

Carbon-Fluorine Spin-Spin Coupling in Carbocations¹Robert J. Spear,^{2a} David A. Forsyth,^{2b} and George A. Olah**Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received July 7, 1975*

Abstract: The ¹³C-¹⁹F coupling constants in a series of *p*- and *m*-fluorophenylcarbenium ions and related carbocationic π systems were determined from ¹³C NMR spectra of the stable ion solutions. The use of stable carbocations permits the examination of C-F couplings over a wide range of systems with varying demand for electronic stabilization by resonance interaction with the fluorine atom. The dominant influence on one-, three-, and five-bond couplings in geometrically similar compounds is the extent of resonance interaction of fluorine with the π system. Other factors, such as carbon hybridization and steric interactions, are also recognized as contributing to variation in ¹J_{CF} in carbocations. A pronounced dependence of ³J_{CF} on the stereochemical alignment (*cis* or *trans*) is demonstrated. The two- and four-bond C-F couplings in the carbocations examined do not show any systematic response to resonance effects, and no other clear trends are evident. It is suggested that future theoretical treatments of C-F couplings should consider the effect on the orbital and dipolar contributions to C-F coupling of changes in *p*-orbital dimensions resulting from changes in charge distribution.

Introduction

The mechanism of ¹³C-¹⁹F spin-spin coupling has been the subject of several recent experimental and theoretical investigations. With the development of pulsed Fourier transform NMR spectrometers, experimental data have become available on long-range C-F coupling measured directly from ¹³C spectra, in addition to C-F coupling constants for directly bonded atoms measured from ¹³C satellites in ¹⁹F NMR spectra.³ Fluoro-substituted aromatics have been an area of particular experimental interest, with studies appearing on fluorobenzenes,⁴⁻¹¹ fluoronaphthalenes,^{6,9,12} fluorophenanthrenes,⁹ fluorobenzofurans,⁸ and fluoropyridines.^{11,13} In this paper, we report C-F couplings in a series of *p*- and *m*-fluorophenylcarbenium ions and related carbocationic π systems. Our purpose in examining these systems is to take advantage of the unique electronic and structural characteristics of carbocations to help elucidate the dependency of C-F couplings on molecular properties. Whereas studies of neutral, substituted fluoroaromatics are confined within the limits of substituents ranging from NH₂ to NO₂, studies of stable carbocations permit the further extension from moderately strong to extremely strong electron-withdrawing substituents.¹⁴ Thus, it is possible to examine the effect on C-F couplings of electron demands on the fluorine atom which vary over a wide range.

Theoretical descriptions of coupling between nuclear spins are based on Ramsey's theory¹⁵ that coupling via the electrons originates from three types of interaction between the magnetic moment due to the nuclear spin and the electrons. The three types are an orbital interaction with the magnetic field due to the orbital motion of electrons, a dipolar interaction with the electron spin, and a Fermi contact interaction with the electron spin. Ideally, the best way to interpret C-F coupling data would be to calculate the contributions of the various nuclear-electron interaction mechanisms to C-F coupling, based on wave functions for each species considered. However, despite successful applications of theory, using only the Fermi contact term, to C-H coupling¹⁶ and, to a lesser extent, C-C coupling,^{17,18} similar theoretical evaluations of C-F couplings are less than satisfactory.¹⁷ Computational approaches which have included the orbital and dipolar interactions show the importance of these contributions to C-F and F-F couplings, but the calculations are still far from accurately reproducing experimental *J*_{CF} values.¹⁹⁻²³ Some of the lack of accuracy may be attributable to the limitations imposed by the inadequacies of approximate wave functions. Because of these dif-

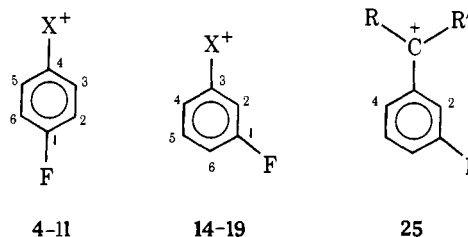
ficulties, we feel it is worthwhile to point out systematic trends in our experimental C-F coupling constant data and to find empirical correlations with other molecular properties which are dependent on the same electronic characteristics of the molecules.

Results and Discussion

Our ¹³C and ¹⁹F NMR data for 18 carbocations and data for six neutral monosubstituted benzenes, chosen as representative of the published data,^{6,7} are summarized in Tables I-III. The carbocations were formed by ionization or protonation of the appropriate substrate in HSO₃F-SbF₅-SO₂ClF or, in the case of acyl halide or α -fluorotoluene precursors, ionization with SbF₅-SO₂ClF or SO₂. Complete details of the methods of preparation of these ions, together with references to previous preparations (where applicable) are described in the Experimental Section.

Chemical Shifts. Carbon-13 assignments were aided by recording off-resonance spectra. Where more than one quaternary carbon was present in an ion, the resonance exhibiting the largest ¹³C-¹⁹F coupling was assigned to the carbon directly attached to the fluorine atom.³

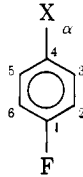
Data for the *p*-fluorophenylcarbocations **4-11** are summarized in Table I. C(1) and C(4) were identified from off-



resonance spectra. The carbons ortho to X⁺, C(3) and C(5), were assigned from their large downfield shift,¹⁴ while C(2) and C(6) resonate at considerably higher field due to their position ortho to the fluorine.²⁴ C(2) and C(6) exhibit only a small gradual deshielding as X changes from NH₂ (**1**) to H-C⁺-CH₃ (**11**), consistent with minimal charge development at carbons meta to charge-bearing substituents.

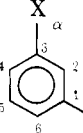
Data for the *m*-fluorophenylcarbenium ions **14-19** are summarized in Table II. The number of such ions applicable to this study was limited by the requirement that X⁺ be a symmetrical substituent in order that spectra not be complicated by rotameric pairs. The single nonsymmetrical example, **16**, is discussed below.

