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^{13}C Nuclear Magnetic Resonance Spectroscopy. Determination of Carbon–Fluorine Couplings[1]

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Abstract: One-, two-, three-, and four-bond carbon–fluorine coupling constants have been observed for a series of substituted fluorobenzenes. The one-bond coupling constants in the para derivatives are proportional to the fluorine chemical shifts, but a similar correlation shows considerable scatter for the meta derivatives and is invalid for the ortho derivatives. The carbon–fluorine coupling constants in fluorobenzene are $J_{CF} = -245.3$, $J_{CCF} = +21.0$, $J_{CCCF} = +7.7$, and $J_{CCCCF} = +3.3$ Hz. Consistent explanations of the substituent effects on the long-range coupling constants have not been found. All the carbons in 1-fluoronaphthalene are coupled to the fluorine with magnitudes of 0.6 to 250 Hz. The fluorine in 2-fluoronaphthalene is coupled to only six carbons, presumably those in the same ring as the fluorine. The carbon–fluorine coupling constants in *n*-hexyl fluoride are $J_{CF} = -166.6$, $J_{CCF} = +19.9$, and $J_{CCCF} = 5.25$ Hz. The one-bond carbon–fluorine couplings in cyclic geminal difluorides vary with ring size. The fluorine substituent effect on the chemical shifts of carbons γ to the fluorine is discussed in terms of proposed steric perturbation mechanisms.

Although carbon–proton nmr couplings seem well understood in terms of hybridization and effective nuclear charge, comparable theoretical understanding does not yet seem available for analogous carbon–fluorine couplings. The problem is not wholly a lack of data, because Muller and Carr[3] and Harris[4] have observed ^{13}C satellites in the fluorine spectra of a wide variety of compounds. Furthermore, Tiers[5] has shown that carbon–fluorine coupling and carbon–proton coupling in dichlorofluoromethane have opposite signs, and also that the one-bond and two-bond carbon–fluorine coupling constants in 1,2-difluorodichloroethylene and 1,2-difluorotetrachloroethane have opposite signs.[6] Experimental difficulties often arise with larger molecules, for example, with the ^{13}C satellites of the fluorine spectrum of fluorobenzene which are rendered complex by fluorine–proton coupling.[7] This particular problem can be greatly lessened by the double-resonance technique,[8] but, in any case, the observation of inner satellites arising from small, long-range carbon–fluorine couplings is hampered by the intense resonances from the molecules with only ^{12}C. Even if the inner satellites could be seen, assigning them to couplings with the proper carbons would be difficult. In this research, we have determined a number of carbon–fluorine couplings by direct observation of the ^{13}C nmr (cmr) spectra.

Experimental Section

Most samples were obtained from commercial sources and used without further purification. The geminal difluorides were available from previous studies.[9] Anilinium cations were prepared

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[1] Supported in part by the National Science Foundation. Some of the data in this paper were reported in preliminary paper: F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 4940 (1969).

[2] National Science Foundation Predoctoral Fellow, 1965–1968.

[3] N. Muller and D. T. Carr, *J. Phys. Chem.*, 67, 112 (1963).

[4] R. K. Harris, *J. Mol. Spectrosc.*, 10, 309 (1963).

[5] G. V. D. Tiers, *J. Amer. Chem. Soc.*, 84, 3972 (1962).

[6] G. V. D. Tiers and P. C. Lauterbur, *J. Chem. Phys.*, 36, 1110 (1962); G. V. D. Tiers, *J. Phys. Chem.*, 67, 928 (1963).

[7] S. Mohanty and P. Venkateswarlu, *Mol. Phys.*, 12, 277 (1967).

[8] See M. A. Cooper, H. E. Weber, and S. L. Manatt, *J. Amer. Chem. Soc.*, 93, 2369 (1970).

[9] (a) S. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *ibid.*, 89, 88 (1967); (b) J. B. Lambert and J. D. Roberts, *ibid.*, 87, 3884 (1965).

Table I. Carbon–Fluorine Couplings in Ortho-Substituted Fluorobenzenes (Hz)

Substituent	$J_{C-1,F}$	$J_{C-2,F}$	$J_{C-3,F}$	$J_{C-4,F}$	$J_{C-5,F}$	$J_{C-6,F}$	
H	245.3	21.0	7.7	3.3	7.7	21.0	
F	248.8	14.1	−3.0	*a*	*a*	20.5	
Cl	248.7	17.5	0	4.05	7.2	20.8	
Br	247.0	20.7	0	3.35	7.1	21.95	
I	245.6	25.2	1.46	3.5	7.2	23.4	
NO_2	264.4		4.25	2.8	8.7	20.6	
NH_2	237.5	12.7	3.8	3.6	6.7	18.4	
NH_3^+	248.6	13.8	0	3.9	7.5	18.4	
OH	238.8	13.7	1.94	3.78	6.6	18.0	
O^-	235.8	12.15	3.4	3.3	7.0	19.0	
CH_3	243.9	17.0	4.8	3.7	7.9	22.1	CH_3 3.8
CHO	257.7	8.2	1.86	3.75	9.1	20.45	CHO 6.4
$COCH_3$	254.2	12.8	2.54	3.4	9.0	23.7	CO 3.2 CH_3 <0.4
2-Fluoropyridine	236.7		14.7	4.2	7.75	37.4	

[a] The average of these two coupling constants is 5.2 Hz.

by dissolving the corresponding anilines in methanolic nitric acid. Phenolate anions were prepared by dissolving the corresponding phenols in methanolic potassium hydroxide. Carbon-13 spectra were obtained in the external-lock mode of the Varian DFS-60 spectrometer, with complete proton decoupling.[10] Theoretical spectra were calculated using the computer program LAOCOON II.[11]

Results

The advantage of using proton decoupling in investigating carbon–fluorine couplings in compounds which also contain hydrogen should be clear from Figure 1, where the undecoupled and proton-decoupled spectra of fluorobenzene are shown. The undecoupled spectrum required 700 scans and on close inspection shows the complexity expected for the X part of an ABB′CC′MX spin system. The decoupled spectrum required 30 scans, and the fine structure arises unambiguously from carbon–fluorine couplings.

