Tetrahedron Vol. 33, pp. 1769 to 1773. Pergamon Press 1977. Printed in Great Britain

^{13}C–^{19}F COUPLINGS AND ^{19}F NMR SHIFTS OF CYCLOALKYL, BICYCLOALKYL AND STEROID MONOFLUORO COMPOUNDS[1]

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(*Received in the UK 6 January 1977; Accepted for publication 19 January 1977*)

Abstract—The stereospecifity of ^{13}C–^{19}F couplings is investigated with 20 alicyclic compounds. One bond couplings, ranging from 168 to 214 Hz, can be represented as a function of the corresponding ^{13}C–H coupling constants. For comparison ^{13}C–^{1}H couplings are determined for norbornane and adamantane and indicate considerable *s* character at the bridgehead C–H bond of the latter compound. One bond and geminal couplings (ranging from 18 to 24 Hz) are found to depend not significantly on the steric environment. With vicinal couplings a strong dependence is established on torsional angles, which is fitted to a Karplus function. Typical values for CCCF *trans* arrangements are around 10 Hz, for *gauche* angles less than 1.5 Hz. Vicinal couplings are substantially altered by electronegative substituents and by hybridization changes of participating carbon atoms. The ^{3}J values observed with cycloalkylfluorides are interpreted on the basis of model geometries for the corresponding hydrocarbons. The influence of solvent and temperature changes is restricted to one bond couplings. ^{19}F shifts in cyclohexane derivatives are constantly at higher field for axial fluorine (by ~20 ppm), but otherwise there is no significant relation to the orientation of neighbouring bonds, nor to ^{13}C shifts of the Cα–F carbon atoms or to the corresponding one bond couplings.

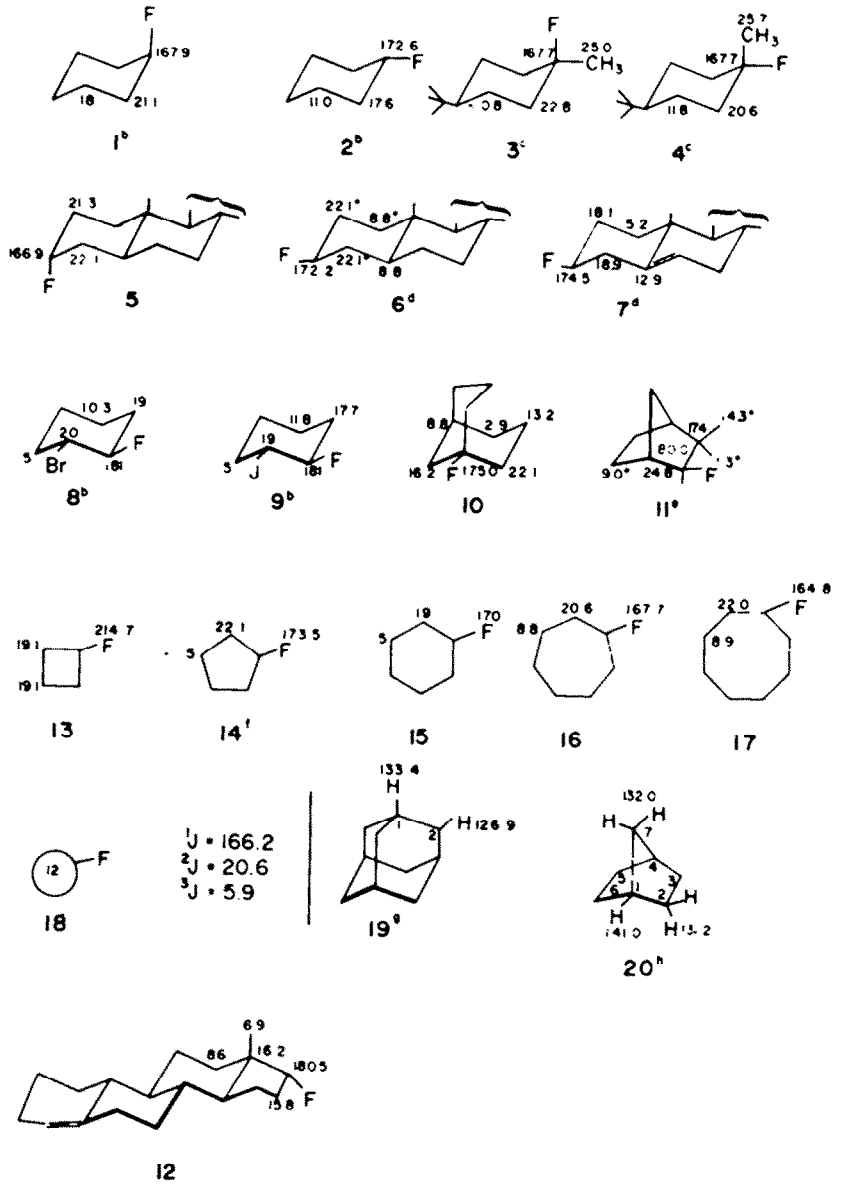
The evaluation of molecular structures by ^{13}C NMR spectroscopy has predominantly rested on chemical shift arguments.[2] Although examples for stereospecific vicinal $^{13}CCC^{19}F$ couplings were known as early as 1970,[3] their relation to torsional angles of participating bonds has not yet been investigated. The potential of vicinal couplings is illustrated with camphene hydrofluoride **11** (Scheme 1), where five constants are available relating directly to the geometry of the molecule.

