Long-Range Proton–Fluorine Coupling in a Rigid System. The Nuclear Magnetic Resonance Spectra of 5-Substituted Difluorotetrachlorobicyclo[2.2.1]heptenes[1]

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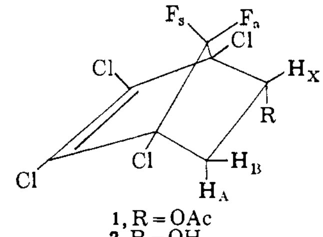
Abstract: The proton and fluorine spectra of six 5-substituted 7,7-difluoro-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-heptenes have been completely analyzed by iterative computer calculation. The signs and magnitudes of 36 long-range (four saturated bonds) coupling constants have been determined in addition to the two- and three-bond coupling constants. The long-range couplings are found to have both positive and negative signs and are found to depend primarily on the relative geometries of the H and F atoms, being largest when the nuclei conform most closely to the coplanar W conformation. The long-range couplings are also slightly dependent on the substituent electronegativity, decreasing algebraically as the substituent electronegativity increases.

The purpose of the present work was to study proton–fluorine spin–spin coupling over four saturated bonds in a rigid system. Although much work has been done on the nmr of fluorocarbons, very little is known about the angular dependence of H–F and F–F couplings over four bonds in saturated systems simply because the requisite conformationally rigid fluorocarbons are not nearly so easily obtained as the corresponding hydrocarbons.

Spin–spin coupling of protons over four saturated bonds has received a great deal of attention recently. From an abundance of experimental data[3] it has been concluded that maximum coupling occurs when the two protons and the three intervening carbon atoms are in the coplanar, zigzag conformation, a conclusion substantiated by theoretical calculations.[4] Our objectives in the present work were to see whether similar behavior is shown by H–F coupling over four saturated bonds and to determine the signs of the coupling constants and the effect of substituents of varying electronegativity on this long-range coupling and thereby to gain some insight into the mechanism of proton–fluorine coupling.

The Difluorotetrachlorobicyclo[2.2.1]heptene System. The system we have chosen to study is a series of 5-substituted 7,7-difluoro-1,2,3,4-tetrachlorobicyclo-[2.2.1]-2-heptenes (**1**–**6**).



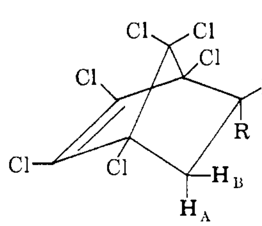
1, R = OAc
2, R = OH
3, R = Cl
4, R = C_6H_5
5, R = COOH
6, R = CN

This system has a number of advantages—the stereochemistry of the atoms is fixed and known, a minimum number of coupling nuclei is present facilitating complete, unambiguous analysis of the spectra, substituents of differing magnetic anisotropy and electronegativity are easily introduced, and a variety of H–F dihedral angles and interatomic distances are present.

The compounds were prepared by the Diels–Alder reaction of 5,5-difluoro-1,2,3,4-tetrachloro-1,3-cyclopentadiene with the appropriate dienophile according to the procedure of McBee, *et al.*,[5] and are assumed, in accordance with the rule of Alder and Stein,[6] to be the *endo* isomers. The hydroxy compound **2** was prepared by hydrolysis of the acetate **1**. McBee prepared the phenyl **4** and carboxyl **5** derivatives in his work. That the CF_2 group is the bridge in this system was demonstrated by the pyrolysis of the dimethyl acetylenedicarboxylate adduct to give an 83% yield of dimethyl tetrachlorophthalate.[5,7] This conclusion is in complete accord with our nmr spectral evidence.

Results and Discussion

We have previously analyzed the nmr spectra of **7**–**12**,[8] which lack the two fluorine atoms on the bridge.



7, R = OAc
8, R = OH
9, R = Cl
10, R = C_6H_5
11, R = COOH
12, R = CN

Our previous work revealed a linear correlation between the three proton coupling constants and the substituent electronegativity as well as a linear correlation

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[1] A preliminary account of this work was given at the International Symposium on Nuclear Magnetic Resonance Spectroscopy, Sept 1965, Tokyo, Japan.