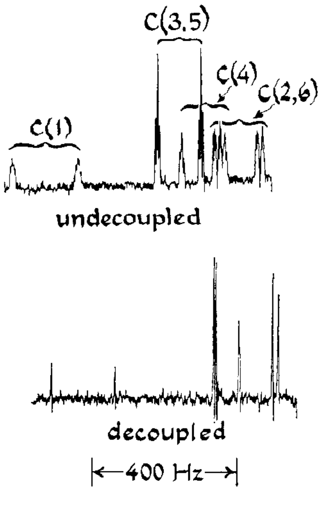

Figure 1. ^{13}C nmr spectrum of neat fluorobenzene at 15.1 MHz. Top, 700 scans, undecoupled. Bottom, 30 scans, proton decoupled.

Substituted Fluorobenzenes. The carbon–fluorine coupling constants obtained for a series of ortho-, meta-, and para-substituted fluorobenzenes are given in Tables I–III. The carbons bonded to the fluorine were easily identified by their considerably downfield shifts[12,13] and their large fluorine couplings[7,13] which are insensitive to the proton-decoupler frequency. The resonance of the carbon bearing the substituent could also be identified by being insensitive to the decoupling frequency, except for those substituents car-

Table II. Carbon–Fluorine Couplings in Meta-Substituted Fluorobenzenes (Hz)

Substituent	$J_{C-1,F}$	$J_{C-2,F}$	$J_{C-3,F}$	$J_{C-4,F}$	$J_{C-5,F}$	$J_{C-6,F}$	
H	245.3	21.0	7.7	3.3	7.7	21.0	
F	245.4	25.3	12.1	3.6	9.8	21.2	
Cl	249.5	24.6	10.0	3.4	8.9	21.3	
Br	250.4	24.5	9.3	3.4	8.4	21.1	
I	249.0	23.2	7.8	3.3	8.1	20.8	
NO_2	250.9	26.5	8.3	3.3	8.2	21.5	
NH_2	241.4	24.6	11.0	2.3	10.2	21.3	
NH_3^+	247.5	25.6	9.8	3.4	8.9	21.2	
OH	244.5	24.8	11.3	3.0	10.2	21.2	
O^-	241.4	21.5	11.4	2.4	11.0	21.4	
CH_3	243.6	21.1	7.2	2.2	8.5	21.2	CH_3 1.75
CHO	248.2	21.7	6.3	2.9	7.8	21.8	CHO 2.4
$COCH_3$	246.3	22.2	5.9	2.9	7.75	21.6	CO 1.9 CH_3 0.68

Table III. Carbon–Fluorine Coupling Constants in Para-Substituted Fluorobenzenes (Hz)

Substituent	$J_{C-1,F}$	$J_{C-2,F}$	$J_{C-3,F}$	$J_{C-4,F}$	
H	(−)245.3	21.0	7.7	3.3	
F	242.0	24.3	8.5	3.8	
Cl	245.5	23.1	8.2	3.1	
Br	246.7	23.7	8.0	3.3	
I	247.4	22.2	7.6	3.4	
NO_2	256.6	24.0	10.2	*a*	
NH_2	233.2	22.4	7.5	1.86	
NH_3^+	246.8	23.7	9.1	3.2	
OH	237.4	23.0	7.9	2.14	
O^-	236.1	22.7	8.0	1.6	
CH_3	243.5	21.1	7.75	2.9	CH_3 0
CHO	255.0	22.4	9.7	2.6	CHO 0

[a] Resonance broadened because of partial quadrupole-induced relaxation of the coupling to the directly attached nitrogen.

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(10) (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 89, 2967 (1967); (b) F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, 90, 1566 (1968). Variable single frequency was used rather than "noise" decoupling: F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, 60, 1152 (1968).

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

(12) H. Spiesecke and W. G. Schneider, *ibid.*, 35, 722, 731 (1961).

(13) G. E. Maciel and J. J. Natterstad, *ibid.*, 42, 2427 (1965).

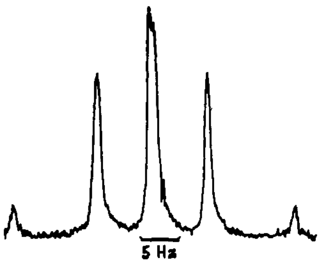

Figure 2. Proton-decoupled ^{13}C nmr spectrum of C-3 of 1,2-difluorobenzene at 1.51 MHz.

rying protons which are coupled reasonably strongly to the ring carbons. With benzaldehydes, for example, optimum decoupling for the directly attached ring carbon was obtained at the aldehyde proton resonance frequency. Additivity of substituent effects on aromatic ^{13}C chemical shifts[14] was primarily used to assign the remaining ^{13}C resonances. The carbons ortho to the fluorines generally appeared upfield and showed about 20-Hz couplings to the fluorines. Where assignments were ambiguous on the basis of the chemical shifts, the proton chemical shifts (as determined from the decoupling frequency of the directly attached hydrogens) were considered in making the assignments.

As part of the study of substituent effects on carbon–fluorine coupling in fluorobenzenes, the three difluorobenzenes were examined. Because the carbon–fluorine coupling constants were not easily determined in these three compounds, the method used will be described in some detail.

There are altogether nine structurally different carbons in the three difluorobenzenes. One resonance in each compound is insensitive to the proton-decoupling frequency, is shifted to low field, and is a doublet of doublets, with the larger coupling being *ca.* 250 Hz. This resonance is assigned to the carbon bearing the fluorine. There is only one other type of carbon in *p*-difluorobenzene. The two 1:2:1 triplets in the meta isomer are assigned to C-2 and C-5, and of these, C-2 is shifted upfield by the *o*-fluorines and has the larger of the two coupling constants. The remaining resonance is assigned to C-4. Of the two resonances in the ortho isomer, the downfield signal is assigned to C-4, which is not adjacent to a fluorine. This resonance is a 1:2:1 triplet which means that either the three- and four-bond coupling constants are equal or that the spectrum is deceptively simple.

