Deuterium Isotope Effect on Geminal Couplings between Proton and Fluorine Nuclei

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AN isotope effect has been observed on the geminal proton–fluorine coupling constant in fluoroform and silyl fluoride and it is hoped that this, together with calculations now in hand, will provide some understanding of the variation of geminal coupling constants with nuclear configuration.

The effect of isotopic substitution on chemical shifts is well known,[1] but few comparable data have appeared on coupling constants;[2–5] previous reports of a positive isotope effect on a coupling constant have been of a *secondary* nature, *i.e.* the effect of substitution on the value of J_{AB}, where neither the A nor the B nucleus is substituted;[2–5] attempts to observe a *primary* effect, *i.e.* the effect on J_{AB} of isotopic substitution of A or B, were negative.[2,4] Preliminary calculations on the model compound CH_3F indicated, however, that such an effect should be just observable in proton–fluorine couplings, and we report here data on fluoroform and silyl fluoride.

Fluoroform and [^{2}H]fluoroform were prepared from CF_3I;[6,9] the silyl fluorides from phenyl trichlorosilane *via* the bromide[8] with antimony trifluoride as the fluorinating agent. The silyl fluoride contained very small amounts of other fluorosilanes, owing to disproportionation, which were just detectable by n.m.r. and i.r. spectra. No hydrogen was detected in the deuteriated compounds. Samples were sealed in n.m.r. tubes at known concentrations with degassed cyclohexane (*ca.* 6 mmoles) and CCl_3F (*ca.* 0·2 mmoles). Spectra were recorded on a Varian HA-100 spectrometer, line positions being measured with the internal frequency counter (V4315 model 6000–4). For the ^{19}F spectra, a Muirhead D-890A decade oscillator modified to reduce drifting, produced the required offset from the CCl_3F lock. To obtain the highest accuracy, line positions were always measured in pairs, to minimise the effect of any drift, and about 25 measurements were made for each pair of lines. No bias was found from measurements made on pairs of lines centred at different fields, thus any errors due to a nonlinear magnetic field sweep are less than those from other sources.

The largest errors arise in the measurements on the deuteriated compounds, mainly because of the small factor $\gamma_D/\gamma_H = 0{\cdot}1535$. This was partially counterbalanced by the larger number of lines for the deuteriated compounds. Table 1 shows a set of typical measurements on CHF_3. Tables 2 and 3 give the overall mean values of J for each sample examined, this mean being calculated by weighting the mean of each paired difference inversely to the square of its standard error.

The results show that $^2J_{HF}$ decreases with decreasing concentration for fluoroform, probably because of changes in hydrogen bonded self-association, but the small variation with concentration in silyl fluoride is not statistically significant over the 10 mole % range studied.

TABLE 1. *Fluoroform* (Sample 7, Table 3) (Lines are numbered from low to high field)

Lines measured	J (Hz)	Error (Hz)	Number of measurements
1,2 ^1H	79·344	0·020	41
2,3 ^1H	79·343	0·014	23
3,4 ^1H	79·334	0·017	43
1,2 ^{19}F	79·334	0·021	25

For fluoroform, the good agreement between the values for CHF_3 in samples 6 and 7 which had very nearly the same total concentration, argues that, as far as the intermolecular interactions causing the concentration dependence are concerned, CHF_3 and CDF_3 should be considered to be at the same total concentration in sample 6.

The value of $^2J_{HF}$ was taken to be that of sample 6b which had the smallest error. This gives an isotope effect for fluoroform of 0·078 ± 0·048 Hz which is just significant. For silyl fluoride the value of $^2J_{HF}$ was taken to be a weighted average of results 1, 2a, and 4; *viz.* 45·764 ± 0·015 Hz, which gives a statistically significant isotope effect of 0·153 ± 0·052 Hz. In both cases the effect is

TABLE 2. *Silyl fluoride in cyclohexane at* 25 ± 1°

Sample number	Concentration mole %	Molecule	J (Hz)	Error (Hz)	Spectrum	Ref.
		SiH_3F	45·8	0·1	^1H	3
1	10	,,	45·758	0·013	^1H	this work
2a	17	,,	45·762	0·017	^1H	,,
2b	,,	,,	45·761	0·030	^{19}F	,,
3	19	SiD_3F	45·611	0·050	^{19}F	,,
4	19	SiH_3F	45·774	0·015	^1H	,,

TABLE 3. *Fluoroform in cyclohexane at* 25 ± 1°

Sample number	Concentration mole %	Molecule	J (Hz)	Error (Hz)	Spectrum	Ref.
	pure liquid	CHF_3	79·72	0·07	^1H	10
	gas *ca.* 45 atmos.	CHF_3	79·74	0·1	^{19}F	11
	10% v/v	CHF_3	79·21	0·1	^{19}F	11
	5% v/v	CHF_3	79·23	0·1	^1H	10
	48/52 mixture	CHF_3/CDF_3	79·5/78·2	— / —	^{19}F	7
5	4	CHF_3	79·267	0·032	^1H	this work
6a	31 { 12	{ CHF_3	79·343	0·026	,,	,,
b		CHF_3	79·339	0·015	^{19}F	,,
c	19	CDF_3	79·261	0·046	,,	,,
7a	32	CHF_3	79·340	0·018	^1H	,,
b	,,	,,	79·334	0·021	^{19}F	,,

such that deuteriation causes a decrease in the absolute magnitude of the coupling constant.

[$J = {}^2J_{HF}$ or ${}^2J_{DF} \times \gamma_H/\gamma_D$, where $\gamma_D/\gamma_H = 0{\cdot}15350609 \pm (8 \times 10^{-9})$.[9] Error quoted is the standard deviation of the weighted mean.]

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