The Nuclear Magnetic Resonance Spectra of Aromatic Fluorocarbons. The *peri* F–F Coupling Constants in Fluoronaphthalenes and Related Compounds

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Summary The *peri* F—F coupling constants in fluoronaphthalenes have been found to be large and probably positive in sign.

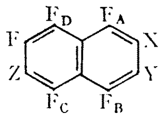
FOLLOWING the recent interest in large "through space" ^{19}F coupling constants,[1] we report that during a study of the n.m.r. spectra of series of fluoronaphthalenes and related compounds we have found that the coupling between *peri*-related fluorines is much larger than any F–F coupling in single-ring aromatic systems.

Values of these constants in fluoronaphthalenes (I), fluoronaphthalic anhydrides (II), fluoroacenaphthylenes (III), and fluoroacenaphthene-1,2-quinones (IV) are given in the Table. Double-resonance experiments carried out on compounds (IIa), (IIb), and (IVa) establish that the coupling is, in each case, of opposite sign to the *ortho* and of the same sign as the *para* coupling. The latter relationship has also been found in (Ie). Since the *ortho* and *para* couplings in both magnitude and sign relationship appear to be "normal" for aromatic systems, where the *ortho* coupling has been shown to be of negative sign,[2] the *peri* couplings here are presumably positive. In view of the general similarity of pattern of the magnitudes of all couplings in the whole series of compounds it is a reasonable assumption that the same relationship exists in all the remaining compounds.

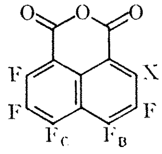
TABLE

		X	Y	Z	J_{AD} (Hz.)	J_{BC}(Hz.)
(I)	a	H	F	F	65·7	59·4
	b	H	F	OMe	63·7	65·2
	c	H	OMe	OMe	61·8	68·2
	d	OMe	OMe	H	63·4	69·3
	e	H	F	NMe_2	62·6	69·7
(II)	a	H				53·9
	b	OMe				58·2
(III)	a	H				32·7
	b	OMe				35·7
(IV)	a	OMe	F			29·4
	b	OMe	OMe			30·7

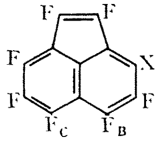
The discussion on "through space" coupling between fluorine nuclei has been reviewed recently by Servis[1] who reports for the 4-F–5F coupling in 4,5-difluorophenanthrenes a very high value (170 Hz.) insensitive to changes in substituent chemical shift of the coupling nuclei, and accounts for this in terms of interaction between the non-bonding electrons of the fluorine atoms. The results reported here are not incompatible with this explanation in that the coupling nuclei are spatially more separated, giving a smaller nonbonding contribution, whilst the greater sensitivity to substituent changes might well arise from a larger contribution *via* the bonding electrons over four, rather than five bonds. A reason for the markedly smaller values in compounds (III) and (IV) is not immediately apparent but it may be significant that the five-membered ring introduces strain into these structures which could result in changes in the geometry of the relevant part of the molecules and hence affect both contributions to the coupling constants.



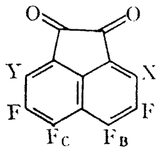
(I)



(II)



(III)



(IV)

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[1] K. L. Servis and K. N. Fang, *J. Amer. Chem. Soc.*, 1968, **90**, 6712.
[2] L. C. Snyder and E. W. Anderson, *J. Chem. Phys.*, 1965, **42**, 3336.