[2] National Science Foundation Undergraduate Research Participant.

[3] For an excellent review of long-range proton coupling see S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).

[4] M. Barfield, *J. Chem. Phys.*, 41, 3825 (1964).

[5] E. T. McBee, D. K. Smith, and H. E. Ungnade, *J. Am. Chem. Soc.*, 77, 387 (1955).

[6] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

[7] This may well have been one of the first (and unrecognized) syntheses of difluorocarbene.

[8] K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

Table I. Chemical Shifts for 7,7-Difluorobicycloheptenes

Compd	Lines matched	Rms error	Chemical shifts, ppm				
			F_s^a	F_a^a	X^b	B^b	A^b
1 OAc	38	0.029	141.7	123.0	5.400	2.804	1.886
2 OH	44	0.092	138.2	122.8	4.507	2.608	1.857
3 Cl	45	0.035	138.9	121.9	4.581	2.952	2.219
4 C_6H_5	53	0.136	140.5	124.0	3.752	2.726	2.426
5 COOH	25	0.024	143.2	123.9	3.539	2.589	2.507
6 CN	46	0.052	143.6	123.4	3.548	2.748	2.280

[a] ϕ^*, parts per million upfield from $CFCl_3$. [b] Parts per million downfield from TMS.

Table II. Coupling Constants for 7,7-Difluorobicycloheptenes

Compd	Electro-negativity[a]	Coupling constants, Hz									
		F_aF_s	F_aX	F_aB	F_aA	F_sX	F_sB	F_sA	BX	AX	AB
1 OAc	3.80	+179	−3.24	−3.46	−1.89	+0.56	−0.76	−5.44	+8.07	+2.69	−13.72
2 OH	3.43	+182	−3.21	−3.48	−1.95	+0.36	−0.45	−5.38	+7.94	+2.88	−12.99
3 Cl	3.25	+178	−3.56	−3.21	−1.56	+0.81	−0.68	−5.27	+8.94	+3.40	−14.11
4 C_6H_5	2.75	+169	−3.04	−2.51	−0.90	+1.04	+0.39	−4.95	+9.28	+4.56	−12.43
5 COOH	2.60	+174	−2.81	−2.72	−1.42	+0.93	+0.89	−5.14	+9.70	+4.54	−13.16
6 CN	2.49	+174	−2.32	−2.74	−1.40	+1.12	−0.32	−4.87	+9.70	+4.37	−13.15

[a] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

between the internal chemical shifts, $\delta_X-\delta_A$ and $\delta_X-\delta_B$, and the substituent electronegativity. With this background we could predict with some certainty the proton coupling constants and chemical shifts in **1–6**, thus greatly simplifying the analysis of this five-spin system.

The easiest member of the series to analyze is the acetate adduct **1**. The electronegative acetate group deshields the X proton so that the proton portion of the spectrum is a true ABX system. The chemical shift between the two fluorine atoms is some 1000 Hz so that the complete analysis of the spectrum is a first-order process, *i.e.*, the two fluorine couplings are simply superimposed on the proton couplings to give 16 well-resolved lines of approximately equal intensity for each nucleus, and the various coupling constants are almost exactly equal to the measured spacings (as confirmed by iterative computation). Although this facilitates analysis it does not allow any conclusions to be drawn concerning the signs of proton–fluorine couplings because, as demonstrated by computation, a change in the sign of J_{HF} for this compound produces changes in the line frequencies and intensities of the ^1H and ^{19}F spectra which are within the experimental errors of measurement.

The analysis of the spectra becomes progressively more difficult as the electronegativity of the substituent becomes smaller because the proton chemical shifts converge to give ABC spectra. However, valuable information can be derived from these ABCXY spectra because a change in the sign of J_{HF} will often produce a marked change in the proton and fluorine spectra. This will be illustrated (*vide infra*) for the carboxyl derivative **5**, a compound in which the chemical shift between the A and B protons is only 0.082 ppm (in contrast with the 0.92 ppm in the acetate **1**).

