

## The Effect of Substituents on $J_{meta}^{FF}$ in Fluorobenzenes

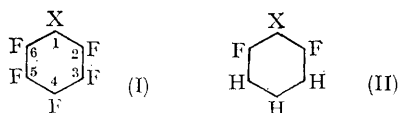
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PROTON-PROTON coupling constants in substituted benzenes are characterised by their invariance to the nature of the ring substituents, falling in the ranges<sup>1</sup> 7—9, 2—4, and 0—2 c./sec. for  $J_{ortho}$ ,  $J_{meta}$ , and  $J_{para}$  respectively. This independence of substituents has been of great value in elucidating the structures of many aromatic compounds. From the limited amount of data available,<sup>19</sup>F-<sup>1</sup>H couplings behave similarly. With <sup>19</sup>F-<sup>19</sup>F couplings, although  $J_{ortho}$  is relatively constant (-20 to -21 c./sec),<sup>2</sup> there has been some evidence<sup>3</sup> to suggest that  $J_{meta}$  varies appreciably and may be of either sign. One of the difficulties encountered is that in the most studied compounds, the pentafluorobenzenes<sup>4,5</sup> (I) the analysis of the AA'XX'R <sup>19</sup>F spectra does not give the signs of any of the three *meta*-couplings ( $J_{2,4}$ ,  $J_{2,6}$ , and  $J_{3,5}$ ) nor does it distinguish between  $J_{2,6}$  and  $J_{3,5}$ .

We report from an analysis (see Table 1) of the

spectra of nine 2,6-difluorobenzenes (II; X = CO<sub>2</sub>H, CO<sub>2</sub>Me, CO-Me, CN, NH<sub>2</sub>, NHCO-Me, NHEt and OCH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>) together with other unpublished<sup>6</sup> data, that  $J_{meta}$  varies between +12 and -10 c./sec. Furthermore, from a computer



analysis of all the available data (some 36 F-F couplings) it is possible to predict these *meta*-couplings to ca. 1 c./sec. on the basis of additive substituent contributions. Substituent contributions for the commonest substituents are given in Table 2. (Values of  $J_{meta}^{FF}$  in compounds with other substituents have been measured but only for one

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TABLE 1  
Coupling constants (c./sec.) in 2,6-difluoro-1-substituted benzenes

	H-H		H-F			F-F
	$J_{3,4}$	$J_{3,5}$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{2,6}$
CN .. .. .	8.67	0.80	9.10	6.60	-0.85	0.00
CO <sub>2</sub> H .. .. .	8.48	0.90	9.50	6.40	-1.40	3.00
CO <sub>2</sub> Me .. .. .	8.52	1.00	9.60	6.35	-1.40	3.90
CO <sub>2</sub> Me .. .. .	8.43	0.90	9.35	6.20	-1.30	2.70
NH <sub>2</sub> .. .. .	8.47	1.30	10.40	6.25	-1.50	12.10
NHCO-Me .. .. .	8.44	1.35	9.50	6.10	-1.90	4.50
NHEt .. .. .	8.34	1.50	11.50	6.00	-1.70	10.90
I .. .. .	8.37	1.20	7.40	6.35	-1.30	2.30
OCH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub> .. .. .	8.40	1.25	10.35	5.88	-1.90	8.00

TABLE 2

Substituent	Contribution to $J_{meta}^{FF}$		(c./sec.)
	<i>ortho-ortho</i>	<i>ortho-para</i>	<i>meta-meta</i>
H .. .. .	0.0	0.0	0.0
F .. .. .	-0.3	-3.8	-0.7
NH <sub>2</sub> .. .. .	+6.3	-8.1	-0.8
Cl .. .. .	-3.3	-0.3	+0.1
NO <sub>2</sub> .. .. .	-7.7	+6.1	+1.9
CN .. .. .	-6.1	+4.4	—
I .. .. .	-3.6	+0.6	+0.6

compound, thus these substituent contributions cannot be tested and are not included here.) The values in Table 2 together with the predicted value of  $J_{meta}^{FF}$  in *m*-difluorobenzene of 6.3 c./sec. make it possible to calculate  $J_{meta}^{FF}$  in all the compounds incorporating these substituents. A best-fit analysis over 36 measured couplings yielded a mean deviation of 0.3 c./sec. As the experimental error in the  $J$ -values due to broad lines, complex analyses, etc., may be as much as 1 c./sec., the agreement obtained is strong support for the validity of the basic assumption of additive substituent contributions. Furthermore, this rule now enables one both to differentiate between  $J_{2,6}$  and  $J_{3,5}$  in the pentafluorophenyl derivatives and to predict the signs of all the  $J_{meta}^{FF}$ -values in these compounds (apart from those cases in which the couplings are small, *i.e.*, < 2 c./sec.).

The values of the substituent contributions we obtain are remarkable in that the contribution for a substituent *ortho* to both coupling nuclei is in general opposite in sign to that of a substituent oriented *ortho* and *para* to the coupling nuclei. There is also a reasonably good linear relationship between the substituent contribution and the Hammett  $\sigma$ -value<sup>7</sup> of the substituent. This is also novel as H-H coupling is considered to operate *via* the  $\sigma$ -bonds of the aromatic system,<sup>8</sup> yet the Hammett  $\sigma$ -value reflects the  $\pi$ -electron perturbation of the substituent. This suggests that there is an additional mechanism in F-F couplings which involves the  $\pi$ -electrons of the ring. We are grateful to Dr. L. F. Thomas for communicating his results prior to publication and to Dr. A. M. Roe, for samples of the 2,6-difluorobenzenes.

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