The proton-decoupled ^{13}C spectra of C-3 of 1,2-difluorobenzene, C-4 of 1,3-difluorobenzene, and C-2 of 1,4-difluorobenzene are shown in Figures 2–4. Each spectrum shows the six lines characteristic of the X part of an ABX spin system.[15] The general ABX spectrum is a function of four variables, the chemical shift between the A and B nuclei and the three coupling constants J_{AB}, J_{AX}, and J_{BX}. If a sufficient number of lines are seen, all the parameters can in principle be extracted directly from the resonance frequencies; however, the resonance frequencies in the X part of the spectrum contain only three pieces of information, $(D_+ + D_-)$, $(D_+ - D_-)$, and $(J_{AX} + J_{BX})$.[15] Without additional information, the four spectral parameters cannot be obtained from this information; however, given one of the four basic parameters from another source, the resonance frequencies in the X part of the spectrum are sufficient to determine the other three parameters. The most helpful and easily available parameter for this purpose is J_{AB}, and Mohanty[16] and McDonald[17] have reported values for this coupling, the fluorine–fluorine coupling, from a complete analysis of the proton and fluorine spectra of 1,3-difluorobenzene. Unfortunately, the reported values differ significantly, although each investigator indicated that his parameters provide a close match between the experimental and calculated proton and fluorine spectra.

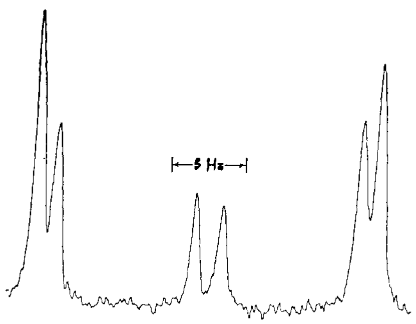

Figure 3. Proton-decoupled ^{13}C nmr spectrum of C-4 of neat 1,3-difluorobenzene at 15.1 MHz.

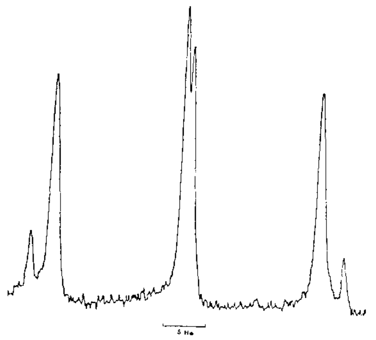

Figure 4. Proton-decoupled ^{13}C spectrum of C-2 of neat 1,4-difluorobenzene at 15.1 MHz.

In general, only one set of nmr parameters will match both the frequencies and line intensities of the X part of an ABX spectrum. Because the intensities of ^{13}C resonances are notoriously sensitive to saturation, magnetization transfer, and Overhauser effects associated with proton decoupling,[18] the intensity information available from ^{13}C spectra is not as reliable as would be desired, but in the absence of accurate values

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(14) P. C. Lauterbur, *J. Amer. Chem. Soc.*, 83, 1846 (1961); *J. Chem. Phys.*, 38, 1406, 1415 (1963).

(15) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in Nuclear Magnetic Resonance," W. A. Benjamin, New York, N. Y., 1962, pp 71–85. That these resonances should be of the ABX type is contrary to expectations based on simple theory, wherein the fluorines would be expected to have *identical* chemical shifts and be, at most, representative of AA'X systems. However, it will be noted that the ^{13}C atoms at C-3 of 1,2-difluorobenzene, C-4 of 1,3-difluorobenzene, and C-2 of 1,4-difluorobenzene are not equivalently located with respect to the fluorines. This means that when we observe the ^{13}C resonances of the carbons in question, there will be a differential ^{13}C isotope effect on the chemical shift of the fluorines in these molecules; *cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Elmsford, N. Y., 1966, pp 875 and 962, for examples and references. The magnitudes of the chemical shifts will be seen to be about right for such differential isotope effects.

(16) S. Mohanty, *Mol. Phys.*, 13, 86 (1967).

(17) D. B. McDonald, *Chem. Commun.*, 686 (1967).

(18) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 86, 2977 (1964).

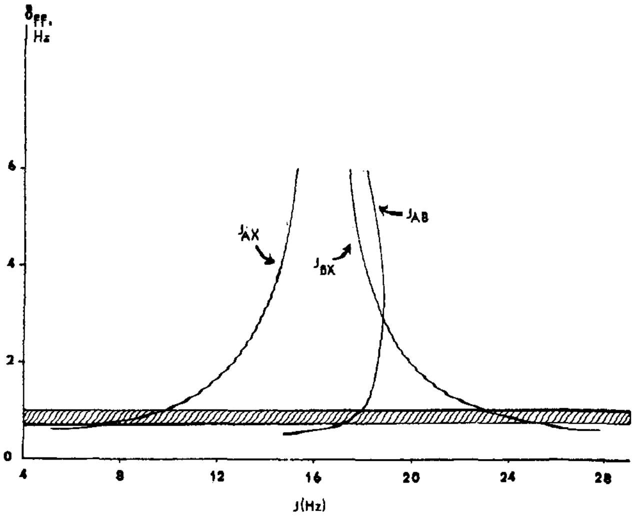

Figure 5. Variation of the coupling constants in the ABX spectrum presented by C-2 of 1,4-difluorobenzene with δ_{AB}. The region of best agreement with the experimental spectrum is indicated by the shaded area.

for one of the parameters, a method of analysis based on intensities has to suffice. The procedure used was first to estimate a value for one of the parameters (usually the chemical-shift difference between the two fluorines) and solve the ABX equations for the other three parameters and the intensities in the X part of the spectrum. The degree of sensitivity of this calculation is demonstrated in Figure 5, which shows the variation of the three dependent variables with the assumed chemical-shift difference for 1,4-difluorobenzene. The region (shaded) which provides the best agreement with the observed intensities is indicated in Figure 5. The ^{13}C spectrum is about five times more sensitive to changes in the fluorine–fluorine chemical shift than it is to changes in any one of the coupling constants. Thus, if the chemical shift is known to within ±0.04 Hz, the coupling constants are known to ±0.2 Hz. The values for the three fluorine–fluorine coupling constants obtained in this work (Table IV) are in reasonable agreement with the corresponding coupling constants found by Evans[19] in some substituted derivatives. The fluorine–fluorine coupling constant determined for 1,3-difluorobenzene agrees with the values reported elsewhere.[8,17] Given the value for the fluorine–fluorine coupling constant in 1,2-difluorobenzene from the analysis of the spectrum of C-3, the ^{13}C spectrum of C-4 can be calculated, using various sets of carbon–fluorine coupling constants in order to determine if, in fact, the spectrum of this carbon is deceptively simple. Indeed, the 1:2:1 triplet was found to persist over a wide range of three- and four-bond carbon–fluorine coupling constants, including a probable value of about 3 Hz for the four-bond coupling. The two carbon–fluorine coupling constants are probably not equal in this case.