C(1) and C(3) in **14-19** were readily identified by off-

Table I. ^{13}C - ^{19}F Coupling Constants^a and ^{13}C ^b and ^{19}F ^c NMR Chemical Shifts for a Series of *p*-Fluorophenylcarbenium Ions and Representative Fluorobenzenes


No. ^d	X	C(1) ^{a, b}	C(2)	C(3)	C(4)	C(5)	C(6)	C _α	φ _F ^c
1	NH ₂ ^e	233.2 (157.0)	22.4 (116.0)	7.5 (117.0)	1.86 (145.2)	7.5 (117.0)	22.4 (116.0)		128.8
2	H ^e	245.3 (163.6)	21.0 (115.5)	7.7 (130.4)	3.3 (124.5)	7.7 (130.4)	21.0 (115.5)		114.2
3	NO ₂ ^e	256.6 (166.3)	24.0 (116.6)	10.2 (126.5)	<i>f</i> (144.9)	10.2 (126.5)	24.0 (116.6)		103.4
4	⁺ CNH ₂ ^g	268.4 (170.1)	23.7 (119.1)	11.9 (140.4)	2.9 (96.0)	11.9 (140.4)	23.7 (119.1)	<i>f</i> (107.4)	88.2
5	⁺ C(OH) ₂ ^g	268.8 (171.3)	23.2 (118.7)	11.7 (136.9)	NRC ^h (116.2)	11.7 (136.9)	23.2 (118.7)	<1 ⁱ (180.8)	89.2
6	⁺ N ₂ ^j	271.9 (170.1)	25.2 (121.6)	13.0 (136.4)	NRC (108.6)	13.0 (136.4)	25.2 (121.6)		82.8
7	H-C-OH ^g	278.1 (174.6)	24.8 (120.7) ^k	13.4 (137.8)	<1 ⁱ (125.2)	13.6 (149.3)	24.8 (119.7) ^k	NRC (202.2)	71.8
8	⁺ CO ^l	285.0 (181.2)	24.6 (121.6)	14.8 (146.2)	NRC (84.6)	14.8 (146.2)	24.6 (121.6)	<1 ⁱ (154.5)	69.3
9	⁺ C(CH ₃) ₂ ^{g, m}	294.2 (180.0)	22.1 (120.9)	16.9 (146.8)	<1 ⁱ (136.9)	16.9 (148.8)	22.1 (120.9)	5.3 (248.0)	60.9
10	⁺ CF ₂ ⁿ	301.0 (182.5)	22.8 (123.6)	18.8 (150.4)	<1 ⁱ (107.6)	18.8 (150.4)	22.8 (123.6)	5.6 (175.9)	47.6
11	H-C-CH ₃ ^{g, o}	303.6 (183.6)	24.5 (123.1) ^k	18.8 (148.6)	<1 ⁱ (138.6)	19.4 (159.3)	24.5 (122.1) ^k	6.5 (223.4)	46.8

^a Coupling constants are in Hz. ^b Carbon-13 chemical shifts are shown in parentheses below the J_{CF} values and are in ppm relative to external (capillary) Me₄Si. ^c Fluorine-19 chemical shifts are in ppm relative to external (capillary) CFCl₃. ^d The carbons in 1-11 are numbered for clarity of comparison and do not necessarily follow the accepted numbering schemes. ^e Data from ref 6 and 7. ^f Broadened by ¹⁴N quadrupole. ^g In FSO₃H-SbF₅-SO₂ClF at -75 °C. ^h NRC indicates that the carbon resonance was broadened, relative to the other carbon resonances, by an unresolved coupling (2-3 Hz). ⁱ The resonance showed no broadening relative to the other carbon resonances. ^j In SO₂ at -40 °C. ^k C(2) and C(6) assignments could be reversed; reported value is the average of $J_{\text{C}(2), \text{F}}$ and $J_{\text{C}(6), \text{F}}$. ^l In SbF₅-SO₂ClF at -75 °C. ^m CH₃, 32.4, $J_{\text{CF}} < 1$. ⁿ In SbF₅-SO₂ at -75 °C, J_{CF} values for the CF₂ fluorines are given in Table III. ^o CH₃, 26.6, $J_{\text{CF}} < 1$.

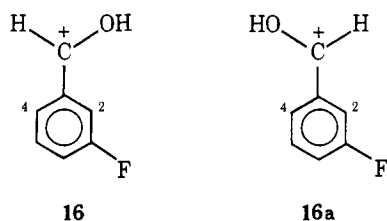
Table II. ^{13}C - ^{19}F Coupling Constants^a and ^{13}C ^b and ^{19}F ^c NMR Chemical Shifts for a Series of *m*-Fluorophenylcarbenium Ions and Representative Fluorobenzenes


No. ^d	X	C(1) ^{a, b}	C(2)	C(3)	C(4)	C(5)	C(6)	C _α	φ _F ^c
12	NH ₂ ^{e, f}	241.4 (164.6)	24.6 (102.6)	11.0 (149.7)	2.3 (111.7)	10.2 (131.3)	21.3 (105.2)		114.4
2	H ^e	245.3 (163.6)	21.0 (115.5)	7.7 (130.4)	3.3 (124.5)	7.7 (130.4)	21.0 (115.5)		114.2
13	NO ₂ ^{e, f}	250.9 (162.0)	26.5 (110.7)	8.3 (148.7)	3.3 (119.0)	8.2 (130.9)	21.5 (121.8)		110.9
14	⁺ CNH ₂ ^g	253.8 (162.3)	26.9 (122.7)	9.0 (101.6)	NRC ^h (133.3)	8.6 (133.5)	21.0 (128.6)	<i>i</i> (105.8)	107.2
15	⁺ C(OH) ₂ ^g	251.4 (163.0)	24.7 (119.4)	8.7 (121.7)	NRC ^h (129.0)	7.2 (133.2)	21.7 (129.4)	NRC ^h (181.7)	108.4
16	H-C-OH ^{g, j}	254.5 (163.3)	22.9 (118.0)	8.8 (129.9)	NRC ^h (143.0)	7.8 (133.9)	22.6 (136.5)	2.3 (205.8)	106.6
17	⁺ CO ^k	259.2 (162.6)	28.0 (126.6)	10.5 (91.1)	3.0 (139.3)	9.1 (135.4)	21.0 (137.1)	3.8 (151.7)	102.2
18	⁺ C(CH ₃) ₂ ^g	256.3 (163.6)	22.0 (125.2)	≈8 ^l (141.4)	NRC ^h (138.6)	7.6 (135.0)	21.6 (141.8)	NRC ^h (262.5)	106.8
19	⁺ CF ₂ ^{k, m}	260.5 (163.9)	23.3 (128.6)	9.4 (112.9)	NRC ^h (143.7)	8.1 (136.5)	21.2 (147.7)	NRC ^h (179.1)	101.4

^a Coupling constants are in Hz. ^b Carbon-13 chemical shifts are shown in parentheses below the J_{CF} values and are in ppm relative to external (capillary) Me₄Si. ^c Fluorine-19 chemical shifts are in ppm relative to external (capillary) CFCl₃. ^d The carbons in 12-20 are numbered for clarity of comparison and do not necessarily follow the accepted numbering schemes. ^e J_{CF} data from ref 6; chemical shifts were determined on neat solutions (12 and 13). ^f Data from H. S. Gutowsky, D. W. McCall, B. R. Garvey, and L. H. Meyer, *J. Am. Chem. Soc.*, 74, 4809 (1952), converted to CFCl₃ using δ_{CFCl₃} (C₆H₅F) = 114.2 ppm. ^g In HSO₃F-SbF₅-SO₂ClF at -75 °C. ^h NRC indicates that the carbon resonance was broadened, relative to the other carbon resonances, by an unresolved coupling (2-3 Hz). ⁱ Broadened by ¹⁴N quadrupole. ^j Data for the minor rotamer (X = ⁺C(OH)H) are not given. ^k In SbF₅-SO₂ClF at -75 °C. ^l Partly obscured by C(4) resonance. ^m J_{CF} values for the -CF₂ group are given in Table III.

