An Experimental and Theoretical Investigation of Orientational Dependence of H–F Couplings in Fluoro-olefins

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The ^{1}H and ^{19}F n.m.r. spectra of several monofluoro-olefins are reported. Coupling of vinylic fluorine to hydrogen bound to sp^3-hybridised carbon has been observed over three, four, and five bonds. The four-bond 'allylic' F–H coupling has been examined in detail, with FPT-INDO calculations for several cases. The *trans*-CH•C:CF coupling changes sign as the HC•C:C torsion angle varies, as predicted, but the *cis*-CH•C:CF coupling is positive for all H•C•C:C angles, contrary to predictions. Alkyl substituents have an appreciable effect on the allylic couplings; this effect is primarily due to changes in geometry on substitution. The $^5J_{HF}$ couplings are also sensitive to orientation; in particular, the observation of a *cis*-$^5J_{HF}$ coupling depends on the proximity of the fluorine and the coupled hydrogen.

The history of fluorine-19 as an 'n.m.r. nucleus' almost rivals that of hydrogen, and fluorine chemical shifts and coupling constants are accordingly well documented.[1–6] Nonetheless, few systematic data are available on the n.m.r. properties of fluorine bound to olefinic carbon, other than in relatively simple vinyl fluorides.[4] We were particularly interested in the possible dependence on orientation of the three- and four-bond fluorine couplings to hydrogen bound to sp^3-hybridised carbon ('vicinal' and 'allylic' couplings) in fluoro-olefins, which are important as possible analogues of peptides.[7]

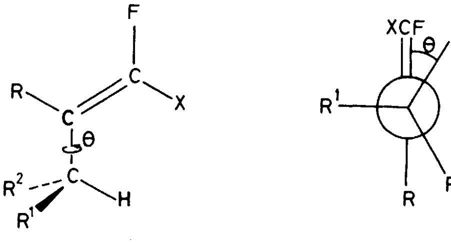
The dependence of $^3J_{HH}$ on orientation is well known.[8] Several studies indicate a similar dependence of $^3J_{FH}$ on orientation,[9–14] though substituent effects on $^3J_{FH}$ are larger than on $^3J_{HH}$. Three-bond couplings of the type F–C(=C)–CR$_2$–H have been observed in a range of systems,[4] including 2-fluoropropene in which the sign of $^3J_{FH}$ was found to be positive.[14] In a conformational study of several halogenoacetyl fluorides, the corresponding coupling constants were found to change sign with orientation.[15] Experimental determinations of the 'allylic' F–H coupling F–C=C–C–H are so far restricted to the two 1-fluoropropenes,[16] in which the sign of the coupling is also positive.

Several calculations of $^3J_{HF}$ in fluoroethane[17–19] agree in predicting a relationship of the form (1), which has been

$$^3J_{FH} = A + B\cos\theta + C\cos^2\theta \qquad (1)$$

confirmed experimentally.[10,12] The $\cos^2\theta$ term is dominant in all the calculations; the best calculation[18] gave the coefficients as A = 0.2, B = 5.0, C = 30.3, agreeing well with observed couplings. Most recent calculations use the 'finite perturbation' (FPT) procedure of Pople *et al.*, with INDO[21] wavefunctions (INDO-FPT). Calculations of the three-bond coupling in olefins are so far restricted to vinyl fluorides,[20,22] and predict that the *trans*-coupling is larger than the *cis*-, in agreement with observation.[4] No calculations of the three-bond fluorine–hydrogen coupling across an olefinic carbon atom have been reported.

A calculation of coupling constants in the 1-fluoropropenes[23] showed that $^4J_{FH}$ changes sign with orientation for both *cis*- and *trans*-couplings. The calculated values at $\theta = 0°$ (Scheme) are negative, whereas the values for $\theta = 120°$ are positive. Five-bond fluorine–hydrogen couplings through an intermediate double bond have not been examined either theoretically or experimentally. The major contributions to the five-bond F–H couplings in 1-fluorobutane have, however, been examined using the INDO-FPT method.[23] Coupling is largest when the hydrogen and fluorine nuclei are closest, in general agreement with observation.[4,23]



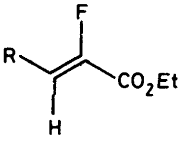
Scheme. Definition of the dihedral angle θ in fluoro-olefins

In this work we examined the fluorine and proton n.m.r. spectra of the α-fluoro-α,β-unsaturated carboxylic esters (**1**)—(**16**) and related compounds. These materials provide examples of several hydrogen–fluorine couplings involving vinylic fluorine which have not been closely studied experimentally. It was hoped that this work would provide information on the important orientation dependence of these couplings.

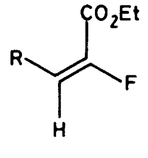
Results

The proton and ^{19}F n.m.r. data for compounds (**1**)—(**8**) are summarised in Table 1. With the exception of (**5**), the proton spectra at 220 MHz show first-order patterns and the chemical shifts and coupling constants are obtained directly. The spectra of (**5**) at 400 MHz were analysed using the iterative computer program LAOCOON III.[24]

The determination of the configuration of these materials relied on the magnitudes of the vinylic fluorine–hydrogen coupling ($^3J_{trans}$ is invariably greater than $^3J_{cis}$ in vinyl fluorides[4]) and the chemical shifts of the vinylic proton and the protons α to the double bond. Both types of resonance are shifted to low field (deshielded) by a *cis*-carboxy group;[25–32]

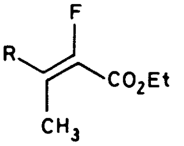


(a)

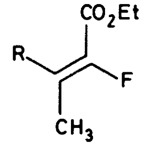


(b)

(1) R = CH_3
(2) R = CH_2CH_3
(3) R = $CH(CH_3)_2$
(4) R = $C(CH_3)_3$
(5) R = CH=CHPh

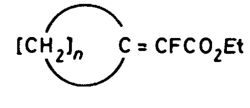


(a)

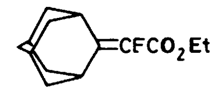


(b)

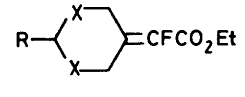
(6) R = CH_3
(7) R = $CH_2C(CH_3)_3$
(8) R = $CH_2CH(OMe)_2$



(9) n = 3
(10) n = 4
(11) n = 5



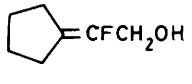
(12)



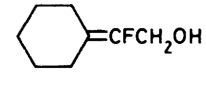
(13) X = CH_2 R = CH_3
(14) X = CH_2 R = Ph
(15) X = S R = H
(16) X = S R = Ph

$CH_2{=}CF{-}CH_3$
(17)

$(CH_3)_2C{=}CFCH_2OH$
(18)



(19)



(20)

consequently the vinyl hydrogen atom in the *Z*-olefin (a) resonates at lower field than in the *E*-isomer (b) and *vice versa* for the α-hydrogen atoms.

