaniline[20]. The purity of the compounds investigated was monitored by TLC using the conditions proposed for the aryl derivatives of phosphorus, arsenic and antimony[22]. Analytical results and physical properties of the compounds not reported in the literature are presented in Table 4. Some typical examples of preparations of the fluoroaryl compounds studied in the present communication are given below.

Diphenyl(p-fluorophenyl)antimony

A solution consisting of 3.1 g (10 mmoles) of diphenylchloroantimony[23] in 20 ml of dry ether was added with stirring to a solution of *p*-fluorophenylmagnesium bromide obtained from 2.27 g (13 mmoles) of *p*-fluorobromobenzene[24] and 0.36 g of magnesium in 30 ml of the same solvent. After refluxing for 1.5 h the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl. The ether layer was separated, washed with water, dried over $CaCl_2$ and the solvent removed. 1.7 g (69%) of the product was obtained as colourless crystals of m.p. 46–47° after recrystallization from methanol.

Diphenyl(p-fluorophenyl)bismuth

To a suspension of 3.98 g (10 mmoles) of diphenylchlorobismuth[18] in 20 ml of dry ether cooled to 0° was added under nitrogen with stirring a solution of *p*-fluorophenylmagnesium bromide obtained from 2.27 g (13 mmoles) of *p*-fluorobromobenzene and 0.36 g of magnesium turnings in 30 ml of dry ether. After stirring for 3 h at 0°, the reaction mixture was decomposed with a saturated aqueous solution of NH_4Cl. The ether layer was washed with water, filtered, dried over $CaCl_2$ and the solvent removed under reduced pressure. The resulting pale-yellow oil crystallized on trituration with methanol. 1.5 g (47%) of the product was obtained as colourless crystals of m.p. 52–54° after recrystallization from ethanol.

Diphenyl(m-fluorophenyl)amine

A mixture of 5.5 g (24 mmoles) of *m*-fluoroiodobenzene[25] 4.25 g (24 mmoles) of diphenylamine, 3.5 g of K_2CO_3 and 0.25 g of copper powder was refluxed in 30 ml of nitrobenzene for 20 h. After cooling, the reaction mixture was filtered, nitrobenzene was removed from the filtrate under reduced pressure and the residue distilled in vacuum; 3.2 g (50%) of a yellow oil with b.p. 188–190°/8 mmHg was obtained, which rapidly solidified. Recrystallization from ethanol afforded pale-yellow crystals of m.p. 102–103°.

Diphenyl(p-fluorophenyl)methane

To a solution of *p*-fluorophenylmagnesium bromide obtained from 5.25 g (30 mmoles) of *p*-fluorobromobenzene and 0.8 g of magnesium turnings in 80 ml of dry ether under nitrogen was added a solution of 2.47 g (10 mmoles) of diphenylbromomethane[26] in 20 ml of the same solvent. After stirring for 3 h at room temperature, the reaction mixture was decomposed with a cooled diluted solution of hydrochloric acid, the ether layer was separated, washed with water, dried over $CaCl_2$ and the solvent removed. The solid obtained was treated with petroleum ether, the solution separated from the insoluble residue and the solvent evaporated. The resulting oil solidified after trituration with methanol. 1.3 g (50%) of the product was obtained as colourless crystals of m.p. 40–42° after recrystallization from methanol.

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