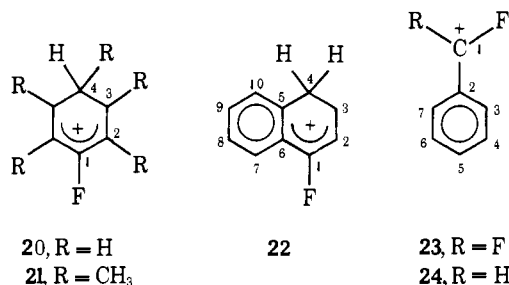
resonance spectra. The remaining four aryl carbons are subjected to a range of shielding and deshielding influences; π -resonance electron withdrawal strongly deshields C(2), C(4), and C(6), while C(5), the meta carbon, is only slightly deshielded.¹⁴ The fluorine atom strongly shields C(2) and C(6),²⁴ and if X⁺ is a nonlinear group possessing α substituents, i.e., **25**, R,R' \neq H, C(2) and C(6) will be subject to the well-documented γ -substituent effect,^{14,25-28} resulting in a mutual shielding of C(2) and R' (and C(4) and R) by 5-15 ppm. Considering these factors and the results for **4-11** (Table I), the carbon resonance weakly coupled to the fluorine was assigned to C(4), and C(5) was assigned by its near constant chemical shift in **14-19** and by the fact that the J_{CF} value was similar to that for C(3). The remaining two carbons, C(2) and C(6), displayed similar J_{CF} values, and, by analogy with the situation in phenylcarbenium ions,¹⁴ the most deshielded resonance was assigned to C(6).²⁹

Protonation of *m*-fluorobenzaldehyde yielded two isomeric ions (**16**, **16a**) in the approximate ratio 3:1. The major isomer was assigned the syn structure (**16**) because the large upfield shift of C(2) required that the hydroxyl



group be syn to C(2).³⁰ Since several carbon resonances of the minor (anti) isomer **16a** were obscured by resonances from **16**, data are not included for this species. An independent study of *m*-fluorobenzaldehyde in superacid media has also identified **16** as the major (72%) isomer.³¹

Data for several fluoroarenium ions (**20-22**) and fluoro-carbenium ions where the fluorine is directly attached to the benzylic carbon center (**23**, **10**, **19**, **24**) are summarized in Table III. The carbon assignments in **20** and **21** were straightforward; C(2) and C(5), the carbons ortho to the protonation site (C(4)) were identified by their strong deshielding relative to C(2) and C(6). In the fluoro-naphthalenium ion (**22**), C(1), C(4), C(5), and C(6) were



identified from off-resonance spectra, while C(3) was assigned from its strongly deshielded position. Consideration of the substantial shielding of neighboring carbons by the fluorine²⁴ allowed the assignment of C(2) and the differentiation of C(6) from C(5). C(7), the carbon syn and γ to the fluorine,³² was identified from its upfield position and

Table III. ¹³C-¹⁹F Coupling Constants^a and ¹³C^b and ¹⁹F^c NMR Chemical Shifts for some Fluorobenzenium Ions and Fluorophenyl Carbenium Ions

System ^d	No.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	ϕ_F^c
	20^e	324.8 (194.3)	19.7 (126.2)	26.7 (188.1)	<i>f</i> (47.7)	26.7 (188.1)	19.7 (126.2)					11.0
	21^g	313.3 (187.0)	17.1 (129.7)	23.1 (202.3)	<i>f</i> (57.1)	23.1 (202.3)	17.1 (129.7)					31.3
	22^e	329.0 (193.0)	21.0 (123.5)	28.6 (187.9)	<i>f</i> (42.6)	18.2 (159.2)	8.5 (124.0)	15.4 (130.6)	NRC ^h (131.6)	NRC (143.9)	NRC (130.3)	24.2
	23 , X = Y = H ⁱ	361.7 (178.2)	8.2 (111.2)	10.7 (145.5)	< <i>i</i> (134.1)	5.7 (159.5)	< <i>i</i> (134.1)	10.7 (145.5)				-12.2
	10 , X = H, ^{i,k} Y = F	358.0 (175.9)	9.8 (107.6)	9.9 (150.4)	< <i>i</i> (123.6)	6.0 (182.5)	< <i>i</i> (123.6)	9.9 (150.4)				-7.3
	19 , X = F, ^{h,m} Y = H	365.1 (179.1)	9.4 (112.9)	9.8 (128.6)	< <i>i</i> (163.9)	5.7 (147.7)	< <i>i</i> (136.5)	11.5 (143.7)				-19.0
	24^l	375.5 (203.7)	< <i>i</i> (129.2)	14.2 (142.1)	<i>n</i> (134.3)	8.4 (163.0)	<i>n</i> (134.3)	23.5 (155.1)				-21.0

^a Coupling constants are in Hz. ^b Carbon-13 chemical shifts are shown in parentheses below the J_{CF} values and are in ppm external (capillary) Me₂Si. ^c Fluorine-19 chemical shifts are in ppm relative to external (capillary) CFCl₃; negative sign refers to downfield (deshielded) from CFCl₃. ^d The carbons in **10**, **19**, and **20-24** are numbered for clarity of comparison and do not necessarily follow accepted numbering schemes. ^e In HSO₃F-SbF₅-SO₂ClF at -80 °C. ^f The protonated carbon [C(4)] in benzenium ions is typically broader than the other carbon resonances and, as such, no estimate of J_{CF} is possible. ^g Data from G. A. Olah, H. C. Lin, and D. A. Forsyth, *J. Am. Chem. Soc.*, 96, 6908 (1974). ^h NRC indicates that the carbon resonance was broadened, relative to the other carbon resonances, by an unresolved coupling (2-3 Hz). ⁱ In SbF₅-SO₂ at -75 °C. ^j The resonance showed no broadening relative to the other carbon resonances. ^k The J_{CF} values for the C(5)-F(Y) are given in Table I. ^l In SbF₅-SO₂ClF at -75 °C. ^m The J_{CF} values for the C(4)-F(X) are given in Table II. ⁿ Resonance slightly broadened by probable near-equivalence of C(4) and C(6) (average shift given) and, thus, no estimate of coupling is possible.

