

High-resolution Fluorine-19 Nuclear Magnetic Resonance Spectroscopy. Studies of some Group V Fluorophenyl Derivatives

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The ^{19}F n.m.r. spectra of $(\text{C}_6\text{F}_5)_n\text{Ph}_{3-n}\text{E}$ and $(\text{C}_6\text{F}_5)_n\text{Ph}_{3-n}\text{PO}$ ($n = 1-3$; $\text{E} = \text{P}, \text{As}, \text{and Sb}$) have been studied, and the spin-spin coupling constants are derived. The causes of broadening in the bis- and tris-pentafluorophenyl compounds are discussed. ^{31}P and ^{19}F N.m.r. shifts of the phosphines; tris-2,6-difluorophenylphosphine, tris-2,5-difluorophenylphosphine, and tris-2,3,6-trifluorophenylphosphine are also reported. The preparations of 2,5-difluoro- and 2,3,6-trifluorophenyl-lithium are given.

MANY pentafluorophenyl compounds have been studied by ^{19}F n.m.r. spectroscopy.¹⁻³ In connection with the study of fluoroaryl Group V compounds and their metal complexes, the spectra of these ligands and some complexes with platinum and rhodium have been measured to determine whether correlations of the chemical shifts and the coupling constants with the structures exist. It has been postulated⁴ that compounds containing more than one pentafluorophenyl group are rigid on the n.m.r. time scale. The compounds in this paper also show this effect and some polyfluorophenyl phosphines were prepared to study this effect further.

EXPERIMENTAL

The pentafluorophenyl compounds were prepared as previously described.⁵ The preparation of 2,6-difluorophenyl-lithium has now been published.⁶ ^{19}F and ^{31}P N.m.r. spectra were obtained on a Varian DA/60 instrument at 56.4 and 19.3 Mc./sec. respectively. PhCF_3 was used as an internal standard for the ^{19}F , and P_4O_6 as an external standard (capillary) for the ^{31}P spectra. Calibration was by means of normal sideband techniques. The compounds were studied in saturated chloroform and methylene dichloride solutions. All operations involving *n*-butyl-lithium were carried out in sodium-dried solvents under an atmosphere of dry nitrogen. The tetrahydrofuran was distilled from LiAlH_4 before use. A Perkin-Elmer 225 model was used to record the i.r. spectra. The m.p.'s were taken with a hot-stage microscope. Molecular weights were determined in chloroform solution with a Mechrolab vapour-pressure osmometer.

2,3,6-Trifluorophenyl-lithium.—Tetrahydrofuran (50 ml.) was added to 1,2,4-Trifluorobenzene (4.0 g.), prepared by the method of Tamborski *et al.*⁷ from 2,3,5,6-tetrafluorophenylhydrazine⁸ and the mixture was cooled to -60°C . Butyl-lithium (1.45-m; 21 ml.) were then added to the mixture during 15 min. and the contents were stirred for 2 hr. at -55°C to produce a colourless solution of the lithium reagent. This was carbonated to yield 2,3,6-trifluorobenzoic acid (3.6 g., 70%) identified by its m.p.⁷ and ^{19}F n.m.r. spectrum.⁷ Addition of phosphorus trichloride to the aryl-lithium yielded tris-2,3,6-trifluorophenylphosphine (1.0 g., 20%) as white crystals (from light petroleum) m.p.

$50-53^\circ\text{C}$ (Found: C, 49.9; H, 1.3; *M*, 434. $\text{C}_{18}\text{H}_6\text{F}_9\text{P}$ requires C, 50.9; H, 1.4%; *M*, 424). Strong i.r. absorptions at 1470, 1240, 1184, 1123, 996, 880, 816, 736, and 342 cm^{-1} ; ^{19}F n.m.r. $\delta + 43.6, +62.1, +78.6$ p.p.m.

