Long-range Carbon–Fluorine Scalar Coupling in some Fluorinated Aromatic Compounds

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Summary The proton-decoupled ^{13}C spectrum of 2-fluoronaphthalene has been reassigned and reveals a six-bond coupling of 2·8 Hz between the fluorine and C-6; a similar coupling is observed in 4-fluorostyrene; long-range ^{13}C–^{19}F coupling constants in other fluorinated aromatics appear to be related to variations in the π-bond orders in the bonds between the interacting spins.

IN a recent paper Weigert and Roberts[1] implied that long-range ^{13}C–^{19}F scalar coupling in fluorinated aromatics attenuates with an increase in the distance between the two nuclei involved. Partly on this basis they assigned the ^{13}C spectrum of 2-fluoronaphthalene stated to consist of six doublets and four singlets; in particular, the four singlets were assigned to carbons in the ring farther removed from the fluorine atom. A doublet, J_{CF} 2·5 Hz, at 2·1 p.p.m. upfield from benzene was stated to be insensitive to the proton-decoupler frequency and assigned to C-10.

^{13}C *Chemical shifts*[a] *(σ) and* ^{13}C–^{19}F *coupling constants*[b] (J_{CF}) *for 2-fluoro-* (I) *and 2-fluoro-*6-*methylnaphthalene* (II)

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
(I)	σ	76·9	32·2	83·6	62·5	62·2	66·5	65·0	66·1	58·3	65·6
	J_{CF}	25·9	248·8	21·0	10·1	c	2·8	1·2	c	9·9	5·1
(II)	σ	76·3	d	81·8	63·0	63·3	57·8	61·6	65·6	60·0	65·4
	J_{CF}	24·9	d	19·1	9·1	c	2·9	1·2	c	8·9	5·5

[a] In p.p.m. upfield from CS_2. Note, the data in ref. 1 can be converted from the benzene scale to the CS_2 scale by adding 64·4
[b] In Hz. [c] No resolvable ^{13}C–^{19}F coupling. [d] Instrumental sensitivity precluded precise determination.

We have re-examined the proton-decoupled ^{13}C spectrum of 2-fluoronaphthalene at 14·1 and 23·5 kG and find that, within the resolution of our instruments, the spectrum consists of eight doublets and two singlets. Off-resonance noise-decoupling experiments[2] show that the doublet assigned by Weigert and Roberts[1] to C-10 results from a protonated carbon, and comparison of the spectra of 2-fluoronaphthlene and 2-fluoro-6-methylnaphthalene (see Table) reveals that this doublet arises from C-6. The resulting chemical-shift parameters compare closely with those for 2-methyl substitution in naphthalene[3] and allow complete assignment of the spectrum of 2-fluoronaphthalene. It is now clear also that C-7 is coupled to the fluorine (J_{CF} 1·2 Hz), whereas C-5 and C-8 are not; *i.e.* long-range ^{13}C–^{19}F coupling does not necessarily decrease as the distance between the interacting spins increases.

Such couplings have also been recorded in other fluorinated aromatic compounds. In 4-fluorostyrene, the fluorine is coupled to C-8 (J_{CF} 1·9 Hz) but not to C-7. In 6-fluoroquinoline, however, no coupling is observed to C-2 although it stands in the same geometric arrangement relative to the fluorine as does C-6 in the 2-fluoronaphthalenes and C-8 in 4-fluorostyrene. In 5-fluoroquinoline, the ^{13}C–^{19}F coupling constants to C-3 and C-4 (J_{CF} 3·5 and 4·7 Hz, respectively) are similar in magnitude to those to the corresponding coupling constants in 1-fluoronaphthalene[1] ($J_{C-7,F}$ 3·3; $J_{C-8,F}$ 5·6 Hz) and 2-fluorostyrene ($J_{C\omega,F}$ 4·7, $J_{C\alpha,F}$ 5·3 Hz). In 8-fluoroquinoline, however, no coupling is observed to C-2.

In recent publications Barfield and Karplus[4] have expressed long-range proton–proton scalar coupling in terms of the total Penney–Dirac bond order between the two centres involved. In the cases discussed above, it is probable that long-range coupling is transmitted *via* the π-framework and that reduction in π-bond orders results in reduction in the coupling constant. For instance, the lack of observable coupling to C-2 in 8-fluoroquinoline may be the result of a reduction in the π-bond orders of the CN bonds relative to those for the corresponding C–C bonds in naphthalene.[5] Further evidence is available from a comparison of the ^{13}C spectra of 4-fluorostyrene with those of 4-fluorobiphenyls[6] and 4-fluorostilbenes.[6] Although in 4-fluorostyrene a coupling of 1·9 Hz is observed over the six bonds from the fluorine to C-8, ^{13}C–^{19}F coupling in the biphenyls or stilbenes is confined to the fluorinated ring. In these cases there are substantial reductions in the π-bond orders between the centres of interest as compared with those in styrene.[5]

Although broad correlations can be made between ^{13}C–^{19}F long-range coupling constants and individual π-bond orders between the interacting centres, quantitative correlations probably involve total Penny–Dirac bond orders.

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