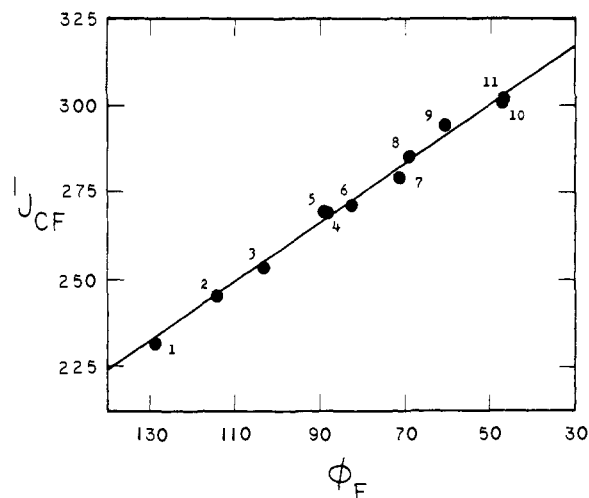


Figure 1. Plot of $^1J_{CF}$ for *p*-fluorophenyl derivatives vs. the corresponding fluorine chemical shifts.

J_{CF} value. Of the remaining three carbons, C(8), C(9), and C(10), which are weakly coupled to the fluorine, C(9) is deshielded due to positive charge delocalization to that position, but C(8) and C(10) are only tentatively assigned in Table III. The carbon assignments in the difluorophenyl-carbenium ion (**23**) were readily derived by off-resonance spectra, which identified C(2), and relative peak intensities, which defined the para carbon C(5). The carbons ortho to the $^+CF_2$ group, C(3) and C(7), were assigned on the basis of their substantial downfield shift relative to the meta carbons C(4) and C(6). The carbon assignments in the monofluorophenylcarbenium ion (**24**) follow by analogy; the shielded C_{ortho} resonance was assigned as syn to the fluorine (C(3)) from consideration of the γ -substituent effect.^{14,25-28} The $\Delta C(3)$, C(7) value (13.0 ppm) is typical of the magnitude of this effect in carbocations.¹⁴

One-Bond Carbon-Fluorine Couplings. ($^1J_{CF}$). The sign of one-bond carbon-fluorine couplings has been established as negative.³ Previous studies of para-substituted fluorobenzenes have demonstrated that substitution by substituents with increasing ability to withdraw electron density from the π system leads to more negative $^1J_{CF}$ values.⁴⁻¹¹ Linear correlations have been noted for $^1J_{CF}$ with the fluorine chemical shifts and with Taft's σ_R values³³ or other chemically derived substituent constants which can be considered as measures of the electron-withdrawing or -donating capabilities of the substituent groups. Although contributions due to π -resonance effects in neutral systems can be assessed by correlation with substituent constants such as Taft's σ_R constants, no such set of parameters is available for the charged substituents considered in the present study. However, changes in the ^{19}F chemical shift (ϕ_F) of *p*-fluorobenzenes³⁴ and *p*-fluorophenylcarbenium ions³⁵ and in the ^{13}C chemical shift (δ_C) of the para carbon in monosubstituted benzenes³⁶ and phenylcarbenium ions¹⁴ have been shown to be linearly related to measures of π -resonance effects, such as the π -electron density of the para position. Lauterbur³⁷ demonstrated the linear relationship between the para δ_C in a series of neutral benzenes and the ϕ_F of the *p*-fluoro analogues. Thus, we will use both para ϕ_F and para δ_C (of the nonfluorinated systems) as quantitative measures of the capabilities of substituent groups to withdraw or donate electrons to the para position via π -resonance effects.

The $^1J_{CF}$ values for the *p*-fluorophenyl derivatives listed in Table I are clearly responsive to the electron-withdrawing capability of the substituent groups. The $^1J_{CF}$ for **11**, the *p*-fluorophenylmethylcarbenium ion, differs from the

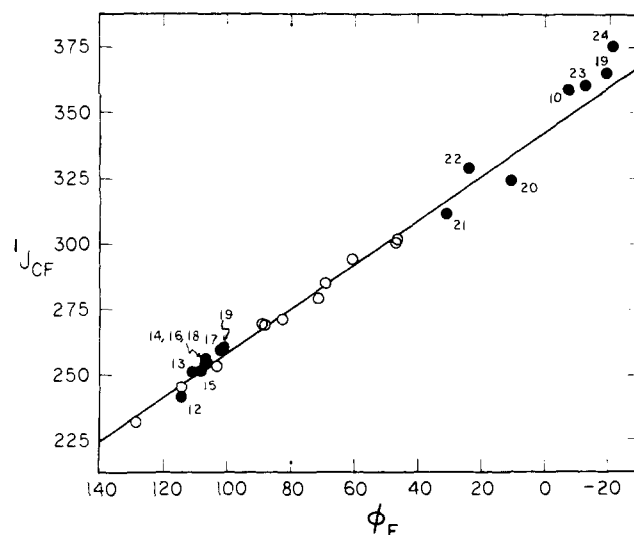


Figure 2. Plot of $^1J_{CF}$ for all systems in Table I-III vs. the corresponding fluorine chemical shifts. The line is the least-squares correlation line for *p*-fluorophenyl derivatives (indicated by open circles), taken from Figure 1.

$^1J_{CF}$ in fluorobenzene by 58 Hz, a fivefold greater difference than that observed for *p*-fluoronitrobenzene. The plot of one-bond C-F couplings (Table I) against the ϕ_F in Figure 1 indicates the precision of the linear relationship between $^1J_{CF}$ and this measure of the electron-withdrawing capability of the substituent groups. The least-squares analysis of the relationship with ϕ_F gives eq 1, and eq 2 is the relationship with para δ_C of the corresponding nonfluorinated phenylcarbenium ions.¹⁴

$$^1J_{CF}(\text{para}) = -0.848\phi_F + 342.9 \quad \begin{array}{l} \text{SD} = 1.9 \\ \text{cc} = -0.997 \end{array} \quad (1)$$

$$^1J_{CF}(\text{para}) = 1.68\delta_C + 31.2 \quad \begin{array}{l} \text{SD} = 2.0 \\ \text{cc} = 0.996 \end{array} \quad (2)$$

The trend to more negative $^1J_{CF}$ values with increasing electron demand on the fluorine atom can be seen to continue in the *m*-fluorophenyl derivatives of Table II and the ions shown in Table III. Although the meta ϕ_F and the ϕ_F values for the ions of Table III are not expected³⁸ to be as accurately representative of π -resonance demand on the fluorine atom as are para ϕ_F values, because of influences other than electron density on the chemical shift, the plot of $^1J_{CF}$ vs. ϕ_F in Figure 2 shows that these points lie close to the line of best fit for the *p*-fluorophenyl derivatives. The linear correlation (eq 3) of all $^1J_{CF}$ in Tables I-III with ϕ_F is still excellent.