The data in Table 1 permit an estimation of ${}^4J_{FH}$ in two distinct orientations. The torsional potential functions for propene and other simple alkenes[33] show that the conformations in which an alkyl group or hydrogen atom eclipses the C=C bond are preferred. The coupling constants ${}^4J_{obs}$ to the hydrogen atoms α to the double bond in acyclic alkenes are therefore simple weighted averages of ${}^4J_0$ and ${}^4J_{120}$, given by equation (2), where n_θ and J_θ are the mole fraction and

$$ {}^4J_{obs} = \sum_{\theta} n_\theta J_\theta \qquad (2) $$

coupling constant respectively corresponding to the conformation characterised by the angle θ. (Strictly speaking, these conformations are all distributions about the potential minima at θ = 0°, 120°, *etc.*) Calculations show that (**3b**) is almost completely restricted to the conformation in which the methine proton eclipses the C=C bond.[34] This is also indicated by the vicinal H(3)—H(4) coupling (10.4 Hz). Using this value for ${}^3J_{HH}(0°)$ with a value of 3.6 Hz for ${}^3J(120°)$ obtained by Garbisch,[35] we find from the value of 9.7 Hz for (**3a**) that this molecule also exists predominantly (90%) in the HCCH *anti* conformation. Since this preference may be attributed to steric interactions between the methyl groups and the *cis*-carboxy group (or fluorine), it is reasonable to assume that (**2a**) and (**2b**) are similarly restricted. Applying this information to the four-bond fluorine couplings in (**1**)—(**3**) gives the following estimates of ${}^4J_{FH}$ for the orientations θ = 0° and θ = 120°:

$$ {}^4J_{cis}(0°) = 1.1\text{ Hz}, \qquad {}^4J_{cis}(120°) = 3.9\text{ Hz} $$

$$ {}^4J_{trans}(0°) = -1.9\text{ Hz}, \; {}^4J_{trans}(120°) = 5.3\text{ Hz} $$

Thus the *trans*-coupling apparently shows the predicted[23] change of sign with orientation, but the *cis*-coupling does not. This study was therefore extended to include a number of cyclic

Table 1. Chemical shifts (δ) and coupling constants[a] of α-fluoro-α,β-unsaturated ethyl ethers C(5)–C(4)–C(3)=C(2)F–CO_2Et[b]

	δH(3)	δH(4)	δH(5)	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{H(3)-F}$	$J_{H(4)-F}$	$J_{H(5)-F}$	δ_F[c]
(**1a**)	6.17	1.79		7.3			33.0	2.9		−130.7
(**1b**)	5.99	2.02		7.8			21.2	2.9		−124.4
(**2a**)	6.11	2.26	1.09	7.7	0.3	7.7	33.3	2.3	N.d.	−131.5
(**2b**)	5.90	2.53	1.07	8.1	0.3	7.5	21.5	1.7	0.9	−123.5
(**3a**)	5.97	2.85	1.07	9.7	N.d.†	6.7	33.7	1.0	0.4	−131.7
(**3b**)	5.72	3.60	1.05	10.4	N.d.	6.7	21.9	2.2	1.0	−125.0
(**4a**)	4.90		1.20				38.7		1.1	−128.8
(**4b**)	4.76		1.22				28.4		0.6	−118.4
(**5a**)[d]	6.76	7.05	6.77	11.41(3)	0.61(5)	15.84(4)	31.08(5)	0.48(5)	N.d.	−128.6
(**5b**)[d]	6.65	7.79	6.81	11.58(3)	1.03(4)	15.83(3)	19.34(5)	1.03(5)	N.d.	−123.4
(**6**)[e] *cis*		1.87		${}^4J_{H-H}$ 0.5				J_{trans} 3.3		
trans		2.11						J_{cis} 4.2		
(**7a**)[e]		2.18 (Me)	0.97					3.3 (Me)	$J_{F-H(6)}$ 1.2	
		2.10						4.2		
(**7b**)[e]		1.88 (Me)	0.95					5.2 (Me)	N.d.	
		2.56						1.7		
(**8a**)[e]		2.15 (Me)	4.54			5.2		3.2 (Me)	0.7	
		2.56						3.6		
(**8b**)[e]		1.92 (Me)	4.49			5.2		4.4 (Me)	N.d.	
		2.84						1.8		

[a] In Hz (±0.05). [b] Ethyl group shifts were 4.300 ± 0.005 (CH_2) and 1.345 ± 0.005 (Me), with J_{H-H} = 7.10 ± 0.05 Hz for all the materials described here. [c] In p.p.m. from external $CFCl_3$. [d] Data quoted are the results of a LAOCOON 3 analysis of the 400 MHz spectra. Sixteen observed lines were assigned to calculated transitions in each case. Final r.m.s. errors: (**5a**) 0.06 Hz; (**5b**) 0.05 Hz. Standard errors in shifts were all less than 0.002 p.p.m. Figures in parentheses are standard errors in the last figure quoted. [e] ${}^{19}F$ Shifts not determined.

† Not determined.

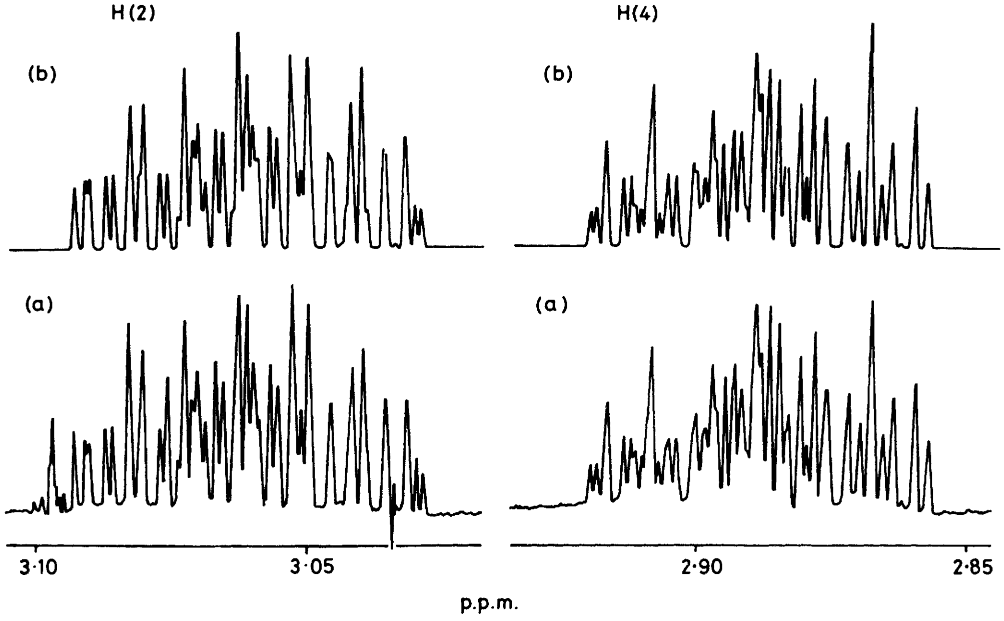


Figure 1. The ^{1}H n.m.r. spectrum of ethyl 2-cyclobutylidene-2-fluoroacetate: the H(2) and H(4) resonances: (*a*) observed spectrum; (*b*) computed spectrum

materials of well defined conformation in search of more direct evidence.