Table IV. Shift and Coupling Parameters from the ^{13}C Spectra of the Difluorobenzenes (Hz)

	J_{CF}	J_{CCF}	J_{CCCF}	J_{CCCCF}	F–F chemical-shift difference[b]	J_{FF}
			1,2-F_2			
C-1	248.8	14.1				
C-3		+20.5	−3.0		0.63	19.0
C-4			*a*	*a*		
			1,3-F_2			
C-1	245.4		12.1			
C-2		25.3				
C-4		+21.2		+3.6	1.25	6.6
C-5			9.8			
			1,4-F_2			
C-1	242.0			3.8		
C-2		+24.3	+8.5		0.85	17.5

[a] The average of these two coupling constants is 5.2 Hz. [b] 56.4 MHz.

In each of the three difluorobenzenes, the carbon giving the clearly discernible ABX spectrum is ortho to one of the fluorines. In 1,3-difluorobenzene, the second fluorine is para to the carbon, while in the 1,2- and 1,4-difluorobenzenes the second fluorine is meta to the carbon. In both of the latter cases the chemical shift between the two fluorines is about 0.5 Hz smaller than in the former case, which is indicative of the difference between the three-bond and four-bond ^{13}C isotope effect on the fluorine chemical shift.[8] The carbon–fluorine coupling constants obtained for the three difluorobenzenes are summarized in Table IV.

Because of the large vicinal proton–fluorine coupling constants in the various substituted fluorobenzenes, both halves of the carbon–fluorine doublet arising from an *o*-carbon could not be sharpened at the same proton-decoupling frequency. In all cases, irradiation at the higher proton frequency sharpened the high-frequency half of the ^{13}C spectrum, and *vice versa*. The ^{13}C–C–F carbon–fluorine coupling constant therefore has the same sign as the H–C–C–F coupling constant in these compounds. The analysis of the ^{13}C spectra of 1,3- and 1,4-difluorobenzene indicates in addition that the two-, three-, and four-bond carbon–fluorine coupling constants all have the same sign. The exception is 1,2-difluorobenzene, C-3 of which shows one small negative coupling which is presumably the ^{13}C–C–C–F coupling. Partial decoupling experiments indicate that, again, the signs of the C–C–F couplings are the same as for the H–C–C–F couplings. Snyder[20] concluded from a complete analysis of a liquid-crystal spectrum of fluorobenzene that the signs of the proton–proton and proton–fluorine coupling constants in fluorobenzene are all positive. The one-bond C–F couplings are probably negative.[5]

Other Aromatic Fluorides. The proton-decoupled ^{13}C spectrum of benzotrifluoride shows four quartets and one singlet, the latter best assigned to the *p*-carbon. The one-bond and two-bond coupling constants of 279.5 and 32.5 Hz are unexceptional. The couplings of 3.9 and 1.56 Hz to the *o*- and *m*-carbons cannot be assigned at present.

An attempt was made to investigate the degree of generality and/or additivity of the fluorine substituent effects on carbon–fluorine couplings by studying some polyfluorobenzenes. Proton-decoupled ^{13}C spectra of the three tetrafluorobenzenes and pentafluorobenzene were obtained. However, the ^{13}C resonances of all the carbons of 1,2,4,5-tetrafluorobenzene and 1,2,3,4-tetrafluorobenzene were second order to such a degree

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(19) D. F. Evans, *Mol. Phys.*, 6, 179 (1963).
(20) L. C. Snyder, *J. Chem. Phys.*, 43, 4041 (1965).

that analyses were not pursued. The fluorine-substituted carbons of 1,2,3,5-tetrafluorobenzene gave first-order spectra, while the ^{13}C spectrum of C-4 again showed second-order features. The only carbon resonance showing three different long-range carbon–fluorine coupling constants was assigned to C-1. The C-2 and C-5 are both on the symmetry axis and their resonances have similar coupling patterns, but they can be easily distinguished because the resonance of C-2 is shifted upfield by the two adjacent fluorines. The doublet splitting is assigned to the *p*-fluorine and the triplet to the two *o*-fluorines. Assignment of the carbon–fluorine couplings to C-1 could not be made from symmetry considerations.

The coupling constants of the two carbons on the symmetry axis of pentafluorobenzene can be assigned by first-order considerations. The unique carbon–fluorine coupling to C-6 is assigned to the *p*-fluorine and the triplet to the *o*-fluorines. From the observed line width, only an upper limit of 2 Hz could be placed on the coupling to the *m*-fluorines. The larger of the two triplets arising from coupling to C-3 is assigned to the *o*-fluorines and the smaller coupling to the *m*-fluorines. The four-bond carbon–proton coupling is 1.7 Hz. The carbon–fluorine coupling constants in the polyfluorobenzenes are summarized in Table V. In general, the fluorine substituent effects as derived from the difluorobenzenes do not seem to correlate with the carbon–fluorine coupling constants in the polysubstituted fluorobenzenes.

Table V. Long-Range Carbon–Fluorine Coupling Constants (Hz) for Polyfluorobenzenes from First-Order Spectral Analysis

Carbon	Obsd couplings[a]
	1,2,3,5-Tetrafluorobenzene
1	5.4 (d), 11.1 (d), 14.9 (d)
2	15.2 (t), 5.8 (d)
5	13.0 (t), 3.8 (d)
	Pentafluorobenzene (6-H)
2	4.0 (d), 7.8 (d), 11.7 (d), 15.5 (d)
3	5.2 (t), 13.2 (t)
6	3.7 (d), 23.4 (t)

[a] d = doublet splitting, t = triplet splitting.