Even with reasonably good knowledge of what the values for the various H–H couplings should be from our previous work we found it impossible to analyze the 60-MHz spectrum of the carboxyl compound **5**. The 100-MHz spectrum contained 20 of the expected 32 lines in the AB region (see Figure 1) which could be matched with a trial spectrum calculated by part I of the LAOCOON II computer program.[9] The experimentally observed lines were matched with the origin number of the corresponding lines in the approximate spectrum and then a least-squares iteration was carried out with part II of the computer program to give the values for the chemical shifts and coupling constants reported in Tables I and II. Because of the inherently greater accuracy of the proton line frequencies compared to the fluorine line frequencies (A-60 spectra *vs.* HR-60 spectra in most cases) only the proton line positions were used to carry out the iterations. The computed fluorine spectrum was then compared with the experimental spectrum for correctness of frequency and intensity fit. The number of lines fitted (a maximum of 48 is possible in the proton region) and the rms error in the

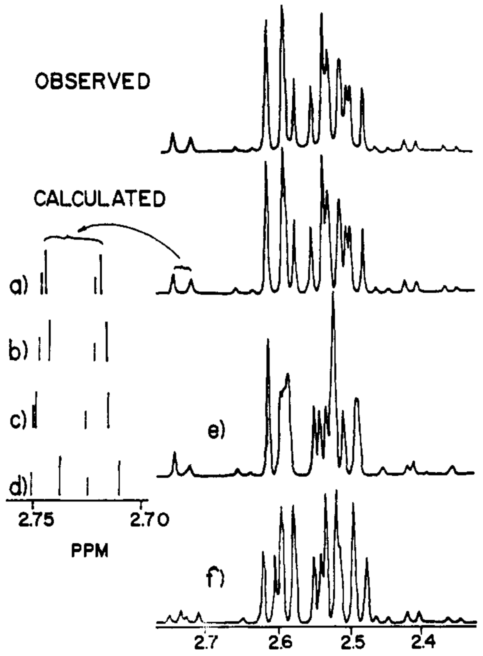

Figure 1. 100-MHz nmr spectrum of the AB region of the carboxyl compound **5**: (a) calculated spectrum employing signs and parameters given in Tables I and II, (b) calculated for J_{F_sB} = +0.5 Hz, (c) calculated for J_{F_sB} = 0.0 Hz, (d) calculated for J_{F_sB} = −0.5 Hz, (e) calculated with J_{F_aA} having a positive sign, all other parameters remain the same, (f) calculated with J_{F_sA} having a positive sign, all other parameters remain the same.

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(9) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964).

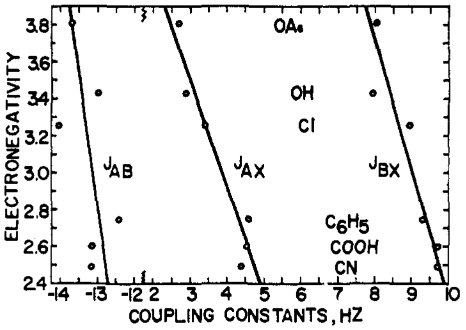

Figure 2. Vicinal and geminal proton coupling constants *vs.* substituent electronegativity.

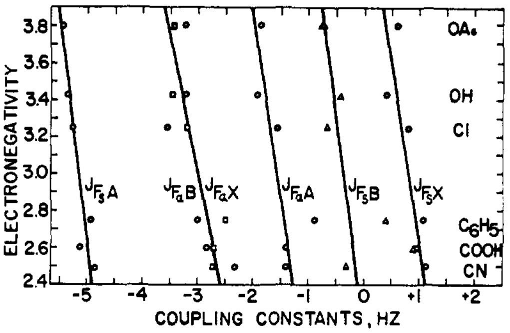

Figure 3. Long-range H–F coupling constants *vs.* substituent electronegativity.

fitting for the assigned lines is also given in Table I. The rms error can be regarded as the upper limit of the error in determining the reported chemical shifts and coupling constants.