The ^{1}H n.m.r. spectra of the cycloalkylidenefluoroacetates (**9**)—(**16**) are, in several cases, too complex to permit full analysis and assignment. Nonetheless, it proved possible to obtain the magnitudes of practically all the four-bond fluorine–hydrogen coupling constants in these materials. The methods employed in each case will be discussed in turn.

Ethyl 2-Cyclobutylidene-2-fluoroacetate (**9**).—The data reported here were obtained by analysis of the 400 MHz proton spectrum, shown in Figures 1 and 2. The proton n.m.r. spectrum of the ring protons in (**9**) forms the AA′BB′MM′ portion of an AA′BB′MM′X spectrum (the usual notation[36] is employed) with the fluorine forming the X part. Suitable parameters for a preliminary calculation of the spectrum were taken from available data on four-membered rings.[37,38] Values for the fluorine couplings were obtained from the 94.1 MHz fluorine spectrum of (**9**) (giving the average four-bond coupling) and the total proton multiplet widths in the 400 MHz spectrum (giving the difference between the two couplings). The five-bond fluorine coupling appears in the proton spectrum as a persistent splitting of *ca.* 0.3—0.4 Hz. The spectral parameters were varied manually to achieve the general form of the spectrum. This was followed by optimisation of a limited number of parameter sets using well resolved transitions until full assignment could be made. The final optimised parameters are given in Table 2 with the probable errors. Figures 1 and 2 compare the observed and computed spectra.

The values obtained are close to those found in methylenecyclobutane,[38] suggesting that the ring geometry is not significantly perturbed by the additional substituents in (**9**).

Ethyl 2-Cyclopentylidene-2-fluoroacetate (**10**) *and Ethyl 2-Cyclohexylidene-2-fluoroacetate* (**11**).—The proton spectra of (**10**) and (**11**) did not admit complete analysis. As usual, the lower-field of the two α-proton multiplets was assigned to the methylene group *cis* to the carboxy group. The remaining ring protons give rise to complex multiplets at 1.7 p.p.m. (**10**) and 1.3 p.p.m. (**11**). The fluorine spectrum of (**10**) (Figure 3) shows three proton–fluorine couplings, of 3.4, 3.4, and 1.8 Hz. Irradiation at 1.7 p.p.m. in the proton spectrum causes collapse of the 1.8 Hz splitting, which was therefore assigned to the *cis*-five-bond coupling by analogy with the acyclic materials (**7**) and (**8**). The remaining two couplings are therefore four-bond 'allylic' couplings. The small separation of the relevant proton signals at 100 MHz, together with the poor resolution of the fluorine spectrum, indicates that the actual couplings may differ significantly from the observed splittings.

The four-bond couplings in (**11**) were obtained from three separate experiments. The 94 MHz fluorine resonance (Figure 4) is a broad multiplet with some unresolved structure. Irradiation of the high-field (1.6 p.p.m.) proton resonance reduces the fluorine signal to a triplet of triplets with splittings of 1.5 and 2.4 Hz. Irradiation of the same region at 220 MHz causes the two methylene proton resonances at 2.35 and 2.73 p.p.m. to collapse to poorly resolved doublets. The measured splittings were 2.1 and 1.3 Hz, respectively. Finally, the appearance of the α-methylene multiplets at 400 MHz is similar to that of the AA′ part of an AA′MM′RR′X system, owing to coupling to the adjacent ring protons and to cross-ring couplings to the other α-methylene group. Irradiation of each α-methylene multiplet therefore reduces the effective spin system to AA′MM′X. Though the resulting signal is still too poorly resolved for full analysis, the characteristic intense transitions of the normal AA′MM′ system are clearly visible [at $\nu_A \pm (J_{AM} + J_{AM'})/2$], split only by the fluorine couplings (Figure 5). The fluorine couplings could thus be measured directly, giving values of 2.7 Hz (*cis*) and 1.6 Hz (*trans*).

Ethyl 2-(9-Tricyclo[3.3.1.1^{3,7}]decylidene)-2-fluoroacetate (**12**).—The proton spectrum of (**12**) shows two multiplets, at 3.80 and 3.16 p.p.m., corresponding to the α-methine protons, with the remaining proton resonances in the range 1.7—2.0 p.p.m. Decoupling experiments on the proton spectrum at 220 MHz were unproductive. Limited information was obtained from decoupling the proton spectrum while observing the fluorine spectrum. Decoupling at 1.8 p.p.m. in the proton spectrum reduced the fluorine resonance to a broad doublet with a separation of 3.7 Hz. Decoupling at 3.1 and 3.8 p.p.m.,