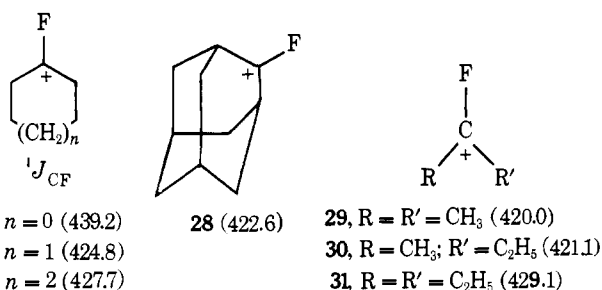
$$^1J_{CF} = -0.892\phi_F + 347.6 \quad \begin{array}{l} \text{SD} = 4.3 \\ \text{cc} = -0.994 \end{array} \quad (3)$$

The points which lie above the *p*-F correlation line in Figure 2, i.e., **10**, **19**, and **22-24**, are from structurally related systems in which the fluorine atom is proximate to a peri hydrogen (**22**) or an ortho hydrogen atom (**10**, **19**, **23**, **24**). The deviations from the line may represent a steric perturbation of the C-F coupling and/or the fluorine chemical shift. A previous study of steric effects on $^1J_{CF}$ values in neutral systems indicated contributions of -5 Hz (i.e., to larger magnitude) in 1-fluoronaphthalene to -10 Hz in 1,8-difluoronaphthalene.⁹ On the other hand, steric influences on chemical shifts are also well known, such as the γ -substituent effect²⁵⁻²⁸ on ^{13}C shifts.

The results for the *m*-fluorophenyl derivatives in Table II reflect the lesser importance of π -resonance effects at the

meta position relative to the para position. The meta ϕ_F and meta $^1J_{CF}$ vary within a relatively narrow range. Similarly, the nonfluorinated analogues of these ions exhibit a small range of meta δ_C , consistent with minimal development of positive charge at the meta carbon.¹⁴ Over this narrow range, there are crude correlations of $^1J_{CF}$ with ϕ_F and δ_C . It has been shown recently that meta δ_C values in phenyl-carbenium ions increase systematically with the increase in the capability of the carbenium ion substituents to withdraw electrons via π -resonance effects;³⁹ however, when the substituting atom attached to the aromatic ring is varied from a sp^2 -hybridized carbon, this correlation is not always adhered to, as in the case of aniline and nitrobenzene, in which the meta δ_C are identical.³⁶ Thus, σ -inductive effects and possibly other influences operate to some extent at the meta position and undoubtedly complicate any simple relationship with ϕ_F or δ_C .

Additional evidence for the importance of π resonance interactions in determining $^1J_{CF}$ values is the carbon-fluorine coupling in ions with fluorine directly attached to a localized carbenium center. As previously reported from our laboratory,⁴⁰ the one-bond couplings in cyclohexyl (**26**, **28**), cycloheptyl (**27**), and acyclic (**29**–**31**) ions are very large and cover a small range. The one-bond coupling in the 1-fluorocyclopentyl cation (**25**) is the largest which has so far been reported and shows the previously described trend to more negative $^1J_{CF}$ values with decreasing ring size.³ Presumably, this is a result of hybridization changes, and one would expect the cyclobutyl analogue to exhibit an even more enhanced value of $^1J_{CF}$.



Two-Bond (Geminal Carbon-Fluorine Coupling Constants ($^2J_{CF}$)). It is more difficult to detect any trends in the variation of $^2J_{CF}$ with the structural and electronic characteristics of the species in Tables I–III. The $^2J_{CF}$ values for the *p*-fluorophenyl derivatives in Table I occur in a narrow range (<5 Hz), with the smallest value (21 Hz) for fluorobenzene itself.⁴¹ The small variations do not conform to any obvious pattern, and resonance effects do not appear to be important. In the *m*-fluorophenyl derivatives (Table II), coupling to C(6) is virtually constant, while coupling to C(2), which is ortho to the substituent, is larger than in fluorobenzene and covers a slightly greater range of values than in the *p*-fluorophenyl derivatives. Again, there are no obvious patterns to the variation, and resonance effects do not appear to be important. Weigert and Roberts suggested that substituent electronegativity was a more relevant parameter than resonance effects for two-bond couplings in fluorobenzenes,⁶ but it is difficult to rationalize the small variations on the basis of electronegativity differences of the substituents, because the ordering of $^2J_{CF}$ values in Table I is not related to the ordering of $^2J_{CF}$ values for the meta-substituted derivatives in Table II.

The two-bond C–F coupling to C(2) in ions **20**–**22** is comparable with the coupling in fluorobenzene, but two-bond coupling to C(6) in **22** is considerably smaller (8.5 Hz). Two-bond coupling from the benzylic fluorines to C(2) in ions **10**, **19**, and **23** is also smaller and is too small to be detected in **24**. Since the signs of these smaller cou-

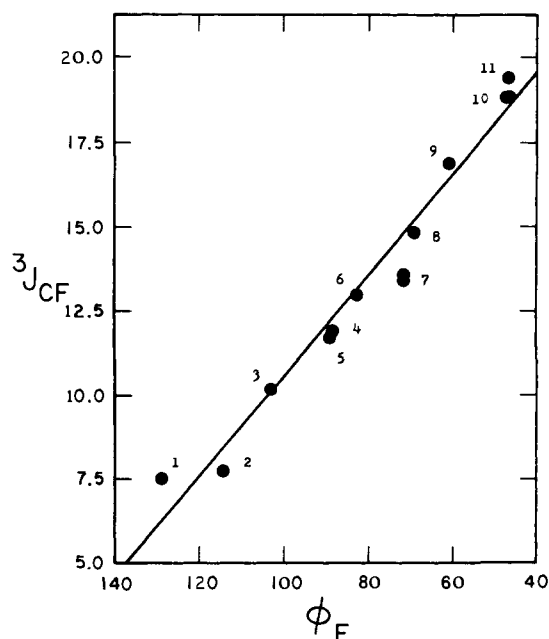


Figure 3. Plot of $^3J_{CF}$ for *p*-fluorophenyl derivatives vs. the corresponding fluorine chemical shifts.

pling constants are unknown, it would be unwise to draw detailed conclusions even about the direction of possible influences on $^2J_{CF}$. That factors controlling $^2J_{CF}$ may be complex is also indicated by the large $^2J_{CF}$ in benzoyl fluoride (61.2 Hz)⁴² and the recent report by Chadwick which suggests that $^2J_{CF}$ in the two rotational isomers of furan-2-carbonyl fluoride have opposing signs.⁴³