Signs of Coupling Constants. From our previous work on compounds **7–12** we concluded that $J_{HH(gem)}$ was negative in sign and $J_{HH(vic)}$ was positive in sign[8] as they are in most other saturated alkanes. Geminal J_{FF} coupling constants are all positive.[10] In the present work then we have assumed that J_{AB} is negative and that J_{AX}, J_{BX}, and $J_{F_aF_s}$ are all positive in sign, leaving only the $^4J_{HF}$ signs to be determined. As stated above, changing the signs of J_{HF} in the calculation of the acetate **1** spectrum gave only minor differences in the calculated line positions and intensities, differences too small to detect experimentally. However, the closely coupled (in the proton region) carboxyl derivative **5** showed rather large changes in line frequencies with changes in some signs of J_{HF}. We made our initial assignment of the $^4J_{HF}$ signs on the basis of the trends in $^4J_{HF}$ with substituent electronegativity, as discussed below. We then calculated spectra with these signs as well as spectra in which one of these signs was reversed and the other five kept constant (although we did not calculate spectra for all 2^6 different possible combinations of sign for $^4J_{HF}$). In those calculations where iteration was performed employing a different set of signs, the rms error was always larger than that reported in Table I.

The signs reported in Table I are in accord with trends in the magnitude of $^4J_{HF}$ as a function of substituent electronegativity. In our previous work on substituent effects on coupling constants in saturated systems[8,11] we have noted that as the substituent electronegativity increases, the vicinal and geminal coupling constants decrease algebraically. In Figures 2 and 3 the vicinal proton–proton couplings and the $^4J_{HF}$ coupling constants are plotted *vs.* the electronegativity of the substituents. Despite some scatter in the points[12] it is seen in Figure 2 that the vicinal H–H coupling constants, J_{AX} and J_{BX}, show a marked dependence on the substituent electronegativity and that this dependence is not so great for the geminal coupling, J_{AB}. In Figure 3 we have plotted the coupling constants for $^4J_{HF}$ *vs.* electronegativity and find exactly the same relationship: that as the substituent electronegativity increases, the coupling constant decreases algebraically. This is most clearly seen for J_{F_sA} which decreases from -4.87 to -5.44 as the substituent electronegativity increases from 2.49 to 3.80 in going from the nitrile **6** to the acetate **1**. J_{F_sX} on the other hand decreases from $+1.12$ to $+0.56$ in going from the nitrile to the acetate which is in accord with the signs determined by computation. J_{F_aX} and J_{F_aB} have very similar values, but are also seen to decrease as electronegativity increases, as do both J_{F_aA} and J_{F_sB}. The latter is most interesting in that some of the coupling constants are slightly positive and some are slightly negative.

One coupling constant, J_{F_sB}, for the carboxyl derivative **5** is off the correlation line and was therefore carefully investigated. It would appear from Figure 3 that it should have a value near zero, yet the iterative calculation gives a value of $+0.89$ Hz for this coupling. If F_sB is given an initial value of -1 or 0 in part II of the LAOCOON II computer program, the final value (best least-squares fit) computed is $+0.89$ Hz. In Figure 1 are presented various calculated spectra for **5**. The first (a) is the best fit calculated from the coupling constants and chemical shifts from Tables I and II. In the second (b) the value of J_{F_sB} has arbitrarily been made $+0.5$, in (c) it has been made 0.0, and in (d) -0.5 Hz. Clearly the best fit occurs when $J_{F_sB} = +0.89$. The effect of changing signs of some of the other $^4J_{HF}$ coupling constants is seen in (e) and (f). Thus from two independent lines of evidence we have arrived at the signs of $^4J_{HF}$ for compounds **1–6**: by the dependence of the coupling constant on substituent electronegativity and by the calculation of theoretical spectra which closely match the experimental spectra in line frequency and intensity. Although we are quite confident about the relative signs here reported, this must be regarded as presumptive evidence; the final answer will come when careful heteronuclear decoupling experiments are performed.

Assignment of F_a and F_s. Having arrived at values for the signs and magnitudes of the six $^4J_{HF}$ couplings the next problem is to decide which fluorine atom is *syn* and which is *anti* to the double bond. We have assigned the *syn* configuration to the upfield fluorine atom and the *anti* configuration to the downfield fluorine atom on the basis of coupling constants and chemical shifts, by analogy with corresponding proton systems.