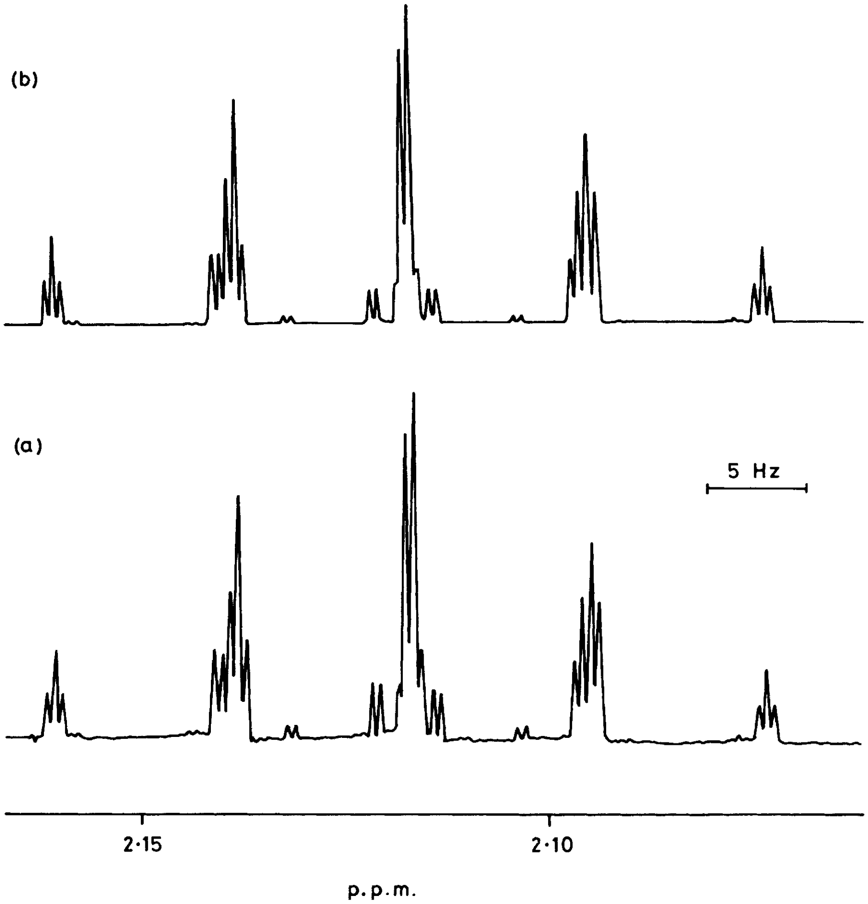


Figure 2. The ^1H n.m.r. spectrum of ethyl 2-cyclobutylidene-2-fluoroacetate: the H(3) resonance: (*a*) observed spectrum; (*b*) computed spectrum

respectively, reduced the fluorine signal linewidth by 1.5 and 3.5 Hz. This leads to estimated magnitudes of 1.5 Hz (*cis*) and 3.7 Hz (*trans*) for the two fluorine couplings in (**12**).

Ethyl 2-*Fluoro*-2-(4-*methylcyclohexylidene*)*acetate* (**13**) *and Ethyl* 2-*Fluoro*-2-(4-*phenylcyclohexylidene*)*acetate* (**14**).—Compound (**13**) provided no useful fluorine coupling constant data despite several approaches, including examination of the fluorine spectrum, selective decoupling experiments, and decoupling experiments following addition of lanthanoid shift reagents. The only data obtained are thus proton shift data.

The spectrum of the 4-phenyl compound (**14**) is very similar in appearance to that of (**13**), although the ring proton shifts are rather more 'spread out' by the phenyl group, allowing a rather more complete assignment of the 400 MHz proton spectrum. An early estimate of the difference in the fluorine couplings to the equatorial α-protons was made by measurement of the total mulitplet widths for the appropriate signals. This gave a value for $^4J_{HF}(trans) - {}^4J_{HF}(cis)$ of *ca.* 2 Hz. The actual magnitudes of these coupling constants were measured directly from a two-dimensional homonuclear *J*-resolved spectrum.[39] Figure 6 shows a part of the 2-D *J*-resolved spectrum of (**14**). The values obtained for the couplings to H_{2e} and H_{6e} (Figure 6) were 2.6 and 1.2 Hz, respectively. These values agree closely with those observed for (**3a**) and (**3b**).

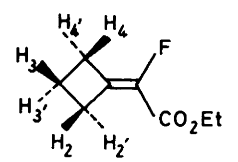
Table 3 summarises the available proton n.m.r. information for (**10**)—(**14**).

Ethyl 2-(1,3-*Dithiacyclohexan*-5-*ylidene*)-2-*fluoroacetate* (**15**) *and its* 2-*Phenyl Analogue* (**16**).—The compounds studied so far provide useful data for conformationally restricted systems. However, a direct demonstration of the difference in sign between the two *trans*-coupling constants was still desired. The two dithianes (**15**) and (**16**) were therefore prepared. It was hoped that the simplicity of these spin systems would provide the required information unambiguously, as the separate couplings to the axial and equatorial hydrogen atoms in (**16**) should be directly observable, while the corresponding values for (**15**) would provide an average value owing to rapid conformational inversion. This assumes that the ring geometry is not perturbed appreciably by the phenyl group; Abraham *et al.* have demonstrated that the solution conformation of 4-phenylcyclohexanone differs only slightly from that of cyclohexanone itself.[40]

Table 4 gives the proton n.m.r. data for the ring protons in (**15**) and (**16**). The two values of $^4J_{HF}$ in (**15**) are 2.8 (*cis*) and 1.9 Hz (*trans*). The average of the two *cis*-couplings in (**16**) is $(4.5 + 0.9)/2 = 2.7$ Hz, in excellent agreement. The possible average values for the *trans*-coupling are $(5.8 + 1.9)/2 = 3.9$ Hz (same sign) and $(5.8 - 1.9)/2 = 2.0$ Hz (opposite signs). The latter is in good agreement with the observed value for (**15**); consequently the two *trans*-couplings are opposite in sign.

This may also be demonstrated directly by a low-power double-resonance experiment.[41] Figure 7 shows the result of irradiation of two separate transitions in the 100 MHz proton spectrum of (**16**). Irradiation of the *low*-field line (actually an unresolved doublet) of the H_{2a} resonance causes a splitting of *ca.* 2 Hz in the *high*-field portion of the H_{2e} resonance [Figure 7(B)]. The two H–F couplings are therefore of opposite sign. Conversely, irradiation of the high-field transition of the H_{6a}

Table 2. Proton and fluorine n.m.r. parameters for ethyl 2-cyclobutylidene-2-fluoroacetate (**9**)[a]



(**9**)

Chemical shifts (p.p.m.)[b]

H(2),H(2′) 3.059 H(3),H(3′) 2.117 H(4),H(4′) 2.889

δ_F −138.9 p.p.m.[c]

Coupling constants (Hz)[d]

^2J: $J(2,2')$ −16.39(2); $J(3,3)$ −9.86(2); $J(4,4')$ −16.16(2)

^3J: $J(2,3) = J(2',3') = 9.66(1)$; $J(2,3') = J(2',3) = 6.25(1)$

$J(3,4) = J(3',4') = 9.70(1)$; $J(3,4') = J(3',4) = 6.15(1)$

^4J: $J(2,4) = J(2',4') = 0.93(1)$; $J(2,4') = J(2',4) = -4.04(1)$

$^nJ_{H-F}$: $^4J[H(2),F] = J[H(2'),F] = 3.92(2)$;

$^5J[H(3),F] = J[H(3'),F] = 0.35(2)$;

$^4J[H(4),F] = J[H(4'),F] = 3.25(2)$

[a] The data were obtained by analysis (LAOCOON 3) of the proton spectrum at 400 MHz. Ninety-six observed lines were assigned to 226 calculated transitions. The final r.m.s. error was 0.07 Hz. [b] Shifts referenced to Me$_4$Si: standard errors are less than 0.001 p.p.m. [c] Referenced to external trichlorofluoromethane. [d] Probable errors in the last figure shown in parentheses.