2,5-Difluorophenyl-lithium.—*p*-Difluorobenzene (3.4 g.) in tetrahydrofuran (50 ml.) was treated with butyl-lithium (1.5M; 20 ml.) as in the above preparation; the mixture was stirred for 4 hr. at -55°C . Carbonation yielded 2,5-difluorobenzoic acid (2.8 g., 60%), m.p. $128-129^\circ\text{C}$ (lit.⁹ $118-119^\circ\text{C}$) (Found: C, 52.7; H, 2.51; *M*, 162. Calc. for $\text{C}_7\text{H}_4\text{F}_2\text{O}_2$ C, 53.0; H, 2.54%; *M*, 158); ^{19}F n.m.r. $\delta + 53.5, +56.7$ p.p.m. Tris-2,5-difluorophenylphosphine, obtained by addition of phosphorus trichloride to the aryl-lithium, was sublimed *in vacuo* at 160°C and the sublimate was crystallized from light petroleum at -30°C to give white crystals (1.5 g., 30%), m.p. $145-150^\circ\text{C}$ (Found: C, 57.6; H, 2.49; *M*, 366. $\text{C}_{18}\text{H}_6\text{F}_6\text{P}$ requires C, 58.4; H, 2.43%; *M*, 370); strong i.r. bands at 1460, 1400, 1252, 1188, 883, 816, 738, and 341 cm^{-1} ; ^{19}F n.m.r. $\delta + 46.9, +54.5$ p.p.m., $J(\text{P}, \text{F}_2)$ 60 c./sec.

Analysis of Spectra.—No attempt was made to analyse the spectra of the polyfluorophenyl compounds. The monopentafluorophenyl compounds $(\text{C}_6\text{F}_5)_2\text{Ph}_2\text{E}$ ($\text{E} = \text{P}, \text{As}, \text{and Sb}$) were analysed as AA'MXX' spin systems. The *para*-resonance consists of a triplet of triplets and from this $J_{2,4}$ and $J_{3,4}$ were calculated. The two overlapping AA' parts (of the AA'XX' system) which make up the *meta*-resonance were 'uncoupled' using the value of $J_{3,4}$; values for $J_{2,3}$, $J_{2,6}$, $J_{2,5}$, and $J_{3,5}$ were then derived. The first-order coupling by the phosphorus $J(\text{P}, \text{F}_2)$ was obtained by comparing the observed *ortho*-resonance with that calculated by using the values of the coupling constants found from the *meta*- and *para*-signals. Figure 1 shows the *meta*-resonance of $(\text{C}_6\text{F}_5)_2\text{Ph}_2\text{Sb}$.

In all the other pentafluorophenyl compounds examined the *meta*- and *ortho*-signals were broadened so that the 20 lines of the A or X parts were not observed. The *para*-resonance was unaltered. Figure 2 shows the *meta*-resonance of $(\text{C}_6\text{F}_5)_2\text{PhSb}$ as an example of this effect. It will be seen that the two outer doublets of the *meta*-resonance in Figure 1 are replaced by broad lines in Figure 2. The spectra of these compounds were analysed by a modification of the AA'MXX' analysis in which it was assumed that the position of the broadened peak corresponded to the midpoint of the two lines which should have been present for each doublet.

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DISCUSSION

The spin-spin coupling constants of the compounds investigated are shown in Table 1. The values fall inside the range of those reported by other workers. The values agree with those of Graham *et al.*¹⁰ who also studied some of the compounds, but the values of $J_{2,4}$ in $(C_6F_5)_3P$ and $(C_6F_5)_3PO$ are in disagreement with those of Emeléus and Miller.¹¹

The phosphorus-*ortho*-fluorine coupling-constants observed vary widely, with no apparent correlation between

Values for $J_{3,5}$ calculated on this basis are all negative and the moduli agree well with those observed, thus justifying the assignment in Table 1 of $J_{2,6}$ and $J_{3,5}$.

The ^{31}P n.m.r. spectra of $(C_6F_5)_2Ph_2PO$ and $(C_6F_5)_2PhPO$ were studied but only broad, structureless lines were observed. Tris-2,6-difluorophenylphosphine and tris-2,5-difluorophenylphosphine showed a septet and a quartet respectively. The spectrum of tris-2,3,6-trifluorophenylphosphine was complicated since the fluorine atoms in the 2 and 6 positions are not equivalent. The

TABLE 1

Spin-spin coupling-constants (c./sec.)