The ^{13}C chemical shifts and carbon–fluorine coupling constants which could be obtained from a first-order analysis of the spectrum of pentafluoroiodobenzene are given in Table VI. The carbon para to the iodine is assigned by its intensity and the fact that the basic carbon–fluorine doublet is further split into a triplet of triplets. Correspondingly, the carbon bonded to the iodine has no large one-bond carbon–fluorine coupling and appears as a doublet (F-4) of triplets of triplets. The remaining carbons are assigned on the basis of their relative bandwidths and chemical shifts. The carbon ortho to the iodine would be expected to be downfield relative to the *m*-carbon because there is one less *o*-fluorine, and for the same reason, the sum of the carbon–fluorine coupling constants as reflected in the bandwidths would be expected to be smaller. The relative signs of the coupling constants cannot be determined from the first-order analysis, nor could the couplings to the *o*- and *m*-carbons be assigned to the proper fluorines. Other pentafluoro derivatives which were investigated included the aniline, phenol, chloride, and bromide. Unfortunately, the ^{13}C multiplets of most of the carbons were found to overlap to such an extent that the carbon–fluorine coupling constants could not be determined.

Table VI. ^{13}C Shift and Coupling Parameters of Pentafluoroidobenzene[a]

Carbon	Chemical shift[b]	J_{CF}	J_{CCF}	J_{CCCF}	J_{CCCCF}
1	127.5		28.4	1.3	4.8
2	45.0	254	(12.2, 6.1, 4.5, 3.4)[c]		
3	55.5	257	(Second-order spectrum)		
4	50.9	255	13.5	4.6	

[a] All couplings are in hertz. [b] In parts per million upfield from carbon disulfide; the carbons of benzene on this scale come at 64.1 ppm. [c] The coupling constants have not been assigned to particular proper fluorines.

Both the ^{13}C satellites of the fluorine spectrum and the ^{13}C spectrum of hexafluorobenzene were taken but, at present, there is not enough information available about substituent effects on the carbon–fluorine and fluorine–fluorine coupling constants to complete the analysis of the spectrum. Although the detailed analysis remains to be done, some qualitative conclusions may be drawn. The one-bond carbon–fluorine coupling constant is close to 250 Hz, rather than 360 Hz as stated by Van Der Kelen.[21] None of the four parts of the pseudo-AX spectrum is symmetrical about its center of gravity, nor are the two halves of the A part or the X parts mirror images of each other. Because of ^{13}C isotope effects on the fluorine chemical shifts, the seven-spin system is best described as ABB'CC'DX. Even assuming that the coupling constants are not affected by the isotopic substitution, there are three relative chemical shifts, three fluorine–fluorine coupling constants, and four carbon–fluorine coupling constants to be determined. The liquid-crystal results for the fluorine–fluorine coupling constants can only be taken as order of magnitude estimates and do not appear to provide a good enough starting point for an iterative analysis.[22]

Fluoronaphthalenes. The ^{13}C chemical shifts, the fluorine substituent effects on the chemical shifts, and the carbon–fluorine coupling constants of 1- and 2-fluoronaphthalene are given in Table VII. The proton on C-8 of 1-fluoronaphthalene is shifted downfield by the peri interaction with the fluorine. The carbon resonance which sharpens on irradiation of the low-field proton resonance is assigned to C-8. The carbon directly bonded to the fluorine is found at low field, is insensitive to the proton-decoupling frequency, and is a doublet of 250 Hz. The carbons ortho to the fluorine show large, positive substituent effects on the carbon chemical shift and have relatively large carbon–fluorine coupling constants. The doublet which is sensitive to the decoupling frequency is assigned to C-2, and the one which is not to C-9. The resonance at lower field which is also insensitive to the decoupler frequency is assigned to C-10. Figure 6 shows a region of the ^{13}C spectrum of 1-fluoronaphthalene under different decoupling conditions. Three separate settings of the decoupler are

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(21) G. P. Van Der Kelen, *Bull. Soc. Chim. Belg.*, **72**, 644 (1963).

(22) L. C. Snyder and E. W. Anderson, *J. Chem. Phys.*, **42**, 3336 (1965).

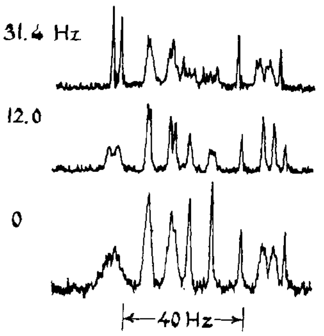

Figure 6. Partial ^{13}C nmr spectrum of 1-fluoronaphthalene with different offset settings of the proton decoupler.

required to sharpen all six resonances in this region. The one doublet which is insensitive to the decoupler frequency has been assigned to C-9. The *m*- and *p*-carbons are assigned on the basis of the expected fluorine substituent effects on the chemical shifts, leaving only C-5, C-6, and C-7 unassigned. There is little to be said for any one particular assignment because all of the carbon–fluorine coupling constants are small and the chemical-shift differences are within 2 ppm of each other. The assignment presented in Table VII is based on a possible (but not proven) correlation of the long-range carbon–fluorine coupling with the distance between the two nuclei involved. The magnitudes of the coupling constants assigned to the carbons in the same ring as the fluorine are very similar to the corresponding coupling constants in fluorobenzene. The signs of the cross-ring coupling constants cannot be assigned at this time.

Table VII. Carbon-13 Shift and Coupling Parameters for Monofluoronaphthalenes

Compound	Carbon	Chemical shift[a]	Substituent effect[b]	J_{CF}, Hz
1-Fluoro	1	−33.1	−33.5	251.1
	2	+16.9	+14.3	19.9
	3	+0.4	−2.2	8.2
	4	+2.1	+1.7	4.0
	5	0.0	−0.4	1.7
	6	−0.9	−3.5	0.8
	7	−1.7	−4.3	3.2
	8	+5.5	+5.1	5.1
	9	+1.9	+7.1	16.4
	10	−9.2	−4.0	4.8
2-Fluoro	1	+11.1	+10.7	25.2
	2	−33.2	−35.8	246[c]
	3	+16.3	+13.7	20.4
	4	−3.1	−3.5	8.8
	5	−0.7	Unassigned	0
	6	−0.2		0
	7	+0.1		0
	8	+0.4		0
	9	−7.0	−1.8	9.2
	10	+2.1	+7.3	2.5

[a] In parts per million upfield from benzene. [b] In parts per million upfield from the corresponding position in naphthalene: T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966). [c] Not precisely determined.