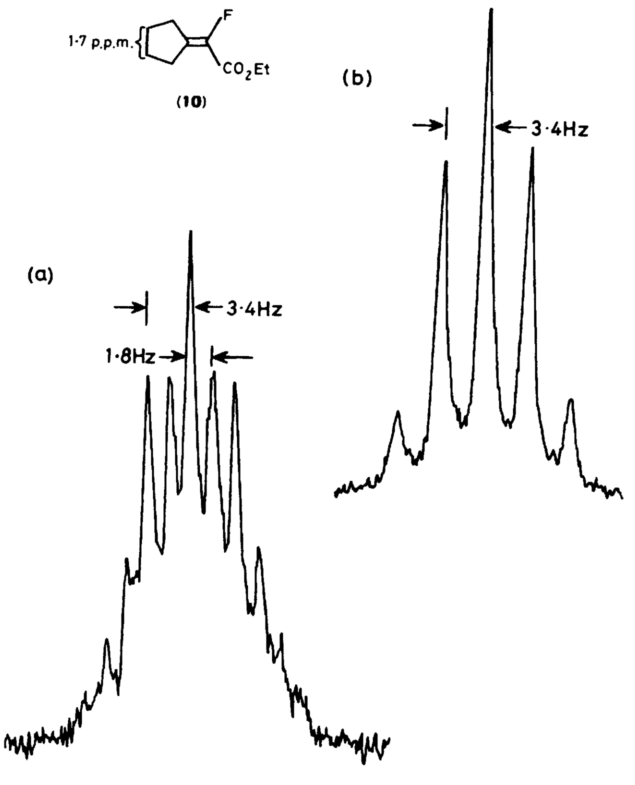


Figure 3. The effect of proton decoupling on the 94.1 MHz fluorine-19 spectrum of 2-cyclopentylidene-2-fluoroacetate (**10**): (a) unperturbed spectrum; (b) spectrum with irradiation at 1.7 p.p.m. (^{1}H)

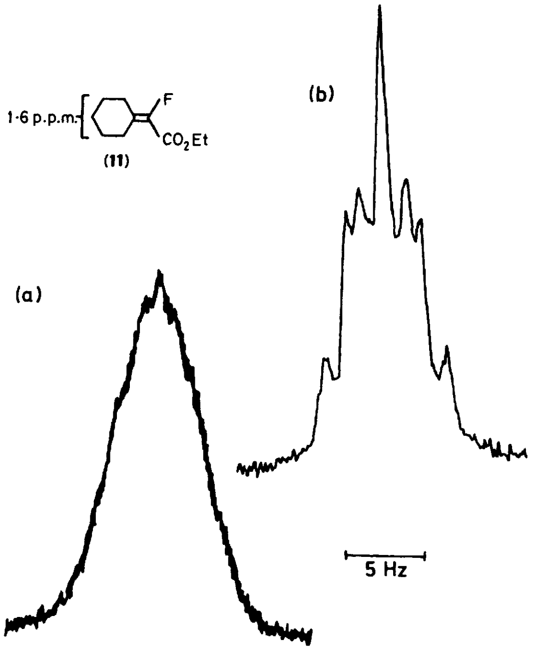


Figure 4. The effect of proton decoupling on the 94.1 MHz fluorine-19 spectrum of ethyl 2-cyclohexylidene-2-fluoroacetate (**11**): (a) unperturbed spectrum; (b) spectrum with irradiation at 1.6 p.p.m. (^{1}H)

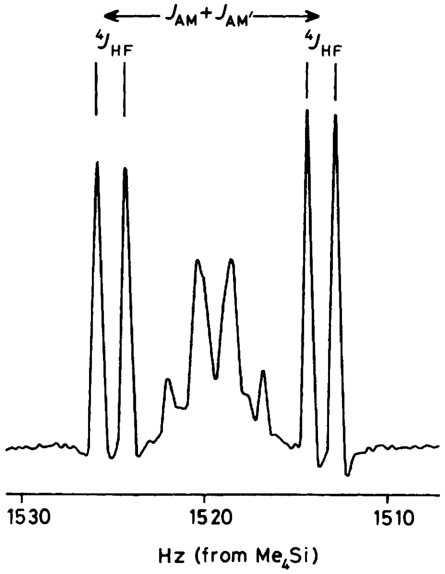


Figure 5. The determination of the allylic fluorine–hydrogen couplings in ethyl 2-cyclohexylidene-2-fluoroacetate (**11**): the H(2) resonance at 400 MHz with irradiation of the H(6) resonance

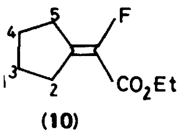
resonance results in a similar splitting of the high-field part of the H_{6e} resonance. The two couplings in this case are therefore of the same sign.

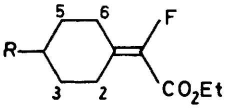
The four-bond fluorine–hydrogen coupling constants in the 1-fluoropropenes are positive.[22] The absolute signs of the various $^4J_{HF}$ in (**16**) are therefore assigned as follows:

$$trans\text{-}^4J_{eq} = -1.9 \text{ Hz}, \quad trans\text{-}^4J_{ax} = +5.8 \text{ Hz}$$

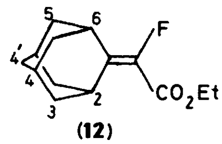
$$cis\text{-}^4J_{eq} = +0.9 \text{ Hz}, \quad cis\text{-}^4J_{ax} = +4.5 \text{ Hz}$$

Table 3. Chemical shifts and fluorine coupling constants for the ethyl 2-cycloalkylidene-2-fluoroacetates (**10**)—(**14**)


(10)


(11) R = H **(13)** R = Me

(14) R = Ph


(12)

Chemical shifts[a]

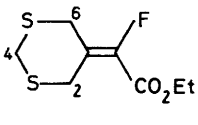
	δ(2)	δ(3)	δ(4)	δ(5)	δ(6)	δ_F[b]
(10)	2.71	(1.73)		2.53		−126.3
(11)	2.73	1.63	1.63	1.63	2.35	−131.5
(12)	3.80		(1.7—2.0)		3.16	−135.9
(13)[c] *eq*	3.52	1.85		1.85	2.92	−131.0
ax	2.00	1.06	1.60	1.06	1.85	δ(Me) 0.91
(14) *eq*	3.67	(2.02)		(2.02)	3.10	−129.9
ax	1.93	1.60	2.67	1.60	(2.02)	δ(Ph) 7.2—7.4