A large body of evidence has been accumulated in the bicyclo[2.2.1]heptene system to show that a proton

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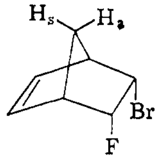
(10) D. F. Evans, S. L. Manatt, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 238 (1963).

(11) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964).

(12) Deviations from a simple correlation might be expected for substituents wih π electrons, second and higher row elements, and fluorine atoms: S. L. Manatt, D. D. Elleman, and S. J. Brois, *ibid.*, **87**, 2220 (1965).

syn to the double bond will couple strongly with a proton in the *endo* configuration on the saturated two-carbon bridge, these two protons being in the coplanar, zigzag conformation.[13] Coupling has not been reported between the 7-*anti* proton and the *endo* protons on C-2 and C-3. To our knowledge none of the signs of long-range proton–proton couplings in the bicyclo[2.2.1] system has been determined.

The largest HF coupling, *ca.* 5 Hz in compounds **1**–**6**, is the coupling of H_A with one of the fluorines. This coupling is 2 Hz larger than the next largest HF coupling. If $^4J_{HF}$ coupling is analogous to $^4J_{HH}$ coupling[14], then we would expect this 5-Hz coupling to occur between the *syn*-fluorine and H_A. In this regard LeBel[15] has observed a coupling of *ca.* 7.5 Hz between the *syn*-proton and the *endo*-fluorine atom in **13**, a dihalonorbornene closely related to the ones he has reported on previously.[13h] It will be noted that these two coupling nuclei have the same geometrical arrangement as F_s and H_A in compounds **1**–**6**.



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In bicyclo[2.2.1]heptenes which bear a substituent on the one-carbon bridge the proton *syn* to the double bond is upfield from the proton *anti* to the double bond.[13i] We find that a similar assignment in compounds **1**–**6**, *i.e.*, the fluorine *syn* to the double bond being upfield from the fluorine *anti* to the double bond, is consistent with the conclusion made on the basis of the magnitude of the $^4J_{HF}$ coupling constant.

The Geometry of H–F Coupling. If the above assignment of the two fluorine atoms is correct, we can draw some conclusions about the effect of geometry on the $^4J_{HF}$ coupling. We have already pointed out that J_{HF} vicinal behaves like J_{HH} vicinal—it follows a Karplus curve dihedral angle dependence and also depends on the bond angle as J_{HH} does.[14] If this similarity extends to $^4J_{HF}$, then we could, as we have done, expect the largest coupling to be between nuclei which have the coplanar, zigzag conformation because this is the conformation in which the largest four-bond proton–proton coupling occurs.[3,4] This coupling, J_{F_sA}, for all six compounds studied falls in the range -5.15 ± 0.28 Hz. In bicycloheptenes $^4J_{HH}$ with this geometry is *ca.* 2–3 Hz.[3,13]

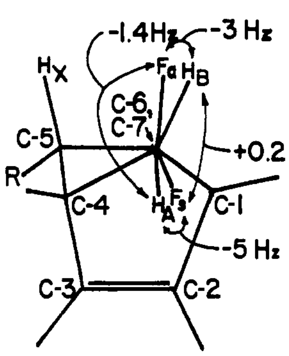

Figure 4. The bicyclo[2.2.1]heptene ring system as seen from above with C-7 directly in front of C-6. Approximate long-range H–F coupling constants are given.

The next largest couplings are J_{F_aB} and J_{F_aX}. All 12 of these coupling constants fall in the range -2.94 ± 0.62 Hz. Both protons B and X are in the *exo* configuration and therefore bear the same geometric relationship to F_a. It is interesting that all 12 couplings fall in such a narrow range when it is noted that the X proton is one bond nearer the substituent than is the B proton.

