Observations on the Angular Dependence of Vicinal ^{19}F–^{19}F Coupling Constants

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Summary Vicinal ^{19}F–^{19}F couplings exhibit a complex angular dependence which includes at least one sign inversion.

As part of a programme concerned with the stereospecific dependencies of heteronuclear coupling constants, the vicinal ^{19}F–^{19}F couplings of the compounds† (1)—(6) have been investigated.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-mannopyranosyl fluoride (2) and the α-D-*gluco*-analogue (3) were available from a previous study.[1] Dissolution of (2) in anhydrous hydrogen fluoride at *ca.* −10° for 15 min. resulted in equilibration[2] to give 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-mannopyranosyl fluoride (1), m.p. 89—90° [from ether–light petroleum (b.p. 60—80°)], $[\alpha]_D^{25}$ +27° ($CHCl_3$). Treatment of 2-deoxy-2-fluoro-D-glucose[1] in sequence with pyridine–acetic anhydride, hydrogen bromide–acetic acid, and silver fluoride–acetonitrile[3] afforded 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranosyl fluoride (4), m.p. 99—101° [from ether–light petroleum (b.p. 60—80°)], $[\alpha]_D^{25}$ +75° ($CHCl_3$).

Reaction of anthracene with 1-chloro-1,2,2-trifluoroethylene at 250° for 20 hr. afforded 7-chloro-7,8,8-trifluoro-(23),5(6)-dibenzobicyclo[2,2,2]octane (5), m.p. (with

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† All new compounds gave satisfactory microanalytical data.

sublimation) 205—206° (from benzene), which was subsequently reduced to 7,7,8-trifluoro-2(3),5(6)-dibenzobicyclo-[2,2,2]octane (6), m.p. (with sublimation) 164—164·5° [from benzene–light petroleum (b.p. 30—60°)], using ethereal lithium aluminium hydride.

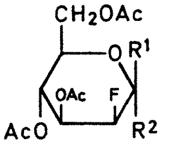
The ^1H–^1H and ^{19}F–^1H couplings‡ of (1)—(6), which will be reported in detail elsewhere, in each case confirmed the assigned structure and, importantly, indicated that the sets of fluorine substituents had the nominal dihedral separations anticipated. The appropriate dihedral angles (ϕ) are listed in the Table together with the corresponding ^{19}F–^{19}F couplings and the total Huggins[4] electronegativity (ΣE) of the first atoms of the substituents attached to C-1 and C-2 for derivatives (1)—(4) and to C-7 and C-8 for derivatives (5) and (6).

Vicinal ^{19}F–^{19}F *coupling constants*[a] *for compounds* (1)—(6)

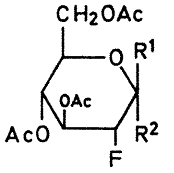
Compound	(1)[b]	(2)[b]	(3)[b]	(4)[b]	(5)[b]		(6)[c]	
					J_{AX}[d]	J_{BX}[d]	J_{AX}[e]	J_{BX}[e]
^{19}F–^{19}F coupling (J Hz)	−20·0	−13·5	−18·8	−15·8	−2·2	+11·4	−1·2	+9·4
Nominal dihedral angle (ϕ°)	180	60	60	60	120	0	120	0
ΣE[f]	18·3	18·3	18·3	18·3	20·1		19·1	

[a] Measured with a modified Varian HA-100 spectrometer in the frequency-swept mode with irradiation of the entire ^1H spectrum.[5] The signs of the couplings were determined by a variant of the selective irradiation technique.[6] [b] In $CDCl_3$–$CFCl_3$ solution. [c] In C_6D_6–$CFCl_3$ solution. [d] Assignment based on ^{19}F chemical shift calculations.[7] [e] Assignment based on vicinal ^{19}F–^1H couplings.[8] [f] Total Huggins electronegativity[4] of the first atom of substituents attached to C-1 and C-2 for derivatives (1)—(4) and to C-7 and C-8 for derivatives (5) and (6).

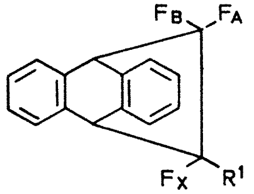
These data imply that the angular dependence of vicinal ^{19}F–^{19}F couplings is more complex than the $\cos^2 \phi$ relationship which has been established for vicinal ^1H–^1H and ^{19}F–^1H couplings.[8,9] The observed maxima and minima at approximate dihedral angles of 0° and 120°, and 60° and 180°, respectively, suggests a possible $\cos^2 3\phi/2$ (or $\cos 3\phi/2$) relationship for ^{19}F–^{19}F couplings.



(1) $R^1 = H, R^2 = F$
(2) $R^1 = F, R^2 = H$



(3) $R^1 = H, R^2 = F$
(4) $R^1 = F, R^2 = H$



(5) $R^1 = Cl$
(6) $R^1 = H$

Since the majority of vicinal ^{19}F–^{19}F couplings previously reported in the literature are of unknown sign and have been derived from compounds of uncertain conformation it is difficult to evaluate the effect of other parameters, such as electronegativity. However, some comments are appropriate.

All of the data reported by Ernst[10] for fluorinated cyclobutane derivatives, and similar data for cyclobutylsilanes (having ϕ = 20—30°) from this laboratory,[11] are in good accord with the present study as also are the couplings obtained[12] by analysis of the low-temperature spectra of 1,1,2-tribromo-1,2,2-trifluoroethane (ΣE = 20·6), J_{gauche} −18·6 Hz, J_{trans} −16·2 Hz.

It has been previously observed[13–15] for fluorinated ethanes that the magnitudes of *time-averaged* vicinal ^{19}F–^{19}F couplings in CF·CF fragments depend on the total electronegativity of the substituents. It would seem that J_{trans} is more susceptible to changes in electronegativity than is J_{gauche} since a collation of the data for fluorinated cyclic compounds and for certain fluorinated ethane derivatives having $\Sigma E < 21$ indicates that $J_{60°}$ varies between −21 and −12 Hz whereas $J_{180°}$ varies between −20 and 0 Hz. Because of this differential effect we consider that caution is necessary at this time in using vicinal ^{19}F–^{19}F couplings as the sole basis for configurational or conformational assignments.

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‡ These data were analysed using a modified version of the LAOCOON III programme with an I.B.M. 360-67 computer.

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