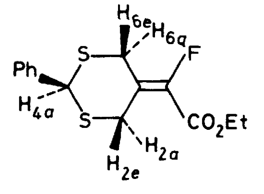
Fluorine coupling constants[d]

	$^4J_{HF}$(*cis*)	$^4J_{HF}$(*trans*)	$^5J_{HF}$
(10)	3.4	3.4	1.8 (*trans*)[e]
(11)	2.7	1.6	
(12)	1.5	−3.7[f]	
(13)	N.d.	N.d.	
(14) *eq*	1.2	−2.6[f]	
ax[g]	4.2	5.8	

[a] Shifts referenced to Me_4Si, taken from spectra at 400 MHz. Values in parentheses are uncertain owing to overlapping multiplets. [b] ^{19}F Shifts referenced to external trichlorofluoromethane at 94.1 MHz. [c] 270 MHz Spectrum. [d] See text for methods of determination. [e] Assumed *trans* by comparison with acyclic materials. [f] Assumed negative by comparison with (**16**) (see text). [g] Calculated from equatorial couplings and data for (**11**).

Table 4. Proton and fluorine n.m.r. data for the dithianes (**15**)—(**16**)


(15)


(16)

(15)[a]

δ[(H(2)] 4.01 J[H(2),F] 1.9 Hz
δ[H(4)] 3.95
δ[H(6)] 3.95 J[H(6),F] 2.8 Hz
δ(F) −132.0

Ethyl H: δ(CH_2) 4.33; δ(CH_3) 1.35; J(CH_2–CH_3) 7.1 Hz

(16)[b]

	H(2*e*)	H(2*a*)	H(4*a*)	H(6*e*)	H(6*a*)
δ(p.p.m.)	4.72	3.59	5.45	3.89	3.44
J(H–F)/Hz	−1.90 ±0.03	5.82 ±0.03		0.94 ±0.03	4.50 ±0.03

Proton–proton coupling constants:

J(2*a*—2*e*) −13.72 ± 0.03; J(6*a*—6*e*) −13.48 ± 0.03
J(2*e*—6*e*) 1.85 ± 0.03; J(2*a*—6*a*) 0.33 ± 0.03

Ethyl H:

δ(CH_2) 4.323, 4.308; δ(CH_3) 1.34
J_{gem} −10.9 ± 0.03; J(CH_2–CH_3) 7.1 ± 0.03

[a] 220 MHz Spectrum in $CDCl_3$. Shifts referred to Me_4Si. [b] Taken directly from the 400 MHz FT spectrum in $CDCl_3$. The quoted errors in the coupling constants are equal to the digitisation of the transformed spectrum.

Discussion

The $^4J_{HF}$ Couplings.—The values of the four-bond fluorine–hydrogen couplings for (**1**)—(**16**) are summarised in Table 5. Comparison of the couplings for (**1**) with those to the methyl groups in (**6**)—(**8**) shows a marked difference in the *cis*-couplings and a smaller, though significant, difference in the *trans*-couplings. The origin of this effect may be explored by comparison of the observed couplings with the results of INDO-FPT calculations.

INDO-FPT calculations[23] on the 1-fluoropropenes using standard geometries[42] predicted that the couplings to the in-plane hydrogen atoms ($\theta = 0°$) were −5.6 and −3.0 Hz for the *cis*- and *trans*-couplings, respectively; the corresponding out-of-plane ($\theta = 120°$) values were 4.2 and 5.4 Hz. Our experimental observations show that the sign of the calculated *cis*-coupling is incorrect. The observed coupling for a particular orientation is the sum of several contributions: (i) a direct[43,44] through-space contribution (negative); (ii) a positive 'rear-lobe' interaction;[23] (iii) several σ-mediated indirect pathways, including the 'through-bond' pathway; and (iv) a π-mediated indirect interaction. The π-mediated contribution is expected to be positive and largest at $\theta = 90°$. The rear-lobe interaction is only important for the *cis*-coupling with θ near 180°. The σ-mediated and through-space terms are both negative, the latter being most important for the *cis*-coupling when θ approaches 0°. Interestingly, it is for this orientation that the observed and calculated couplings differ most. It thus appeared that the 'through-space' interaction was exaggerated in the calculation. A possible cause is the poor reproduction of geometry in the 'standard'[42] model, which gives much smaller values of the relevant F–H distance than optimised or experimental geometries.[7] We have therefore recalculated these coupling constants using fluoropropene geometries calculated elsewhere,[7] and found a considerable reduction in the magnitude of the *cis*-coupling (−5.6 Hz to −3.1 Hz). Unfortunately, the overall agreement between experiment and calculation is reduced by a similar decrease in the calculated out-of-plane couplings.

The values of $^4J_{HF}$ in 2-fluorobut-2-enoic acid have also been calculated using 'standard' and improved geometries. Table 6 summarises the results, compared with values obtained in this work. We note that, while the calculated *cis*-coupling is still negative for $\theta = 0°$, the value is *smaller* than the corresponding *trans*-value, in confirmation of our initial assertion that the through-space effect is over-estimated by the standard geometry.

The addition of a 3-methyl group also decreases the negative contribution to the *cis*-coupling. The calculated values were, for the *cis*-couplings, −1.7 ($\theta = 0°$) and 4.1 Hz ($\theta = 120°$), and for the *trans*-coupling, −2.4 ($\theta = 0°$) and 4.5 Hz ($\theta = 120°$). These values clearly predict the correct order of the coupling constants observed for (**14**) and (**16**), though the magnitudes leave room for improvement.