One bond and geminal couplings. For a number of aromatic compounds ^{13}C–^{19}F couplings have been described by the Fermi contact mechanism.[4a–c] Although other interactions have to be included,[4d,e] there is evidence for an increase of $^{1}J_{^{13}C,^{19}F}$ couplings, notably bearing a negative sign, with increasing *s* character of the C–F bonds.[4] Since the reported $^{1}J_{^{13}C,^{19}F}$ values for 1-fluoro-adamantane (186 Hz)[5] and for *exo*-2-fluoro-norbornane (182 Hz)[6b] are unusually large, we have for comparison measured the corresponding ^{13}C–^{1}H couplings in the ^{1}H-gated decoupled ^{13}C spectra. The observed $^{1}J_{^{13}C,^{1}H}$ values (Scheme 1) in fact indicate a substantial distortion of the bond angles at the bridgehead of adamantane (not so at C2). Similarly, an increased *s* character in the C2–H and C7–H bonds of norbornane is seen, although only an average value for the *endo* and *exo* C2–H position could be obtained. If one includes the known ^{13}C–H couplings of other cycloalkanes[6] a correlation between $^{1}J_{^{13}C,^{19}F}$ and $^{1}J_{^{13}C,^{1}H}$ is observed (Fig. 1). The deviation observed for fluorocyclobutane is not unexpected, since orbital terms have been shown to contribute significantly to CF couplings of larger magnitude.[4e] Stereochemical assignments on the basis of one bond couplings do not seem to be feasible. Although in compounds **1**, **2**, **5**, **6** and **7** (Scheme 1) the couplings with axial oriented fluorine are 5 Hz smaller than with equatorial fluorines, these differences disappear in the tertiary compounds **3** and **4**.

The observed geminal couplings (Scheme 1) do not show a significant dependence on stereochemistry and on electronegativity of additional substituents. Their constant values make them useful for ^{13}C line assignments, particularly in natural products such as steroids.

