

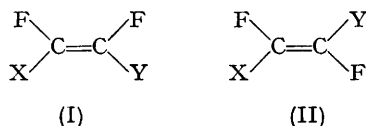
The Effect of Substituents on J_{vic}^{FF} in 1,2-Difluoroethylenes

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VICINAL proton-proton coupling constants in monosubstituted ethylenes have been correlated with the electronegativity of the ethylene substituent,¹ J_{trans} being usually greater than J_{cis} . With ^{19}F - ^{19}F coupling constants, J_{trans} is also of greater magnitude (ca. 118 c./sec.) than J_{cis} (33—58 c./sec.),² although usually of opposite sign to it.³ However no correlations of these coupling constants have been presented.

Values for the vicinal F-F coupling constants in a variety of *cis*- and *trans*-1,2-difluoroethylenes of the type (I) and (II) [X and Y = H, I, Br, Cl, CF_3 , $\text{N}(\text{CF}_3)_2$, and F] have been determined and these, together with certain literature values,^{2,4} are shown



parameters; a best-fit analysis of the data yields the values given in Table 2, the mean deviation being 1.0 c./sec. for J_{cis}^{FF} and 0.7 c./sec. for J_{trans}^{FF} . The agreement obtained offers good support for the validity of the basic assumption of additive substituent contributions, being, for J_{trans}^{FF} in particular, not much greater than the probable experimental error in the J -values.

There is no obvious correlation of the substituent contributions with, for example, the electronegativity of the substituent, although there is a trend to larger values of the contribution to J_{cis} and to J_{trans} (J_{trans}^{FF} is probably negative³) across the first-row elements C to F, or up the periodic Group I to F. This latter trend within a group may not be general however, since the values reported for several silicon-, germanium-, and tin-substituted fluoro-olefins⁵ indicate no such trend in Group IV if

TABLE I

Vicinal coupling constants (c./sec.) in 1,2-difluoroethylenes

| | H | I | Br | Cl | CF_3 | $\text{N}(\text{CF}_3)_2$ | F | |
|---------------------------|---|----------------------------|---|---|-------------------------------|---|----------------------------|---|
| H | $\overline{\text{H}}$ 132.7 ^a | — | — | — | — | — | — | } |
| I | — | $\overline{\text{I}}$ — | — | — | — | — | — | |
| Br | — | — | $\overline{\text{Br}}$ 34.3 ^d | — | — | — | — | |
| Cl | — | — | — | $\overline{\text{Cl}}$ 37.5 ^e | — | — | — | |
| CF_3 | — | — | — | — | $\overline{\text{CF}_3}$ — | — | — | |
| $\text{N}(\text{CF}_3)_2$ | — | — | — | — | — | $\overline{\text{N}(\text{CF}_3)_2}$ — | — | |
| F | — | — | — | — | — | — | $\overline{\text{F}}$ — | |
| | 119 ^c | 129.2 | 124 ^c | 115 ^c | 120.2 ^f | 115.3 | — | |

^a See ref. 4a.

^b cf. Ref. 4b.

^c See ref. 2.

^d See ref. 4b.

^e See ref. 4c.

^f See ref. 4d.

in Table 1. These coupling-constant values may be expressed as the sum of pairs of substituent

an additive substituent-contribution is assumed. The effect of substituent changes further removed

TABLE 2

| Substituent | Contributions to J^{FF} | | | | | | | | |
|----------------------------------|---------------------------|------|------|------|-----------------|----------------------------------|------|--|--|
| | H | I | Br | Cl | CF ₃ | N(CF ₃) ₂ | F | | |
| Contribution to J_{cis}^{FF} | -7.9 | 12.5 | 17.5 | 18.8 | 1.6 | 18.1 | 39.0 | | |
| Contribution to J_{trans}^{FF} | 67.3 | 78.4 | 71.4 | 64.5 | 69.7 | 62.9 | 51.4 | | |

from the double bond has not yet been investigated in any great detail, but the indications are that, although for certain cases these have a comparatively minor effect upon the coupling constants, particularly J_{trans} (cf., CF₂:CF-CF₃,^{4d} CF₂:-CF·CF₂Cl,^{6a} CF₂:CF·CHF·CF₃, CF₂:CF·CF:CF₂, and CF₂:CF·COF,^{6b} where J_{cis} is 40.3, 39, 36.6,

32.4, and 36.8, and J_{trans} is 120.2, 118, 118.4, 118.8, and 114 c./sec., respectively), in others, this is not so (cf., CF₂:CF·SF₅,⁷ and CF₂:CF·SO₂F where J_{cis} is 57.2 and 42.4, and J_{trans} is 117.6 and 121.5 c./sec., respectively).

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