Three-Bond (Vicinal Carbon-Fluorine Couplings ($^3J_{CF}$)). The magnitudes of vicinal carbon-fluorine couplings in neutral *p*-fluorobenzenes encompass a relatively small range,^{6,7} typified by entries 1–3 in Table I, and increase with the increase in electron-withdrawing power of the substituent group.⁷ It should be noted, however, that the sign of this coupling is as yet undetermined, although experiments by Roberts suggest a positive sign in fluorobenzenes.⁶ The $^3J_{CF}$ values in the cationic *p*-fluorophenyl species 4–11 show a range considerably extended from 1–3, reaching a maximum of 19.4 Hz in **11**. A plot of $^3J_{CF}$ against ϕ_F (Figure 3) illustrates the trend of increasing $^3J_{CF}$ with increasing resonance interaction of the fluorine electrons with the π system. An excellent linear correlation is observed, as described by eq 4.

$$^3J_{CF(\text{para})} = -0.151\phi_F + 25.7 \quad \begin{array}{l} \text{SD} = 0.8 \\ \text{cc} = -0.985 \end{array} \quad (4)$$

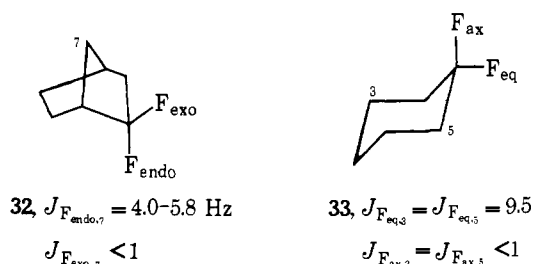
As expected, excellent correlations are also obtained between $^3J_{CF}$ and $^1J_{CF}$ or the para δ_C of the nonfluorinated analogues.

The expectation that resonance effects should be less important at the meta position is confirmed by Table II, in which $^3J_{CF}$ values in *m*-fluorophenyl derivatives are seen to vary over a much smaller range. The only consistent pattern is that coupling to the substituent-bearing carbon (C(3)) is larger in each species than coupling to C(5). As in the case of two-bond couplings, substituent electronegativity has been suggested as a possible influence on $^3J_{CF}$ values,⁶ but there is no apparent relationship between $^2J_{CF}$ and $^3J_{CF}$, nor between $^3J_{CF}$ and meta ϕ_F .

The trend to larger three-bond couplings with increased electron demand on the fluorine atom continues in the arenium ions **20**–**22** (Table III) where $^3J_{CF}$ is now larger than $^2J_{CF}$. The magnitudes of $^3J_{CF}$ excellently mirror the order

expected on the basis of resonance interaction between the fluorine and the coupled carbon, i.e., $J_{F,C(3)}$, $\mathbf{22} > \mathbf{20} > \mathbf{21}$ (cf. ϕ_F), with $J_{F,C(5)}$ in $\mathbf{22}$ exhibiting the smallest magnitude.

Vicinal coupling between the benzylic fluorines and the ortho carbon atoms in entries $\mathbf{23}$, $\mathbf{10}$, and $\mathbf{19}$ (Table III) is much smaller than in comparable resonance interacting systems such as $\mathbf{8}$ – $\mathbf{11}$ (Table I). The vicinal couplings in $\mathbf{24}$ display the expected enhancement (over $\mathbf{23}$) due to π resonance. Since the vicinal couplings in $\mathbf{23}$, $\mathbf{10}$, and $\mathbf{19}$ are the average of ${}^3J_{\text{transoid}}$ (which corresponds to the fluorobenzene coupling pathway) and ${}^3J_{\text{cisoid}}$, the reduced value of ${}^3J_{CF}$ in comparison with $\mathbf{8}$ – $\mathbf{11}$ could be attributed to a marked diminishing of ${}^3J_{\text{cisoid}}$. That this may, indeed, be the case is supported by the widely differing values for ${}^3J_{\text{transoid}}$ (23.5) and ${}^3J_{\text{cisoid}}$ (14.2) in $\mathbf{24}$ (Table III). The large difference is not due to differential effects of substituent electronegativity (which are usually more enhanced in transoid pathways)⁴⁴ because the magnitude is much too large in relation to the results for systems $\mathbf{12}$ – $\mathbf{19}$, for example. A marked steric dependence for vicinal carbon–fluorine coupling in some saturated systems has previously been observed ($\mathbf{32}$, $\mathbf{33}$),⁴⁵ with the transoid coupling predominating



over the cisoid coupling. Whether this is due to enhancement of the transoid coupling by back-lobe orbital overlap⁴⁵ or diminishing of the cisoid coupling by a through-space coupling of opposing sign to the through-bond coupling cannot be ascertained, although the results for $\mathbf{23}$, $\mathbf{10}$, $\mathbf{19}$, and $\mathbf{24}$ suggest reduced ${}^3J_{\text{cisoid}}$ values when compared with the large ${}^3J_{\text{transoid}}$ values in $\mathbf{20}$ – $\mathbf{22}$ and Table I. Differences between ${}^3J_{\text{cisoid}}$ and ${}^3J_{\text{transoid}}$ in large π systems, such as 1-fluoronaphthalene^{6,46} and protonated 1-fluoronaphthalene ($\mathbf{22}$) are undoubtedly also affected by differences in the coupling pathway through the π system, in addition to effects due to the spatial alignment.

Long-Range Carbon–Fluorine Couplings (${}^4J_{CF}$, ${}^5J_{CF}$). Four-bond couplings between carbon and fluorine in *o*-, *m*-, and *p*-fluorobenzenes are the smallest C–F couplings observed in benzene derivatives.^{6,7} The largest ${}^4J_{CF}$ value (3.8 Hz) was observed for 1,4-difluorobenzene. Most types of substituents lead to smaller coupling constants than in fluorobenzene, with no consistent pattern due to resonance effects or substituent electronegativity. The ${}^4J_{CF}$ results for the *p*-fluorophenyl cations (Table I) tend toward vanishingly small values, and no four-bond couplings were resolved in the *m*-fluorophenyl cations (Table II) or in the cations listed in Table III.

Long-range couplings between fluorine and carbons up to six bonds away have been observed in 1- and 2-fluoronaphthalene.^{6,11,12} In previous studies on fluorobenzenes, no coupling was observed between the fluorine and the sp^2 -hybridized α carbon (${}^5J_{CF}$) in *p*-fluorobenzaldehyde, *p*-fluoroacetophenone, and *p*-fluorobenzoic acid or its methyl ester.^{6,7} Similarly, no coupling is observed between the fluorine and the α carbon in the *p*-fluorophenylcarbocations $\mathbf{5}$, $\mathbf{7}$, and $\mathbf{8}$ (Table I), but the ions in which resonance interaction between fluorine and the π system would be expected to be strongest, namely $\mathbf{9}$ – $\mathbf{11}$ (Table I), exhibit substantial

couplings over this pathway. Furthermore, the carbenium ions with benzylic fluorines ($\mathbf{23}$, $\mathbf{10}$, $\mathbf{19}$, $\mathbf{24}$, Table III) also exhibit large couplings to the para carbon, again five bonds distant; the enhanced value for $\mathbf{24}$ relative to the previous three entries is indicative of the π transmission of these couplings. Indeed, all give characteristic π -transmission data, with negligible couplings to the carbon only four bonds removed, i.e., C(4) in $\mathbf{9}$ – $\mathbf{11}$, C(4) and C(6) in $\mathbf{23}$, $\mathbf{10}$, $\mathbf{19}$, and $\mathbf{24}$. The proton and fluorine NMR spectra of some of these ions are also characterized by exceptionally large long-range couplings, i.e.: $\mathbf{9}$, ${}^7J_{\text{CH}_3,\text{F}} = 1.2$ Hz;⁴⁷ $\mathbf{11}$, ${}^7J_{\text{CH}_3,\text{F}} = 2.7$ Hz;⁴⁷ $\mathbf{10}$, ${}^6J_{\text{F},\text{F}} = 19.8$ Hz,⁴⁸ again presumably via a π mechanism. Couplings over five or six bonds were not resolved in the fluoronaphthalenium ion ($\mathbf{22}$).