Vicinal couplings and cycloalkane conformations. The vicinal couplings observed for the conformationally fixed compounds **1**–**11** (Scheme 1) can be represented as a function of the torsional angle θ around the C2–C3 bond. Some values for torsional angles near to 30° and 100°, which are difficult to realize in other model compounds were obtained from 17α-fluorester-4-ene **12**. Although the D ring geometry is flexible, the possible vicinal angles for the known conformational alternatives[7] do not differ substantially and are estimated as follows: for C15 as 100° in the twist conformation (95° in the envelope forms); for C14 as 75°(80°); for C12 as 30°(35°). The 22 experimental values (Scheme 1) together with 7 additional literature[4e,5,6a,8,9] data for ^{3}J can be fitted to a Karplus-function $^{3}J = 11.0 \cos^2 \theta$ (Fig. 2); the corresponding curve obtained by least square treatment of the data predicts the vicinal couplings with a standard deviation of ±1.6 Hz (r = 0.937). In view of the scatter of points the fit to a two term equation does not seem to be warranted. The empirical nature of the correlation should be emphasized, particularly since the sign of the couplings is not known. The calculation of torsional angles from vicinal couplings is hampered as in the case of the corresponding HH couplings[7] by the strong influence of the electronegativity of additional substituents (compare **8** and **9**, Scheme 1) and of the hybridization of interacting bonds. This is clearly seen in the abnormal value of $^{3}J = 19$ Hz for cyclobutane, for which the torsional angle must be 100–130°.[10]

The other fluorocycloalkanes **14**–**18** contain less severe deviations from normal sp^3 states and their vicinal couplings can be analyzed in terms of known model geometries of the corresponding cycloalkane conformations. Only with cyclohexyl fluoride could coupling constants be obtained for individual conformers ^{11}(**1**, **2**); the other fluorocycloalkanes equilibrate too fast at the ^{13}C-NMR time scale even at −100°. For those compounds, **13**–**18**, torsional angles θ for each possible flu-



Scheme 1. ^{13}C-^{19}F and ^{13}C-^1H coupling constants.[a]

[a] In [Hz]; couplings not denoted are below spectrometer resolution (~1.5 Hz). Signals labeled[a] overlap with other ^{13}C signals. ^{13}C spectra were measured at 300 ± 10 K, 30–40% solution in $CDCl_3$, except in the following cases: [b] 180 K, 20% $CFCl_3$; [c] 20%, $CDCl_3$; [d] 10%; [e] 250 K, 20%, $CFCl_3$; [f] 20%, $CFCl_3$; [g] 10% in $CDCl_3/C_6H_6$ (1/2); [h] 50%, $CDCl_3$ (measured by E. Weigand).

orine position were estimated from Dreiding models and an average value $\bar{\theta}$ obtained from the summation over all single θ values. In view of the very similar steric requirements of fluorine and hydrogen, pseudoaxial as well as pseudoequatorial positions were taken into account.

For the twist half chair geometry of cyclopentane[12] an equally distributed population of fluorine in pseudoequatorial positions would yield an average value of $\bar{\theta}_e = 145°$, for pseudoaxial positions $\bar{\theta}_a = 95°$; the corresponding average angles in the envelope conformation[12] are $\bar{\theta}_e = 150°$, $\bar{\theta}_a = 90°$. The observed value of ^3J 1.5 Hz suggests substantial populations of pseudo-*a* besides pseudo-*e* positions.

Cycloheptane is considered in the twist chair form TC as well as in the twist boat conformation TB.[13] Pseudo-*e* substitution including an isoclinal site at C1 in TC would lead to $\bar{\theta}_e = 150°$, in TB to $\bar{\theta}_e = 145°$; the corresponding values for pseudo-*a* positions are $\bar{\theta}_a = 65°$ (TB) and $\bar{\theta}_a = 90°$ (TC). The large coupling of $^3J = 8.8$ Hz would predict average angles above 150°, as occurring in pseudo-*e* populations of the more stable TC[13] conformation.

The most probable conformation of cyclooctane is a boat chair form BC[14] with $\bar{\theta}_e = 150°$ and $\bar{\theta}_a = 80$–$90°$. Energetically close comes a chair chair conformation CC with $\bar{\theta}_e = 150°$ and $\bar{\theta}_a = 20°$. The observed $^3J = 8.9$ Hz is compatible with these conformations except dominant pseudo-*a* populations in CC.