It is concluded from the foregoing comparisons that the results of INDO-FPT calculations cannot accurately reproduce

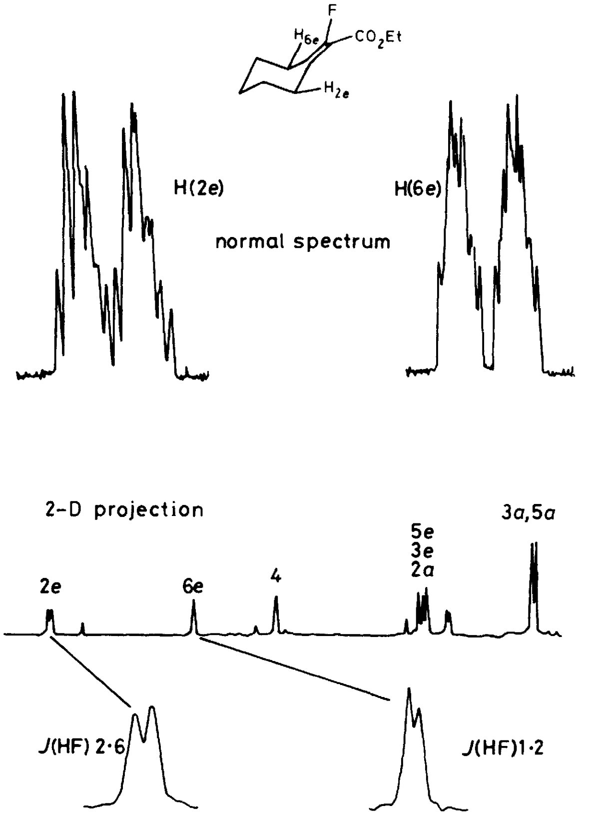


Figure 6. The two-dimensional *J*-resolved 400 MHz ^{1}H spectrum of ethyl 2-fluoro-2-(4-phenylcyclohexylidene)acetate (**14**)[a]

[a] Spectrum obtained by Mr M. Bulsing and Dr. J. K. Saunders, University of Cambridge

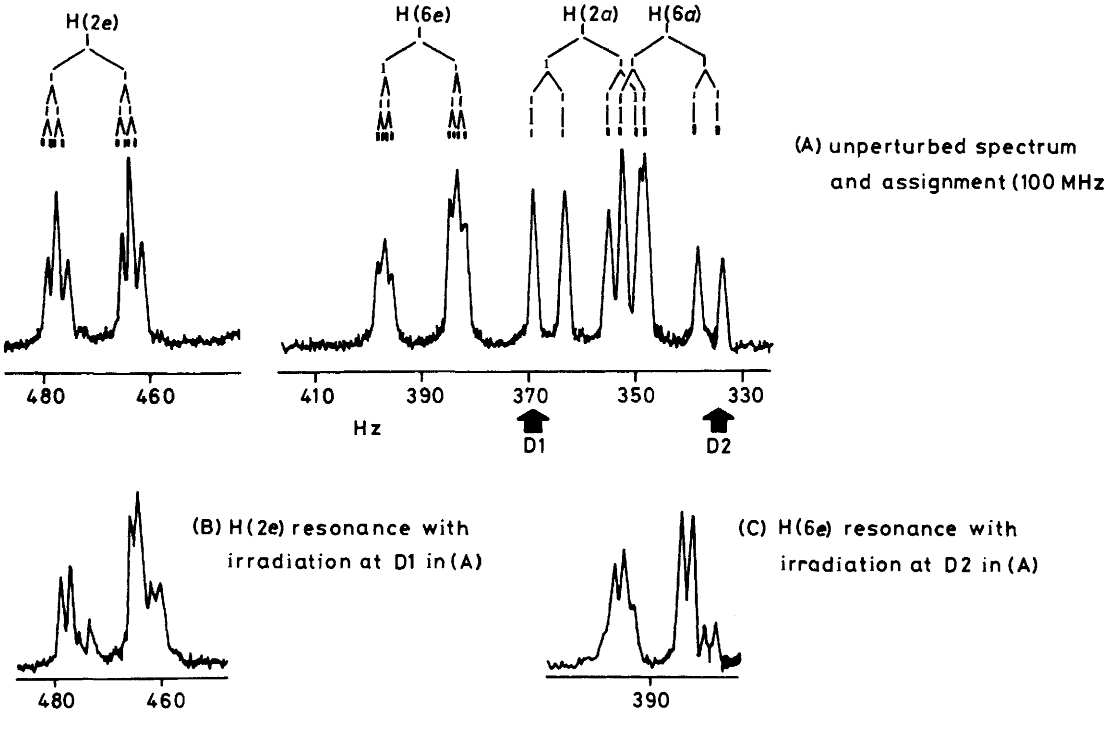
the couplings in these molecules. However, the observed order of the couplings is well reproduced once suitable geometries are employed. The calculations then give a valuable insight into the effects of substituents on $^4J_{\mathrm{HF}}$. With regard to the origin of the observed effect of 3-alkyl substitution, it is clear from the calculated effects of structure on the couplings in 2-fluorobut-2-enoic acid that the total *cis*-coupling to the methyl group is expected to *increase* with decreasing methyl–fluorine separation. It is thus likely that the large effect of alkyl substitution at the 3-position on the *cis*-coupling is primarily the result of geometric changes. The electronic effect on the coupling due to the additional methyl group appears small in comparison.

The $^3J_{\mathrm{HF}}$ *Couplings*.—The α-fluoro-α,β-unsaturated esters (**1**)—(**16**) do not possess $^3J_{\mathrm{HF}}$ couplings to a saturated proton. However, reduction of the esters gave the alcohols (**18**)—(**20**), which do have these couplings. Table 7 gives the n.m.r. data for these compounds.

Comparison of the values of these couplings (22.9 and 24.0 Hz) with the analogous coupling in 2-fluoropropene (**17**)[4] of 16.0 Hz shows clearly the pronounced conformational preference of the OH group in (**18**)—(**20**).

Assuming that $J_g \approx J_t/4$ and that the coupling in 2-fluoropropene is $(J_t + 2J_g)/3$, the calculated couplings for the two rotamers about the C–C bond in (**18**)—(**20**) are 8.0 (OH *anti* to F) and 20.0 Hz (OH *gauche* to F), suggesting 100% population of the *gauche* form. This is not surprising given the well known *gauche* OH–F attraction and the OH–CH$_2$ repulsion.

The $^5J_{\mathrm{HF}}$ *Couplings*.—Table 8 summarises the five-bond fluorine–hydrogen coupling constants measured during this work. The most prominent single effect on these couplings appears to be that of the 3-methyl group in (**6**)—(**8**). For example, (**2**) and (**3**) show appreciable *trans*-couplings, but small or undetectable *cis*-couplings. In contrast, in (**7**) and (**8**) the *trans*-coupling is the smaller coupling. The five-bond



(A) unperturbed spectrum and assignment (100 MHz)

(B) H(2e) resonance with irradiation at D1 in (A)

(C) H(6e) resonance with irradiation at D2 in (A)

Figure 7. The determination of relative signs of fluorine–hydrogen couplings in the dithiane (**16**); low-power decoupling in the 100 MHz ^{1}H spectrum