Compound	$J(P, F_2)$	$J(P, F_3)$	$J(P, F_4)$	$J_{2,4(+)}$	$J_{3,4(-)}$	$J_{2,3(-)}$	$J_{2,5(+)}$	$J_{3,5(-)}$	$J_{2,6}$
$(C_6F_5)_3Ph_2P$	38.0	<0.5	<0.5	4.0	20.4	24.2	10.0	4.4	1.6
$(C_6F_5)_3Ph_2As$				3.2	19.8	25.4	9.8	4.8	1.5
$(C_6F_5)_3Ph_2Sb$				2.9	20.2	26.9	10.8	5.8	1.5
$(C_6F_5)_2Ph_2P$	31.0	<0.5	<0.5	4.0	20.0	23.3	8.9	3.6	
$(C_6F_5)_2Ph_2As$				3.1	18.9	27.3	10.3	5.2	
$(C_6F_5)_2Ph_2Sb$				3.1	19.7	25.0	9.2	5.5	
$(C_6F_5)_3P$	36.5	<1.0	<1.0	4.3	20.0	24.2	8.8	4.6	
$(C_6F_5)_3As$				3.9	19.6	24.8	9.8	4.5	
$(C_6F_5)_3Sb$				3.4	19.5	25.2	9.7	5.7	
$(C_6F_5)_2Ph_2PO$	6.5	3.6	2.3	6.3	20.8	23.5	9.5	5.5	
$(C_6F_5)_2Ph_2P$	15.0	4.9	2.7	6.6	19.9	23.9	8.6	7.2	
$(C_6F_5)_3PO$	37.4	<1.0	<1.0	4.4	20.5	26.3	11.5	3.6	
$[(C_6F_5)_2Ph_2P]_2PtCl_2$	<1.0	<0.5	<0.5	4.8	20.4	24.0	8.6	6.3	
$[(C_6F_5)_2Ph_2P]_2RhCOCl$	<1.0	<0.5	<0.5	4.6	20.6	23.0	7.7	5.8	
$[(C_6F_5)_2Ph_2As]_2PtCl_2$				4.6	20.0	24.9	9.2	6.5	0.8
$[(C_6F_5)_2Ph_2As]_2RhCOCl$				4.2	20.5	24.7	9.2	7.7	

the values and the structures. However, when the phosphine is complexed no detectable coupling occurs, although $J(P, F_2)$ for the free phosphine is large.

The absolute sign of the *ortho*-coupling in C_6F_6 was found to be negative.¹² Since *ortho* F-F couplings fall in a small range (26–18 c./sec.) they are very likely all negative in sign. A similar argument indicates a positive sign for *para* F-F coupling. Thus, in Table 1, $J_{3,4}$ and $J_{2,3}$ are negative while $J_{2,5}$ is positive.

Graham *et al.*¹⁰ have found that a linear relationship exists between $J_{2,4}$ and the chemical shift of the *para* (δp) in pentafluorophenyl compounds. A similar relationship between $J_{2,4}$ and δp is found for the compounds studied here if $J_{2,4}$ is positive in sign.

In polyfluorobenzenes it has been found¹³ that the *meta*- and *para*-F-F coupling-constants are determined by additive substituent contributions from the other groups present, and that the *ortho-ortho* contribution of a substituent to *meta* J_{F-F} varies in a linear fashion with the Hammett constant σp .¹³ The chemical shift of the *para*-fluorine (δp) in pentafluorophenyl compounds (C_6F_5X) is mainly determined by $\sigma p(X)$ too.² Thus, the *ortho-ortho* contribution of X should vary linearly with δp . This is found to be so for compounds already in the literature, and for the compounds studied here the knowledge of δp enables the *ortho-ortho* contribution of $X = Ph_2P$ etc. to be evaluated.

^{31}P chemical shifts (Table 2) show a nearly linear correlation with the total number of *ortho*-fluorine atoms. This suggests that *ortho*-contributions to the chemical-shift are dominant.

The monopentafluorophenyl compounds studied here show typical AA'MXX' spectra. When two or more

TABLE 2

 ^{31}P N.m.r. chemical shifts in p.p.m. upfield from (85%) H_3PO_4 .

Compound	Chemical shift	No. of <i>ortho</i> -fluorine atoms
Ph_3P^a	8.0	0
$Ph_2(C_6F_5)P^b$	26.3	2
$2,5(C_6H_3F_3)_2P$	34.5	3
$Ph(C_6F_5)_2P^b$	49.7	4
$(C_6F_5)_3P^b$	75.5	6
$2,3,6(C_6H_2F_3)_3P$	78.5	6
$2,6(C_6H_3F_3)_3P$	78.5	6

^a J. R. Van Wazer, C. F. Callis, J. H. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715. ^b M. Fild, I. Hollenberg, and O. Glemser, *Z. Naturforsch.*, 1967, **22b**, 253.

pentafluorophenyl groups are present the *meta*-resonance lines are broadened and, in particular, the two outer doublets are collapsed to two broad lines (Figures 1 and 2). The trispolyfluorophenylphosphines also have broad lines while the spectra of the corresponding benzoic

¹⁰ M. G. Hogben, R. S. Gay, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1966, **88**, 3457.