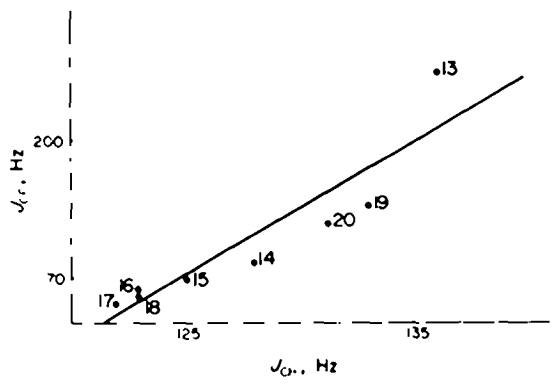


Fig. 1. Correlation between one bond ^{13}C–^{19}F and ^{13}C–^{1}H couplings constants. Compound number see Scheme 1.

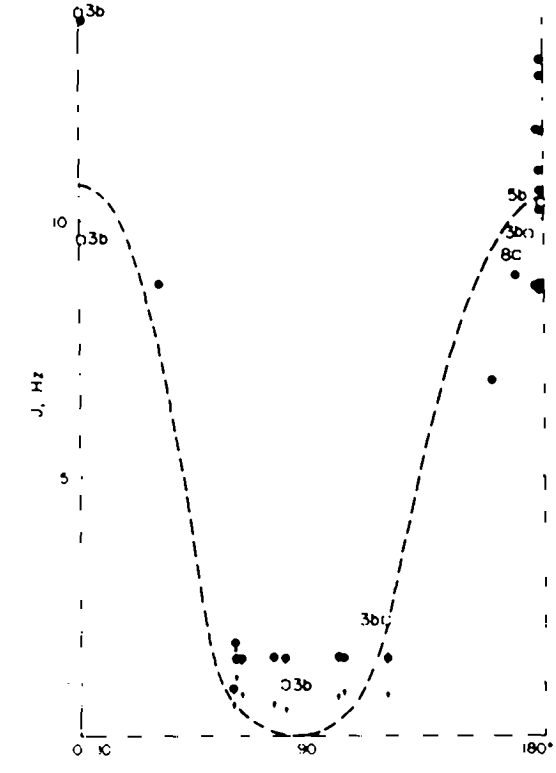


Fig. 2. Correlation between vicinal $^{13}CCC^{19}F$ coupling constants and torsional angles θ. ^{3}J values are taken from Scheme 1 (filled circles), some are literature[16,19,a] values as indicated. Points denoted by an arrow represent upper limits only.

Cyclododecane possesses a particularly stable conformation of D_4 symmetry[17] with elements of similar geometry as cyclohexane. It has been shown recently by low temperature ^{13}C NMR spectroscopy that the skeleton can accommodate substituents with very small energy differences in corner as well as in non-corner positions.[18] In both positions a fluorine will have one γC atom *gauche* ($\theta = 60°$) and another one *trans* ($\theta = 180°$) to the Cα–F bond, which is in accordance with the observed average coupling of $^{3}J = 5.9$ Hz.

Temperature and solvent effects. The application of ^{13}C–^{19}F coupling constants to the analysis of conformational equilibria requires knowledge of the influence of external factors on individual couplings. The conformationally homogeneous fluorides **3** and **4** show no measurable difference ($\Delta J < 0.5$ Hz) in ^{2}J and ^{1}J between CD_3CN and $CDCl_3$ as solvents. Only the one bond coupling increases in the more polar solvent by 4 Hz, which can be explained by an increase of polarity and *s* character at the C–F bond.[17] The same mechanism could be responsible for the observed increase of the one bond coupling with temperature (~1.5 Hz/100°; **3** and **4**, 20% in $CDCl_3$); another factor to consider is an increasing population of higher vibrational ground states. Whereas for **14** and **16** only the usual increase of ^{1}J with temperature (~2 Hz/100°) is observed, ^{1}J in fluorocyclobutane **13** remains temperature invariant while the strongly conformation-dependent vicinal coupling decreases by ~2.5 Hz/100°. This would be consistent with an increase of the pseudo-*a* conformer, which is distinguished from the pseudo-*e* conformer in the folded cyclobutane geometry by a lower torsional angle ($\theta_a \approx 100°$, $\theta_e \approx 130°$).