The ^{13}C spectrum of 2-fluoronaphthalene, with each signal optimally decoupled, consisted of six doublets and four singlets. The doublets are assigned to the carbons in the same ring as the fluorine. The directly bonded carbon is shifted downfield, is insensitive to the decoupling frequency, and is a doublet of *ca.* 250 Hz. The two *o*-carbons are shifted upfield and have carbon–fluorine coupling constants of about 20 Hz. The downfield resonance was assigned to C-1, and the upfield resonance to C-3 by analogy with naphthalene.[23] The two bridge carbons are insensitive to the proton-decoupler frequency and are distinguished by their carbon–fluorine coupling constants and the upfield shift of C-10, which is para to the fluorine. The remaining carbon which is coupled to the fluorine is assigned to C-4. At present, there is no way of distinguishing between possible assignments of the four carbon in the other ring. If, as was suggested earlier, distance between the carbon and the fluorine is the relevant factor in the inter-ring couplings, no inter-ring coupling would be expected in 2-fluoronaphthalene because the carbons in the far ring are more distant from the fluorine than any of the carbons in 1-fluoronaphthalene.

Aliphatic Compounds. The ^{13}C spectrum of *n*-hexyl fluoride obtained with complete proton decoupling consisted of three doublets and three singlets. The three singlets were assigned to C-4, C-5, and C-6 because they show no chemical shift relative to the corresponding carbons in *n*-hexane.[24] The resonance of C-1 was easily identified by its downfield chemical shift, the downfield shift of the directly bonded protons, and the large carbon–fluorine coupling constant. The resonance of C-2 was identified by the slight downfield shift of the directly bonded protons, the downfield ^{13}C chemical shift, and the fact that J_{CF} was large enough so that the relative sign of the coupling constant could be determined by partial decoupling techniques. Three-bond proton–fluorine couplings are generally larger than the corresponding four-bond couplings in unstrained aliphatic systems. The remaining resonance, which is considerably upfield of C-3 in *n*-hexane, was assigned to C-3. The ^{13}C chemical shifts, the substituent effects of the chemical shifts, and the carbon–fluorine coupling constants of *n*-hexyl and some other fluorides are summarized in Table VIII.

Table VIII. ^{13}C Chemical Shifts and Carbon–Fluorine Coupling Constants in Some Continuous-Chain Primary Fluorides

Fluoride	Carbon	Chemical shift[a]	Substituent effect[b]	J_{CF}, Hz
Methyl		53.3[c]	−77.5	158[d]
Ethyl	1	49.4[c]	−73.4	
	2	114.1[c]	−7.7	
n-Hexyl	1	44.9	−69.9	166.6
	2	97.5	−8.3	+19.9
	3	103.0	+6.3	5.25
	4	96.4	−0.3	
	5	105.5	−0.3	
	6	114.6	−0.2	

[a] In parts per million upfield from benzene. [b] In parts per million upfield from the corresponding position in the continuous-chain alkane. [c] Reference 12. [d] Reference 4.

Only three of the carbons of 4-methyl-4-ethyl-1,1-difluorocyclohexane (**1**) are significantly coupled to the

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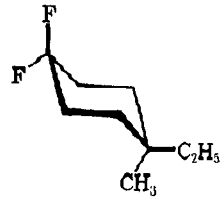
(23) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966).

(24) (a) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964); (b) J. D. Roberts, F. J. Weigert, J. Kroschwitz, and H. J. Reich, *ibid.*, **92**, 1338 (1970).



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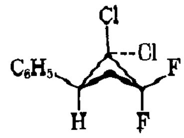

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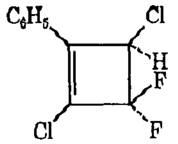

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fluorine. Rapid ring inversion between the nearly identically populated conformers[9a] renders the coupling between the carbons and the two fluorines equal to within experimental error.[25] The resonances of the α, β, and γ carbons can be identified by their distinctive chemical shifts and relative intensities. The two-bond and three-bond C···F coupling constants are quite similar to those in *n*-hexyl fluoride.

The four cyclobutane carbons in 3-phenyl-1,1-difluoro-2,2-dichlorocyclobutane (**2**) are easily identified. The one-bond and two-bond coupling constants are unexceptional. There is an interesting 9-Hz difference between the two C–C–C–F carbon–fluorine coupling constants, but so far it has not been determined which of the fluorines is involved in the larger coupling. Conformational effects probably are the relevant factor because a 1-kcal/mol preference has been estimated for the phenyl group in the pseudoequatorial position.[9b] Only three of the ring carbons in 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene-2 (**3**) are easily distinguished. The carbon bonded to the fluorine shows the large, characteristic, one-bond carbon–fluorine coupling constants. The two-bond carbon–fluorine coupling constants identify the two carbons ortho to the fluorines, and these two are further distinguished by the sensitivity of C-4 to the proton decoupling frequency and the chemical-shift difference expected between alkenic and aliphatic carbons. The resonances of the *o*-and *m*-carbons of the phenyl ring are distinguished from the one of the *p*-carbon by their intensity, and that of the *p*-carbon from C-1 of the phenyl by its sensitivity to the decoupling frequency. Both C-1 of the phenyl and C-3 of the cyclobutane ring are coupled to the fluorines, are insensitive to the decoupling frequency, and have similar chemical shifts. The assignments in Table IX were made assuming that the four-bond carbon–fluorine couplings would be of similar magnitude in the cyclobutene and cyclobutane derivatives when account is taken of the difference in planarity of the rings.

The carbon–fluorine coupling in cyclic geminal difluorides appears to be sensitive to the hybridization of the carbon orbital. The coupling becomes more *negative* as the s character in the carbon orbital increases. The coupling is 240 Hz in the cyclohexane, 280 Hz in the cyclobutanes, and 330 Hz in hexafluorocyclopropane.[26]

Table IX. Carbon–Fluorine Coupling Constants in Some *gem*-Fluorides

Compound	Carbon	Carbon–fluorine coupling constant, Hz
1	1	240.7
	2	+23.9
	3	5.0
	4	~0
2	1	284, 270
	2	26.1, 25.1
	3	15.1, 4.0
	4	23.3, 21.5
	1′	2.05, 2.05
	2′, 3′, 4′	0
3	1	281.2, 279.8
	2	28.6, 27.2
	3	17.0, 12.1
	4	26.0, 23.9
	1′	3.3, 2.3
	2′, 3′, 4′	0
Diethyl difluoromalonate	CF_2	260
	CO	30.8
	CH_2, CH_3	0

Discussion

The most desirable way to interpret substituent effects on carbon–fluorine coupling would be to calculate wave functions for each compound and compare the predicted and observed coupling constants. Extended-Hückel wave functions were calculated for fluorobenzene and the Fermi contact contribution to the coupling constant was evaluated, using the Pople–Santry formalism.[27] Table X compares the results of this calculation with the experimental values of fluorine-carbon and fluorine–proton coupling constants. The agreement for the one-bond coupling is impressive, but the Pople–Santry recipe is specifically designed to reproduce this carbon–fluorine coupling. The long-range carbon–fluorine coupling constants are less well predicted. The discrepancies may arise from significant contributions to the carbon–fluorine coupling from other mechanisms or may be the result of the inadequacy of the extended-Hückel wave functions. At present, it seems more practical to attempt to find correlations between the carbon–fluorine coupling constants and other kinds of couplings or molecular properties.