Conclusions

Our study of C–F couplings in carbocationic systems demonstrates, over a very wide range of ${}^1J_{CF}$ values, that the dominant influence on ${}^1J_{CF}$ in structurally similar compounds is the extent of resonance interaction of fluorine with the π system. Thus, our results confirm previous observations of correlations between ${}^1J_{CF}$ and ϕ_F (or other measures of resonance effects) which lead to the conclusion that increasing the amount of π bonding between carbon and fluorine results in larger values of $|{}^1J_{CF}|$.^{3–11} Furthermore, this study of carbocations demonstrates that fluorine π -resonance interaction is also a major influence on three- and five-bond C–F couplings. The ${}^3J_{CF}$ values in *p*-fluorophenyl cations correlate excellently with ϕ_F (para), and unusually large ${}^5J_{CF}$ values are observed in carbenium ions in which there is strong demand for charge stabilization by resonance interaction with the fluorine electrons.

Increased π bonding to fluorine results in more negative values of ${}^1J_{CF}$ and more positive values of ${}^3J_{CF}$.⁴⁹ The sign of ${}^5J_{CF}$ has not been determined.

It seems likely that C–F spin–spin coupling is transmitted via the π -electron system in the case of one-, three-, and five-bond couplings, although other possible paths of transmission (through σ framework or through space) will also be affected by the changes in the C–F bond length and in the distribution of electrons around the atoms due to increased π -resonance interactions. The conclusion that transmission of C–F coupling occurs at least partially via the π system holds regardless of the detailed mechanism (orbital, dipolar, or Fermi contact) by which the spin information is transferred. In MO formulations, the Fermi contact contribution to coupling, which arises from polarizations of the intervening electron spins, is dependent upon the s electron density at each nucleus.^{16–21,50} For C–H and C–C coupling, the Fermi contact contribution on the square of the P_{s-s} element of the first-order density matrix accounts generally for the observed relation of C–H and C–C coupling to the hybridization of the carbon atom involved.^{16,17} Calculation of the Fermi contact term using a finite perturbation method⁵¹ gave somewhat improved agreement with experimental trends, and it was suggested that further improvement could be made if corrections were made for the variation of s -orbital densities at both nuclei.^{16,17} However, the P_{s-s^2} term does not account for trends in C–N or C–F coupling, and, indeed, the carbon orbital hybridization is not expected to change significantly in a closely related series of compounds such as at the para position of the *p*-fluorophenyl derivatives of Table I. Calculations of the P_{SCSF} element of the density matrix show virtually no change for a series of *p*-fluorobenzenes.¹⁷ Furthermore, calculation of the Fermi contact contribution to ${}^1J_{CF}$ values in *p*-fluorobenzenes and other fluoro compounds using SCF finite perturbation method also did not account for the experimental trend.¹⁷ Thus, while the Fermi contact

contribution is probably a large part of the total $^1J_{CF}$,^{17,20} it is unclear at present what the importance of variations in the Fermi contact contribution is in determining experimental trends of C–F coupling. The failure of a calculated Fermi contact term to account for the trends may be due to the importance of orbital and dipolar mechanisms of coupling, but several other sources of failure are also possible.¹⁷

Theoretical treatments of the orbital and dipolar contributions to coupling have emphasized interactions utilizing the 2p electrons of the two coupled atoms.^{20,21,50} Mathematical expressions for the orbital and dipolar terms are complex. Approximate evaluations of these terms using perturbation methods with INDO–MO's have suggested the importance of the orbital and dipolar mechanisms in determining experimental trends of C–F and F–F coupling.^{20,21} The expressions for these terms for coupling between atoms A and B indicate a proportionality to the product $\langle r^{-3} \rangle_A \langle r^{-3} \rangle_B$, where $\langle r^{-3} \rangle_N$ is the mean inverse cube of the distance from the nucleus for the 2p atomic orbitals on nucleus N. The customary approach is to treat $\langle r^{-3} \rangle_N$ as a parameter to be determined to fit the experimental data^{20,51} or as a constant value determined for an isolated atom.²¹ Then, variations in the orbital and dipolar contributions are accounted for by evaluation of the rest of the expressions for these terms. However, the $\langle r^{-3} \rangle_N$ for atoms in molecules probably should *not* be considered as constants, particularly when there are large variations in charge densities, as in carbocations. The 2p orbitals are expected to contract as electrons are removed from an atom, and, in fact, the dependence of NMR chemical shifts on electron densities has been explained in terms of change in the 2p-orbital dimensions.⁵² As the 2p orbitals contract, the contribution of the orbital and dipolar coupling mechanisms should increase. Thus, future theoretical treatments of C–F couplings should explore the relationships between charge distributions, orbital dimensions, and the effect on the orbital and dipolar contributions to C–F coupling. As mentioned above, inclusion of variation in s-electron density may lead to improved calculations of the Fermi contact term,^{16,17} and similar considerations may improve calculations of the orbital and dipolar terms.

The experimental data show dependence of $^1J_{CF}$ and $^3J_{CF}$ on factors other than π -resonance interactions. $^1J_{CF}$ in ions **10**, **19**, **22–24** may be affected by the sterically proximate hydrogen atoms. A contribution to $^1J_{CF}$ from a hybridization change is suggested by comparing ion **25** with ions **26–31** and also by other observations of ring-size dependence.³ A pronounced dependence of $^3J_{CF}$ on the stereochemical alignment is demonstrated in ion **24**, where $^3J_{trans}$ (23.5 Hz) is nearly 10 Hz greater than $^3J_{cis}$ (14.2 Hz). Substituent electronegativity influence on coupling through the σ framework is suggested by the greater three-bond coupling to the substituent-bearing carbon [C(3)] than to C(5) in *m*-fluorophenyl derivatives (Table II). Likewise, $^2J_{CF}$ to C(2) is greater than $^2J_{CF}$ to C(6) in each *m*-fluorophenyl derivative.