^{19}F Shifts. The wide range of chemical shifts holds much promise for stereochemical applications of ^{19}F NMR spectroscopy.[18] The known shielding of axial as compared to equatorial fluorine[19] is substantiated in the observed shifts ($\Delta\delta \approx 20$ ppm) of the cyclohexane analogues **1–9** (Table 1). Similar trends are known in fluorosteroids[20] and fluoropyranoses;[21] in fluorocyclohexanes additional substituents have been found to lead to unpredictable shift variations.[22]

Whereas α-methyl groups lead to a rather constant deshielding (**3**, **4**, **11**) as compared to secondary fluorides (**1**, **2**, **5–9**), other substituents in non-α position do not alter the ^{19}F shifts significantly (**5–9**). ^{19}F shifts of the conformationally inhomogenous compounds (**13–18**) resemble those of equatorial fluorocyclohexanes, with the notable exception of cycloalkanes of higher *s* character in the CF bond (**13**).

Comparison of ^{19}F shifts with ^{13}C shieldings in the corresponding compounds[23] yields no correlation, thus

Table 1. ^{19}F Shifts,[a] $^{1}H_\alpha$ shifts[b] and geminal $^{1}HC^{19}F$ coupling constants.[c]

Compound	$\delta^{19}F$[a]	$\delta^{1}H$[b]	$^{2}J_{HCF}$
1	185.8[d]	(4.25[e])	49
2	165.4[d]	(3.87[e])	49[e]
3	153.77	—	—
4	127.16	—	—
5	181.4[f]	4.77	49
6	168.2[f]	4.45	48
7	168.4[g]	—	48
8	167.98	4.6	—
9	160.06	4.6	—
11	134.28	—	—
12		4.53	56
13	160.22	4.93	55
14	170.54	5.07	53
15	174.2	4.50	49[e]
16	164.92	4.67	47.5
17	160.16	4.60	46.5
18[h]	177.04	4.63	47

[a] In [ppm] from $CFCl_3$. Measured at 290 ± 5 K, (20 ± 5)% in $CDCl_3/CFCl_3$(1/1), if not indicated otherwise. [b] In [ppm] from TMS. Measured at 300–310 K, 10–20% in CCl_4 or $CDCl_3$. [c] In [Hz], taken from ^{19}F and ^{1}H spectra. [d] At 180 K, $CFCl_3$; literature[a] values: 185.96 and 165.46 Hz. [e] Literature values for 4-t-butylcyclohexylfluorides.[22] [f] In $CDCl_3/CFCl_3$ (3/7), 10–20%.

excluding any dominant common shift mechanism. The ^{19}F shieldings do not depend significantly on the corresponding $^{1}J_{CF}$ couplings and hence bond order changes. Geminal $^{1}HC^{19}F$ couplings as well as ^{1}H, shifts (Table 1) show no stereochemically usable trends.

EXPERIMENTAL

NMR spectroscopy. ^{19}F spectra were obtained at 22.63 MHz in PFT mode using a Bruker HX90/Nicolet 1080 spectrometer at expanded sweep width corresponding to 0.03 ppm digital resolution. The same equipment was used for measuring ^{19}F spectra at 84.67 MHz. ^{1}H spectra at 60 MHz were recorded on Varian instruments A60 and EM 360.

Materials. Some compounds were commercially available or were synthesized according to literature methods: **5**, **6** (Ref. 24, but using tetraethylammonium fluoride); **8**, **9**,[25] **10**,[26] **13**,[27] **14**, **16**,[28] **18**.[16]

1-Fluoro-1-methyl-4-t-butylcyclohexane **3**, **4**. A mixture of 1-methyl-4-t-butylcyclohexene[29] (7.6 g, 0.05 mol) and 50 ml $CFCl_3$ was stirred at −80°C with three successive 0.7 g portions condensed hydrogen fluoride under anhydrous conditions. After 3 h at −80° the mixture was brought to room temp. during 5 h, poured on ice, neutralized with $NaHCO_3$ solution and dried ($MgSO_4$). Since the fluorides decomposed during an attempted destillation, the products were directly investigated by NMR after evaporation of the solvent. The residue (6.2 g, 72%) contained 88% **3** and 12% **4** (by ^{19}C NMR) and less than 3% olefin (by ^{1}H NMR).