¹¹ H. J. Emeléus and J. M. Miller, *I. Inorg. Nuclear Chem.*, 1966, **28**, 662.

¹² L. C. Synder and E. W. Anderson, *J. Chem. Phys.*, 1965, **42**, 3336.

¹³ R. J. Abraham, D. B. Macdonald, and E. S. Pepper, *J. Amer. Chem. Soc.*, 1968, **90**, 147.

acids are sharp. Jolley and Sutcliffe⁴ have found similar effects in some Group IV derivatives and have attributed the broadening to the large pentafluorophenyl groups; these cause a restriction of the rotation of the groups around the central atom, thus preventing an averaging out of the dipole-dipole interactions and leading to a broadening of the lines.

That the broadening can be attributed to second-order effects, unresolved couplings, or quadrupole interactions by the central atom, or interannular couplings may be rejected. The ratios of chemical shifts to coupling constants are such that in the monopentafluorophenyl compounds second-order effects are greater. Unresolved coupling or quadrupole interaction will not explain the broadening of the germanes and silanes since ²⁹Si and ⁷³Ge

the explanation for the broadening, while dipole-dipole broadening should affect all the lines. The line widths of the transitions 1 and 2, and 3 and 4 do tend to be

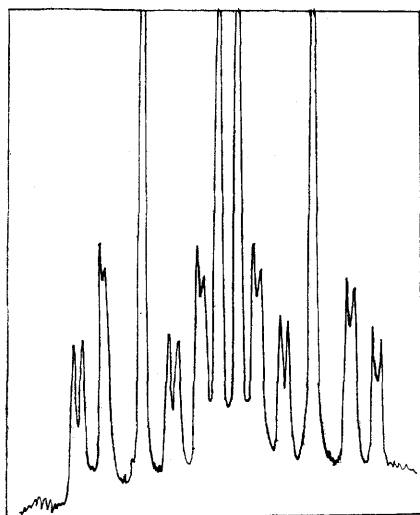


FIGURE 1 ¹⁹F N.m.r. *meta*-resonance of (C₆F₅)Ph₂Sb

are in low abundance. Although interannular coupling between pentafluorophenyl rings has been postulated by Haszeldine *et al.*¹ this does not explain a further observation that Me₂Sn(C₆F₅)₂ is not broadened while Ph₂Sn(C₆F₅)₂ is.

The doublet splitting which depends on the value of $J_{2,6}$ will be unresolved if $J_{2,6}$ is small (0.5 c./sec.). Other lines in the *meta*-resonance will not be affected if this is

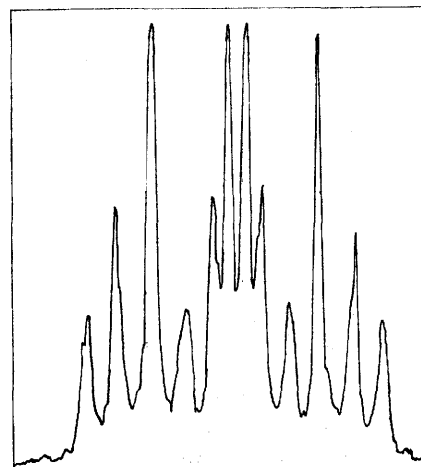


FIGURE 2 ¹⁹F N.m.r. *meta*-resonance of (C₆F₅)₂PhSb

larger in the bis- than in the mono-pentafluorophenyl compounds in the compounds studied here.

No change was observed in the *meta*-resonance of (C₆F₅)_nPh_{3-n}E (E = P, As, or Sb; $n = 2, 3$) at temperatures up to +150°C or in (C₆F₅)Ph₂E (E = As or Sb) down to -60°C. If the broadening is due to steric hindrance then the barrier to rotation must increase sharply on going from the mono- to the bis-pentafluorophenyl compounds.

Although the evidence for nonrotation of the pentafluorophenyl groups is indirect it suggests that the bis- and tris-pentafluorophenyl compounds here are rigid on the n.m.r. time scale.

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