Similarly the coupling of the *syn*-fluorine atom with H_B and H_X shows the same behavior. All twelve coupling constants fall in the range $+0.18 \pm 0.94$ Hz. Here again we must conclude that the more important factor governing H–F coupling is the relative geometry of H and F and not the fact that one proton (H_X) is two bonds from an electronegative substituent and another proton (H_B) is three bonds from the substituent. Finally the six couplings between the fluorine *anti* to the double bond and the *endo*-A proton, J_{F_aA}, all fall in the range -1.42 ± 0.52 Hz.

In Figure 4 we have drawn the bicyclo[2.2.1]heptene ring from a point of view which emphasizes the relative H–F geometry. The plane described by C-1, C-6, and C-7 is seen edge-on and is represented by a line. If H_a and F_s had a perfect coplanar W conformation, they would lie on the same line. It is seen that H_a and F_s lie closer to this plane than any other pair of nuclei and have, as noted previously, the largest four-bond coupling.

Barfield has calculated the angular dependence of long-range proton coupling across four bonds. This theoretical calculation predicts that the largest coupling should be between protons in the coplanar W conformation and that the smallest should occur between protons which are 90° out of the C–C–C plane. However, in the present work we find that the coupling of F_a and H_B (which are close to 90° out of the C-1, C-6, C-7 plane) is not too different (−3 Hz) from J_{F_sA} (−5 Hz) which is close to the coplanar W conformation. Comparison of the other $^4J_{HF}$ couplings with the theoretical values of $^4J_{HH}$ reveals similar discrepancies.

Since the early observation by Roberts[16] many reports of H–F over five bonds have appeared.[17] In each case "direct" or "through space" coupling

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(13) (a) J. Meinwald and Y. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963); (b) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963); (c) J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965); (d) C. W. Jefford, B. Waegell, and K. Ramey, *ibid.*, **87**, 2191 (1965); (e) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964); (f) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964); (g) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (h) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, 30, 2624 (1965); (i) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966); (j) K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Am. Chem. Soc.*, **89**, 2401 (1967).

(14) We have recently demonstrated that $J_{HF(vic)}$ shows a dihedral angle dependence that is very similar to $J_{HH(vic)}$; $J_{HF(vic)}$ is also dependent on the H–C–C^1 and C–C^1–F bond angles in the same way that J_{HH} is: K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *ibid.*, **88**, 5678 (1966).

(15) N. A. LeBel, private communication.

(16) D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

(17) (a) M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); (b) A. Lewin, *ibid.*, **86**, 2304 (1964); (c) A. D. Cross and P. W. Landis, *ibid.*, **86**, 4005 (1964); (d) J. Burdon, *Tetrahedron*, **21**, 1101 (1965); (e) P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Am. Chem. Soc.*, **88**, 2459 (1966); (f) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967).

of H and F have been considered as explanations of the observed coupling. In the latest work on this problem Myhre[17e] found that the magnitude of H–F coupling was extremely sensitive to the internuclear separation and Brewer, *et al.*,[17f] similarly concluded that their results could be best explained in terms of a "through space" coupling involving angular dependence as well as a proximity factor. Unfortunately none of these workers has determined the signs of any of these long-range couplings.

Inspection of the data for the six compounds reported upon in the present work does not reveal any trend in the size of $^4J_{\mathrm{HF}}$ that can be rationalized in terms of a "through space" coupling. The couplings in compounds **1–6** are through four bonds while those cited above are through five bonds, but a more important factor is undoubtedly the lack of close proximity of hydrogen to fluorine in **1–6**. Significant "through space" coupling seems to occur only when H and F are less than 2.5 Å apart.[17f]

It is hoped that the present work will stimulate more theoretical work on what has turned out to be a perplexing problem, the angular dependence of long-range coupling.

Experimental Section

Proton nuclear magnetic resonance spectra were run on a Varian A-60 spectrometer as 10% w/v solutions in carbon disulfide containing 2% tetramethylsilane as an internal reference. Fluorine nuclear magnetic resonance spectra were run on a Varian DP-60 at 56.4 MHz using fluorotrichloromethane as an internal reference. The spectra were calibrated by the audio side-band technique. In addition spectra of the carboxyl derivative were run at 100 and 94.1 MHz.

Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrometer as 10% solutions in chloroform. Melting points were taken on a Thomas-Hoover capillary melting point apparatus.

7,7-Difluoro-1,2,3,4-tetrachloro-5-*endo*-acetoxybicyclo[2.2.1]-2-heptene (1) To 5.01 g (0.021 mol) of 1,1-difluorotetrachlorocyclopentadiene[5] was added 7.16 g (0.083 mol) of vinyl acetate. After refluxing for 8 hr the excess vinyl acetate was removed by distillation at atmospheric pressure and the product at 39 mm. Redistillation on a spinning-band distillation column gave 4.7 g (70%) of the vinyl acetate adduct, bp 105–109° (10–11 mm). The infrared spectrum showed bands at 5.77, 6.72, 8.1–8.3, and 11.22 μ.

Anal. Calcd for $C_9H_6Cl_4F_2O_2$: C, 33.15; H, 1.84; Cl, 43.52. Found: C, 33.24; H, 1.95; Cl, 43.55.

7,7-Difluoro-1,2,3,4-tetrachloro-5-*endo*-hydroxybicyclo[2.2.1]-2-heptene (2). A mixture of 0.252 g (0.77 mmol) of the acetoxy adduct **1**, 0.4 ml of concentrated hydrochloric acid, and 1 ml of ethanol was refluxed for 5 hr. The initially clear solution turned light brown. The reaction mixture was poured into 5 ml of water and extracted into three 5-ml portions of ether. The combined ether extracts were washed with water and dried over anhydrous calcium chloride. The ether was removed under reduced pressure to leave a light brown oil which showed an infrared absorption band at 2.85 μ (hydroxyl) and the absence of the band at 5.72 μ (carbonyl). This material was used without further purification.

7,7-Difluoro-1,2,3,4,5-*endo*-pentachlorobicyclo[2.2.1]-2-heptene (3). In a Pyrex tube was placed 0.145 g (0.6 mmol) of 5,5-difluorotetrachlorocyclopentadiene and 0.23 g (3.7 mmol) of vinyl chloride was condensed in. The tube was sealed and heated for 7 hr at 100°. Upon opening it lost 0.13 g (2.1 mmol) of vinyl chloride. The light yellow residue was used without further purification. It showed significant bands in the infrared spectrum at 5.92, 6.2, 6.9, 7.55, 7.75, 7.9, 8.4, 8.62, 8.71, 8.9, 9.64, 10.24, 10.62, and 11.3 μ.

7,7-Difluoro-1,2,3,4-tetrachloro-5-*endo*-phenylbicyclo[2.2.1]-2-heptene (4) was prepared by the method of McBee[5] in 80% yield as a light yellow viscous oil having bands in the infrared at 3.32, 6.23, and 6.87 μ and having ultraviolet absorption at 208 mμ (ε 1500). McBee[5] reports a 95% yield of crystalline material, mp 45–46°.

7,7-Difluoro-1,2,3,4-tetrachloro-5-*endo*-carboxy[2.2.1]-2-heptene (5) was prepared in 55% yield by the method of McBee.[5] The colorless plates had mp 116–177° and showed bands in the infrared spectrum at 5.77, 6.22, and 11.14 μ (lit.[5] mp 116–116.5°, yield 72%).

7,7-Difluoro-1,2,3,4-tetrachloro-5-*endo*-cyanobicyclo[2.2.1]-2-heptene (6). To 3.30 g (0.013 mol) of 1,1-difluorotetrachlorocyclopentadiene was added 0.701 g (0.013 mol) of freshly distilled acrylonitrile. The mixture was allowed to stand at room temperature in the dark for 3 months. At the end of that time thin layer chromatography indicated only one component. That reaction was complete was indicated by the absence of peaks at 3.27, 3.32, 10.3, and 10.4 μ which were in the starting material. A sample of the viscous liquid was sublimed at 10 mm for analysis.

Anal. Calcd for $C_8H_3Cl_4F_2N$: C, 32.79; H, 1.02; Cl, 48.43. Found: C, 32.51; H, 0.92; Cl, 48.55.

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