Table X. Comparison of the Fluorine–Fluorine and Carbon–Fluorine Coupling Constants in Fluorobenzene with Those Calculated Using Extended-Hückel Wave Functions

Coupling	Calcd, Hz	Obsd, Hz
CF	−207	−245.3
CCF	+4.5	+21.0
CCCF	+9.6	+7.7
CCCCF	−0.8	+3.3
HCCF	+17.5	+8.5[a]
HCCCF	+1.0	+1.1[a]
HCCCCF	+4.1	+0.4[a]

[a] J. E. Loemker, J. M. Read, Jr., and J. H. Goldstein, *Mol. Phys.*, **13**, 433 (1967).

A reasonably successful correlation of carbon–proton couplings in benzene has been made with proton–proton coupling in ethylene, using the Karabatsos relationship between carbon–proton and proton–proton coupling for sp^2 hybridized carbon, $J_{CH} = 0.4J_{HH}$.[10a]

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(25) It is clear from other work that the C–C–C–F couplings in cyclic compounds have a high degree of stereochemical specifity: J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970); D. A. Doddrell, C. Charrier, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **67**, 1649 (1970).

(26) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

(27) See Weigert and Roberts[10a] for the carbon and hydrogen parameters used. In addition, the fluorine exponent was 2.61 and the Coulomb integrals were −39.0 eV for the 2s orbital and −20.9 eV for the 2p orbital.

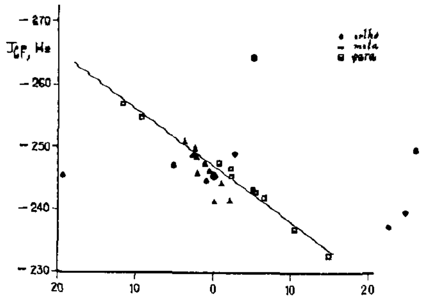
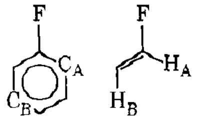


Figure 7. Variation of $^1J_{CF}$ of disubstituted fluorobenzenes with the chemical shift of the fluorines for ortho, meta, and para derivatives. The double-filled circle is for C_6H_5F.

This relationship, if applied to carbon–fluorine couplings in fluorobenzene and proton–fluorine couplings in vinyl fluoride, predicts a geminal carbon–fluorine coupling of +33.9 Hz and a vicinal coupling of +21.0 Hz. Although the signs and the relative magnitudes are predicted correctly, the values of the coupling constants are only in qualitative agreement with the observed values (**4**).[28] Some of the discrepancy is likely to arise from the greater importance of spin–orbit or dipole coupling mechanisms for carbon–fluorine coupling than for proton–fluorine coupling.



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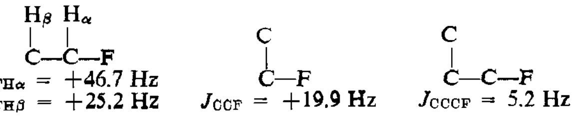
The one-bond carbon–fluorine couplings in para-substituted fluorobenzenes (Table III) correlate very well with the fluorine chemical shifts, as shown in Figure 7. This indicates the importance of resonance effects on these couplings because fluorine chemical shifts in the same compounds correlate well in turn with σ_p, a widely accepted indicator of π resonance effects.[29] The corresponding correlation of one-bond carbon–fluorine coupling with fluorine chemical shift shows a great deal of scatter for the meta derivatives and breaks down completely for the ortho derivatives.

If resonance effects dominate the two-bond or more carbon–fluorine coupling constants, the substituent effects would be expected to be of both signs, especially for nitro and amino groups. However, the substituent effects for the two-bond and three-bond coupling constants in the para derivatives are all positive. Because all of the substituents studied are expected to be electronegative relative to hydrogen, this suggests that for these couplings the electronegativity may be a more relevant parameter than resonance effects. All the substituent influences on the four-bond coupling are negative except for fluorine. Electron-supplying (by resonance) substituents such as amino and hydroxyl exert the largest effect but again, because electron-attracting (by resonance) substituents such as aldehyde groups influence the couplings in the same direction, there appears to be no simple correlation with resonance effects.

None of the long-range coupling constants in the meta derivatives correlates with σ_p, and the two-bond carbon–fluorine coupling constants involving C-6 are quite independent of substituent effects (Table II). All the coupling constants involving C-2 are larger than that of fluorobenzene itself. The electronegativity of the substituent correlates fairly well for the trends seen for C-3, the substituent carbon, although carbonyl substituents seem to have more negative substituent effects than would be otherwise expected. All substituent effects on the other vicinal coupling constant are positive and, again, the general trend is for the more electronegative substituents to show the largest effects. For four-bond coupling, the trend is to lower values, but why the carbon substituents should have the largest effect is not known.

The substituent effects in the ortho derivatives (Table I) are generally larger than those of the meta or para derivatives. All the substituent effects involving C-2 are negative, but they do not correlate well with electronegativity because, for example, the substituent effect for amino is greater than for fluoro. The other two-bond coupling constant shows both positive and negative substituent effects but does not accord with σ_p because nitro and amino have quite similar effects. The variation in the two-bond couplings involving C-6 are smaller than those involving C-2. The largest substituent effects occur in the three-bond couplings involving C-3, although all the substituent effects are negative. However, these coupling constants are small, and because not all of the signs are known, any detailed correlation with substituent character might be hazardous. Electronegativity may be an important factor, because the fluorine substituent effect seems to be most negative. The other three-bond couplings show much smaller variations with substituents of erratic sign. The variations of the four-bond coupling constants are small and no pattern can be seen here.

