Long-range Coupling in α- and β-Fluoro-substituted Pentafluorostyrenes

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FOLLOWING the report[1] that long-range coupling of the 4-fluorine only occurs with the β- and not with the α-fluorine atoms of (I), which is similarly supported[2] by the absence of coupling of the 4-fluorine with the olefinic fluorine atoms of (II), it is suggested that this behaviour is characteristic of fluorinated styrenes. However, in a preliminary investigation of the ^{19}F spectra[3] of a number of fluorinated 1-pentafluorophenylethylene derivatives (III), we found in every instance that coupling occurs between the 4- and α-fluorine atoms and only in one example (III, vii) was coupling between the 4- and β-fluorine atoms observed. The chemical-shift data of these compounds (III), in ϕ^* values, *i.e.*, in p.p.m. from internal CCl_3F, are shown in the Table.

It is immediately obvious from the Table, that the chemical shifts of the olefinic fluorine atoms are dependent upon the nature of the other two substituents and, had these compounds not been obtained by unambiguous synthesis,[4] the tendency would have been to suggest that in compound (III, iii) the olefinic fluorine was not at X but at Y, which would have lead to the supposition that coupling occurs between the 4- and β-fluorine atoms.

The coupling of the 4-fluorine to α-hydrogen and α-fluorine atoms is quite general, that of the coupling of the 4-fluorine to the trifluoromethyl group and to the methyl group (J = 1·4 c./sec.) in octafluoro- and pentafluoro-toluene has been reported,[5] a rather larger coupling, J = 3·3 c./sec. is found in the fluoropentafluorophenylacetamides C_6F_5·CHF·$CONR_2$ (IV). The 4–α-fluorine couplings found in the present work are of the same order as in (IV), being 2·8 c./sec. in (III, iii) and 3·7

TABLE. *Chemical shift data of pentafluorophenylethylenes* (III)

				Shifts, ϕ^*-values					
	X	Y	Z	F 2·6	F 3·5	F 4	X	Y	Z
(i)	H	H	H	144·3	163·8	156·8	—	—	—
(ii)	H[a]	Cl	H	142·7	162·7	155·4	—	—	—
(iii)	F	Cl	Cl	136·0	160·8	148·7	95·6	—	—
(iv)	F[b]	F	F	137·4	161·6	149·7	171·0	96·4	112·7
(v)	Cl	Cl	Cl	138·0	161·0	150·6	—	—	—
(vi)†	F[c]	F	Cl	136·1	160·8	148·7	126·9	96·4	—
(vii)†	F[d]	Cl	F	136·9	161·1	149·2	142·5	—	112·8
(viii)†	F[e]	F	Cl	139·8	152·5	(NMe_2)	124·8	98·57	—
(ix)†	F[f]	Cl	F	139·8	152·5	(NMe_2)	140·4	—	114·8

[a] *trans*-Isomer J_{xz} = 14·2 c./sec., $\delta_x = \tau$ 2·92, $\delta_z = \tau$ 3·21

[b] J_{xy} = 35·5 c./sec., J_{xz} = 118·8 c./sec., J_{yz} = 61·1 c./sec., J_{4x} = 3·7 c./sec., $J_{y2} = J_{y6}$ = 2·3 c. /sec., $J_{x2} = J_{x6}$ = 7·1 c./sec.

[c] J_{xy} = 13·8 c./sec., $J_{x2} = J_{x6}$ = 4·9 c./sec., J_{x4} = 3·75 c./sec., $J_{y2} = J_{y6}$ = = 2·6 c./sec.

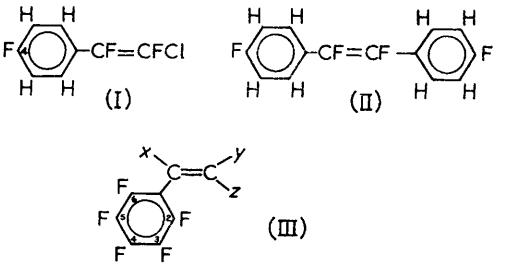
[d] J_{xz} = 134·5 c./sec., $J_{x2} = J_{x6}$ = 7·25 c./sec., J_{x4} = 2·8 c./sec., $J_{z2} = J_{z6}$ = 11·7 c./sec., J_{z4} = 1·9 c./sec.

[e] J_{xy} = 11·6 c./sec., $J_{x2} = J_{x6}$ = 5·55 c./sec., $J_{y2} = J_{y6}$ = 2·5 c./sec., δ_{NMe_2} = 6·92τ, $J_{NMe_2\text{-}3} = J_{NMe_2\text{-}5}$ = 2·5 c./sec.

[f] J_{xz} = 129·5 c./sec., $J_{x2} = J_{x6}$ = 7·25 c./sec., $J_{z2} = J_{z6}$ = 11·75 c./sec., δ_{NMe_2} = 6·92τ, $J_{NMe_2\text{-}5} = J_{NMe_2\text{-}3}$ = 2·5 c./sec.

† Spectra of mixed *cis*- and *trans*-isomers recorded.

c./sec. in (III, iv). The coupling between the 4- and α-fluorine atoms in (III, iii) is clearly seen in the n.m.r. spectrum, which shows the olefinic fluorine (X in III) resonance as a triplet of doublets (triplets arising from coupling to the two *ortho*-fluorine atoms) and the 4F resonance a triplet of quartets, (triplet arising from the 4–3- and 4–5-coupling, and quartets from the similarity of the 4–α-, 4–2-, and 4–6-coupling constants). The α-fluorine resonance of octafluorostyrene (III, iv) is basically a doublet of doublets arising from the *trans*-XZ coupling = 118·8 c./sec., and *cis*-XY coupling = 35·5 c./sec., and each component is a triplet of doublets for the same reasons as discussed above. Further evidence for the 4–α-coupling is obtained by comparison of compounds (III, vi and viii) and (III, vii and ix) since in (III, viii and ix) the 4-fluorine has been substituted by the dimethylamine group resulting in the simplification of the α-fluorine resonance signal. Further, it was this comparison which revealed the single instance of 4–β-fluorine coupling which occurred in the *trans*-isomer (III, vii).



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[1] N. N. Shapet'ko, N. M. Sergeev, E. M. Panov, and R. S. Sorokina, *Zhur. strukt. Khim.*, 1965, **6**, 641.
[2] N. N. Shapet'ko, N. M. Sergeev, O. N. Petrie, T. V. Talalaeva, and A. A. Makhina *Zhur. strukt. Khim.*, 1965, **6**, 158.
[3] The ^{1}H and ^{19}F spectra were recorded at 60·0 and 56·4 Mc./sec. respectively using a Perkin-Elmer R. 10 spectrometer; the ϕ^*-values were determined with precision using the calibrated "decade-shift" facility. All the spectra were recorded in carbon tetrachloride solution.
[4] D. D. Callander, P. L. Coe, and J. C. Tatlow, unpublished work.
[5] I. J. Lawrenson, *J. Chem. Soc.*, 1965, 1117.