Table 5. Allylic fluorine–hydrogen couplings in α-fluoro-α,β-unsaturated esters

	J_{cis}	J_{trans}	Contributing orientation[a]
(1)	2.9	2.9	$J_0 + 2J_{120}$
(2)	2.3	1.7	$J_0 + J_{120}$
(3)	1.0	-2.2^b	J_0
(5)	0.5	-1.0^b	J_0
(6)	4.2	3.3	$J_0 + 2J_{120}$
(7) Me	5.2	3.3	$J_0 + 2J_{120}$
CH_2	4.2	1.7	$J_0 + J_{120}$
(8) Me	4.4	3.2	$J_0 + 2J_{120}$
CH_2	3.6	1.8	$J_0 + J_{120}$
(9)	3.3	3.9	$J_{60\pm15}$
(10)	3.4	3.4	$J_{60\pm30}$
(11)	2.7	1.6	$J_{0+}J_{120}$
(12)	-1.5^b	3.7	J_0
(14) *eq*	1.2	-2.6^b	J_0
ax	4.2^c	5.8^c	J_{120}
(15)	2.8	1.9	$J_0 + J_{120}$
(16) *eq*	0.9	-1.9	J_0
ax	4.5	5.8	J_{120}
1-Fluoropropene[d]	2.6	3.3	$J_0 + 2J_{120}$

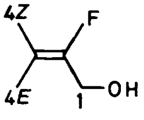
[a] See Scheme. [b] Assumed negative. [c] Calculated from J_{eq} and data for (**11**). [d] Ref. 15.

Table 6. Experimental and calculated coupling constants for ethyl 2-fluorobut-2-enoates

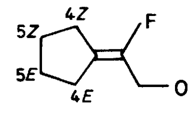
	trans			*cis*		
Method	J_0	J_{120}	J(av.)[c]	J_0	J_{120}	J(av.)
INDO-FP[a]	-3.2	5.4	2.5	-5.1	4.9	1.9
INDO-FP[b]	-3.1	4.8	2.2	-2.5	4.3	2.0
Experimental			2.9			2.9

[a] Standard geometry. [b] Modified geometry. [c] $(J_0 + 2J_{120})/3$.

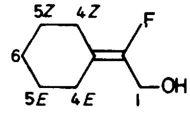
Table 7. Proton n.m.r. data for the 2-fluoroallylic alcohols (**18**)—(**20**)[a]



(18)



(19)



(20)

	H(1)	H(4*E*)	H(4*Z*)	H(5*E*)	H(5*Z*)	H(6)
(**18**)[b] δ	4.20	1.68^c	1.68^c			
J(F–H)	22.9	3.2^c	3.2^c			
	$J(1,4Z) = J(1,4E) = 0.6$ Hz[c]					
(**19**) δ	4.20	$(2.30)^e$		(1.51)		
J(F–H)[d]	24.0					
	$J(1,4Z) = J(1,4E) = 0.9$ Hz					
(**20**) δ	4.23	(2.18)		(1.55)		
J(F–H)[d]	22.9					

[a] Taken from 100 MHz FT spectra: 500 Hz sweep width, 4 K data points. [b] 220 MHz Frequency sweep spectrum. [c] The H(4) methyl signals show some fine structure not due to coupling to ^{19}F or H(1), and hence form an A_3B_3 multiplet. The apparent couplings to these methyl groups are therefore averages of the *cis*- and *trans*-couplings. [d] Only $^3J_{FH}$ determined. [e] Parentheses indicate multiplet overlap: the shift given is the centre of the resulting signal.

Table 8. Five-bond fluorine–hydrogen coupling constants for α-fluoro-α,β-unsaturated esters[a]

	cis		*trans*
(2)			0.9
(3)	-0.4^b		1.0
(4)	-1.1^b		0.6
(7)	1.2		
(8)	0.7		
(9)		0.35	
(10)			1.8^c

[a] Signs of these coupling constants were not determined. [b] Presumed negative; see text. [c] Assignment uncertain.

couplings in (**4**) are also interesting, since in this case also the *cis*-coupling is the larger. The value in this instance (1.0 Hz) is very close to the value (1.2 Hz) observed for the five-bond coupling in 1-fluoro-2,4,6-tri-t-butylbenzene,[4] and is probably also due to a through-space effect. This provides a clue to the reason for the reversal of the relative magnitudes of the *cis*- and *trans*-couplings caused by the addition of a 3-methyl group. It was argued earlier that the molecules (**2**) and (**3**) exist primarily in the HCCH *anti* conformation for steric reasons. Consequently, the direct through-space contribution to the five-bond coupling is expected to be small. The presence of the 3-alkyl group (R = Me) is likely to cause a shift to the HCCH *gauche* conformation, again on steric grounds. The importance of through-space coupling is thereby substantially increased.

Thus, the data in Table 8 suggest that the fluorine coupling $^5J_{cis}$ to a methyl group eclipsing the carbon–carbon double gond is close to -3 Hz, taking the coupling to the out-of plane methyl groups as zero [*cf.* (**3a**)]. The corresponding coupling in the *trans*-series is apparently close to zero, while the *trans*-coupling to the out-of-plane methyl groups is *ca.* 1 Hz, probably positive on the basis of calculated couplings for 1-fluorobutanes.[23]

Experimental

Fluorine-19 n.m.r. spectra were obtained with a Varian XL-100 spectrometer operating at 94.1 MHz. Chemical shifts were referenced to external trichlorofluoromethane.

Proton n.m.r. measurements were carried out with a variety of instruments. Routine spectra were run with a Perkin-Elmer R34 instrument operating at 220 MHz, using tetramethylsilane as combined reference and field/frequency lock. A frequency counter was used to determine chemical shifts, which are accurate to 0.01 p.p.m.

Measurements of coupling constants were taken from scale expansions at usually 1.1 Hz cm^{-1}, and were generally determined as an average of at least three values. They are believed accurate to ±0.05 Hz or less. Other instruments used from time to time as appropriate include; Bruker WH 400 (400 MHz; 32—64 K FT with appropriate Lorentzian-Gaussian multiplication); Bruker WM 250 (250 MHz; 32 K FT); Bruker WH 270 (270 MHz; 16 K FT); JEOL FX 200 (200 MHz; 16—32 K FT).

For analysis of closely coupled spectra the program LAOCOON III was used, operating on an IBM 4341 computer with double precision. Simulated spectra were produced using the Bruker Spectrospin program PANIC running on an ASPECT 2000 data system.

Synthesis.—The compounds were synthesized by the modified Horner reaction of triethyl fluorophosphonoacetate $(EtO)_2P(O)CHFCO_2Et$ with aldehydes and ketones.[45] Aldehydes gave mixtures of *Z*- and *E*-isomers which were not separated, but analysed as such, configuration being identified by measuring $^3J_{HF}$ ($J_{trans} > J_{cis}$). Full details of the chemistry and properties of these compounds have been published elsewhere.[46]

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