It is of interest to compare the aliphatic carbon–fluorine coupling constants with corresponding proton–fluorine coupling constants in ethyl fluoride.



$J_{FH\alpha}$ = +46.7 Hz
$J_{FH\beta}$ = +25.2 Hz
J_{CCF} = +19.9 Hz
J_{CCCF} = 5.2 Hz

The two examples we have for two- and three-bond couplings fit crudely to $J_{CF} = 0.3J_{HF}$. The noteworthy facts are that the relative signs are the same and that the three-bond coupling is smaller than the two-bond coupling for both carbon–fluorine and proton–fluorine couplings. The carbon–fluorine couplings here may be compared with the various couplings in norbornyl compounds.[25]

Carbon Chemical Shifts. The upfield shift of C-3 in *n*-hexyl fluoride is typical of what is found for the γ-carbons in primary continuous-chain alkanes.[24,30] The methyl substituent effect has been explained in terms of gauche interactions which result from coiling of the hydrocarbon chain[24a] wherein nonbonded interactions between the hydrogens change the electron

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[28] The starting point for the Karabatsos treatment of proton–proton and proton–carbon coupling is the average-energy approximation; however, the more general treatment only requires that the two fragments of the wave function being considered be similar. Thus, the average-energy approximation may fail for both carbon–fluorine and proton–fluorine coupling, but if the degree of failure is similar for each, the treatment could turn out to be fortuitously valid.

[29] R. W. Taft, *J. Amer. Chem. Soc.*, 79, 1045 (1957).

[30] T. D. Brown, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1966.

density at the carbons to which they are attached.[31] This mechanism is not possible for a fluorine substituent because there is no proton on the fluorine, and it may be significant in this connection that chemical-shift changes of the opposite sign may be induced at the fluorine by nonbonded interactions.[32]

The ^{13}C chemical shift of C-8 in 1-fluoronaphthalene is 5.1 ppm upfield of the corresponding shift in naphthalene itself. The two other carbons which are three bonds removed from the fluorine, but which are not in close proximity to it, are shifted downfield by 2.2 and 4.0 ppm. The methyl carbon of 2-fluorotoluene is shifted upfield relative to the methyl carbon in toluene by 7.3 ppm. The corresponding effects on the meta and para derivatives are +1.5 and +0.9 ppm.[33] Clearly, a carbon is shifted upfield by a γ-fluorine which is either eclipsed or gauche to the carbon in question.

The C-1 chemical shift in pentafluoroiodobenzene actually appears upfield of the methyl resonance in methyl fluoride. This large shift can be explained on the basis of additive substituent parameters for fluorobenzene and iodobenzene,[12] where $^1\delta_I$ is the substituent effect of

$$\begin{aligned} \delta &= {}^1\delta_I + 2({}^2\delta_F) + 2({}^3\delta_F) + {}^4\delta_F \\ +63.5 &= +32.3 + 28.6 + 1.8 + 4.4 \end{aligned}$$

iodine on C-1 iodobenzene, $^2\delta_F$ is the substituent effect of fluorine on the *o*-carbon of fluorobenzene, etc. The predicted value of +63.5 ppm agrees fortuitously well with the observed shift. Additivity relations appear to hold reasonably well for ^{13}C chemical shifts in aromatic compounds, but not usually to this precision.

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[33] P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

The Fluorine-19 Nuclear Magnetic Resonance Spectra of Some Fluoroaromatic Compounds. Studies Using Noise Decoupling of Protons[1a]

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Abstract: The ^{19}F nmr spectra of a number of fluorobenzenes and other fluoroaromatic molecules have been examined at 94.1 MHz under conditions of complete proton decoupling by noise modulation, which allowed ^{19}F chemical shifts and $F \cdots F$ coupling constants to be extracted conveniently without recourse to complete analyses. Details of the digital frequency sweep and the double-tuned probe provisions for a Varian HA-100 spectrometer are given. Where a proton-decoupled spectrum is a single line, the values of $^1J_{^{13}C-F}$ and the $^{13}C-^{12}C$ isotope shifts may not always be extracted uniquely from the ^{13}C satellites, although the $F \cdots F$ coupling constants can be measured directly. Data on the solvent dependence of $F \cdots F$ couplings and ^{19}F chemical shifts in some polar fluorobenzenes are reported. The behavior of $^3J_{FF}$ in these systems shows no correlation with solvent dielectric constant, which is interpreted to mean that "reaction field" mechanisms are not important here. However, the smaller variations in $^4J_{FF}$ and $^5J_{FF}$ are reasonably correlated with the dielectric constant of the solvent, which suggests that the "reaction field" mechanism is more significant here. No simple dependence of the ^{19}F chemical shifts on solvent dielectric constant was found in contrast to some previous results; possible explanations for this are discussed. Accurate values for the long-range $F \cdots F$ couplings for a number of difluoronaphthalenes, -biphenyls, and -phenanthrenes are presented for the first time.

Because of the difficulties in the theoretical understanding of fluorine–fluorine nmr spin–spin coupling constants, there is continuing interest in the nmr spectra of fluorinated benzenes. To cite but a few examples, there have recently been several careful spectral analyses, including the extraction of $F \cdots F$ coupling relative sign information, on the pentafluorobenzenes.[2,3] It has been shown[4] that a considerable part of the discrepancies found between values of $^3J_{FF}$ in earlier work arises from a large solvent dependence of this coupling. Very recently further evidence from a range of compounds has been presented[5–7] in support of the proposal[8] that the nuclear spin–spin coupling between two fluorine atoms may be transmitted "through space" where the

[1] (a) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration. Partial support was received from the Jet Propulsion Laboratory Director's Discretionary Fund. (b) NASA Resident Research Associate, 1968–1970.

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[4] M. A. Cooper, *Org. Magn. Resonance*, **1**, 363 (1969).

[5] (a) K. L. Servis and K.-N. Fang, *J. Amer. Chem. Soc.*, **90**, 6712 (1968); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **90**, 3577 (1968); (c) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970).

[6] S. L. Manatt and M. T. Bowers, *J. Amer. Chem. Soc.*, **91**, 4381 (1969), and unpublished work of E. A. Cohen and S. L. Manatt quoted therein.

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[8] L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961).