3β-Fluorocholest-5-ene **7**.[29] *3β-Iodocholest-5-ene*[30] (3 g, 6 mmol) was stirred for 10 min at room temp. in the dark with silver (I) fluoride (1.52 g, 12 mmol) in 200 ml of a dry benzene/acetonitrile (1:1) mixture. After filtration and exposure to light for several days and another filtration the solvent was removed in vacuo and the residue crystallized from acetone, which yielded 1.5 g (64%) colorless material.

Attempted preparation of 3α-fluorocholest-5-ene and observation of 6β-fluoro-3α,5α-cyclocholestane. Since the reaction of 3β-cholesteryl tosylate with tetraethylammonium fluoride in acetone yielded no product after 3 days, the occurrence of the α-epimer during the preparation of **7** was investigated spectroscopically. 10 min after AgF addition one observed besides signals of the accumulating **7** an additional ^{1}H NMR doublet at 4.1 ppm ($^{2}J_{HF}$, 48 Hz, $W_{1/2}$ 6–8 Hz) and small signals at 0.5–0.7 ppm. Further ^{19}C NMR signals at 12.46, 12.16 and 96.00 ($^{1}J_{CF}$ 166.8 Hz) ppm indicated the intermediate formation of the cyclosteroid, which is slowly converted to the more stable **7**.

Camphene hydrofluoride **11**.[31] 17.25 (0.1 mol) camphene in 100 ml $CFCl_3$ were stirred at −80° for 3 h with 2.7 g (0.14 mol) hydrogen fluoride. After the same work up as for **3** and **4** the product was immediately investigated at −20°C by ^{19}C NMR; the fluoride decomposes rapidly if not worked up and stored over $CaCO_3$ and if petrol ether or higher temperature was used in the preparation.

17α-Fluoroester-4-ene **12**. 2 g (4.8 mmol) tosylate, obtained from 17β-hydroxyestr-4-ene[32] and tosylchloride in pyridine, were stirred for 35 h at 100°C with dry tetrethylammonium fluoride (8 g) in 40 ml N-methylpyrrolidone-2. The product (80% reaction by ^{1}H NMR) was chromatographed on alumina, eluting with 25% benzene in ligroin. 100 mg **12** were obtained free from other olefinic products.

Cyclooctylfluoride **17**. Attempts to synthesize **17** by addition of HF to cyclooctene in ether at −70°C yielded only polymeric material, also in the presence of pyridine.[33] In the reaction of cyclooctyl tosylate with potassium fluoride in ethylene glycol at 120°C as well as of cyclooctyl chloroformate with thallium fluoride, only cyclooctene was obtained, in addition to cyclooctylchloride from the latter reaction. **17** was found to be accessible from the bromofluoro compound:

2-Bromofluorocyclooctane. N-Bromoacetamide (42 g, 0.3 mol) was mixed with 50 ml liquid HF in 125 ml ether at −70°C; cyclooctene (27 g, 0.25 mol) in 75 ml ether was added dropwise. The mixture was stirred for 14 h at −70°C, brought to room temp. for 2 h and again to −70°C before pouring on ice. After neutralization (Na_2CO_3), drying (Na_2SO_4), evaporation of the ether and destillation, 15 g (30%) product of $bp_{0.002}$ 57–58° were obtained.

Fluorocyclooctane **17**. Tri-n-butyltin hydride[34] (5 g, 17.2 mmol) was added dropwise under N_2 to 2-bromo-fluorocyclooctane (3.5 g, 16.8 mmol) at 170°. The product **17** (1.4 g, 64%) was obtained in a trap connected to the condenser, which was cooled by dry ice.

Acknowledgement—Support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Prof. M. Ashworth for help with the translation of the manuscript.

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