The $^2J_{CF}$ and $^4J_{CF}$ data in Tables I–III do not show any systematic response to resonance effects, and it is difficult to detect any other clear trends. The four-bond C–F couplings are of small magnitude, and no conclusions can be drawn about the mechanism of spin transfer for this coupling. Substituent effects on two-bond (geminal) C–F couplings are by far the most difficult to rationalize.^{6,7,11} In general, geminal coupling constants are much more sensitive to effects of geometry,⁵³ substituents,^{54,55} and solvents⁵⁶ than other types of coupling constants, hence, this is not entirely unexpected. Stothers³ suggested that an increase in the π -bond character of the C–F linkage leads to increased $^2J_{CF}$ values, based on results from acyl fluorides,

but the results for ions **10**, **19**, **23**, and **24** do not fit such a hypothesis.

Finally, the carbon–fluorine couplings should be useful for assignment of carbon resonances in ^{13}C NMR spectra, particularly in strongly conjugating or charged systems. The excellent correlations observed between ϕ_F , δ_C (para), and $^1J_{CF}$ for the *p*-fluorophenyl cations suggest that this latter parameter could be a useful probe of charge distributions in stable carbocations. However, it would be necessary also to account for hybridization changes, steric effects, and possible inductive influences on $^1J_{CF}$. Despite these limitations, it is clear that carbon–fluorine coupling is an informative physical property for studies of electronic interactions in molecules and ions.

Experimental Section

m-Fluoroaniline, *m*-fluoronitrobenzene, *p*- and *m*-fluorobenzonitrile, *p*- and *m*-fluorobenzoic acids and acid chlorides, *p*- and *m*-fluorobenzaldehyde, benzotrifluoride, *p*- and *m*-fluorobenzotrifluoride, 1-(*p*-fluorophenyl)ethanol, fluorobenzene, and 1-fluoronaphthalene were commercially available samples which were used without further purification. *p*-Fluorobenzediazonium tetrafluoroborate and α,α -difluorotoluene were available from previous studies. 2-(*p*- and *m*-Fluorophenyl)-2-propanol were prepared by standard procedures.

Preparation of Ions. The general procedure for preparations of solutions of the ions was to add in small portions a precooled solution or suspension of the precursor in SO_2ClF or SO_2 to a vigorously stirred (Vortex mixer) solution of superacid in SO_2ClF or SO_2 at -78°C . Details of individual ions prepared in this manner are summarized below by the information: ion, precursor compound, ionizing acid, solvent; previous preparations of the ions are also indicated: **4**, *p*-fluorobenzonitrile, $\text{HSO}_3\text{F}\text{-SbF}_5$ (MA), SO_2ClF ; **5**, *p*-fluorobenzoic acid, MA, SO_2 ; **7**, *p*-fluorobenzaldehyde, MA, SO_2ClF ; **8**,^{57,58} *p*-fluorobenzoyl chloride, SbF_5 , SO_2ClF ; **9**,^{35,47} 2-(*p*-fluorophenyl)-2-propanol, MA, SO_2ClF ; **10**,⁴⁸ *p*-fluorobenzotrifluoride, SbF_5 , SO_2 ; **11**,^{35,47} 1-(*p*-fluorophenyl)ethanol, MA, SO_2ClF ; **14**, *m*-fluorobenzonitrile, MA, SO_2ClF ; **15**, *m*-fluorobenzoic acid, MA, SO_2ClF ; **16**,³¹ *m*-fluorobenzaldehyde, MA, SO_2ClF ; **17**,⁵⁷ *m*-fluorobenzoyl chloride, SbF_5 , SO_2ClF ; **18**,⁴⁷ 2-(*m*-fluorophenyl)-2-propanol, MA, SO_2ClF ; **19**,⁴⁸ *m*-fluorobenzotrifluoride, SbF_5 , SO_2 ; **20**,⁵⁹ fluorobenzene, MA, SO_2ClF ; **22**,⁶⁰ 1-fluoronaphthalene, MA, SO_2ClF ; **23**,^{14,48} benzotrifluoride, SbF_5 , SO_2 ; **24**,¹⁴ α,α -difluorotoluene, SbF_5 , SO_2ClF .

Carbon-13 Nuclear Magnetic Resonance Spectra. ^{13}C NMR spectra were obtained on a Varian Associates Model XL100-15 spectrometer operated in the pulsed Fourier transform mode. Complete details of the instrumentation and methods have been described elsewhere.⁶¹ Ion concentrations were dilute, in the range 5–10%, and 1000–2000 transients were generally required for acceptable signal-to-noise ratios. The spectra were initially recorded at wide sweep widths (6000–7000 Hz) to obtain the chemical shifts, which were measured from a 1.75-mm capillary of 5% ^{13}C -enriched Me_4Si . At these sweep widths, line positions are accurate to about 0.1 ppm. No corrections to shifts have been made for bulk susceptibility differences. However, in several instances unrelated to the present study, we have measured shifts where Me_4Si was present as both an internal and external reference; in these cases, the shift difference between the two Me_4Si signals was on the order of 0.2 ppm. Smaller sweep widths (1000–3000 Hz) were then used to measure accurate coupling constants; 8192 words of memory were used, giving a digital resolution of 0.24 Hz at 1000 Hz to 0.73 Hz at 3000 Hz sweep width. Determination of coupling constants at widely differing sweep widths indicated no systematic trends to larger or smaller values at smaller sweep widths. The experimental resolution under these conditions was 1–3 Hz, and estimates of unresolved couplings were made from consideration of line widths at half-height. For compounds **10** and **19**, which contain two types of fluorines, it is assumed because of the very large differences in chemical shifts for the interacting nuclei that the spectral spacings represent the real values of the coupling constants. Specific peak assignments were aided by recording off-resonance spectra.

Acknowledgment. Support of this work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

References and Notes

- (1) Stable Carbocations. 185. Part 184: G. A. Olah, G. Liang, K. Babiak, and R. J. Murray, Jr., *J. Am. Chem. Soc.*, **98**, 576 (1976).
- (2) (a) Postdoctoral Research Associate; (b) National Institutes of Health Postdoctoral Fellow, 1974–1975.
- (3) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 196–205.
- (4) N. Müller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).
- (5) S. Mohanty and P. Venkateswarlu, *Mol. Phys.*, **12**, 277 (1967).
- (6) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2361 (1971).
- (7) G. Miyajima, H. Akiyama, and K. Nishimoto, *Org. Magn. Reson.*, **4**, 811 (1972).
- (8) R. J. Abraham, D. F. Wileman, G. R. Bedford, and D. Greatbanks, *J. Chem. Soc., Perkin Trans. 2*, 1733 (1972).
- (9) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Am. Chem. Soc.*, **95**, 975 (1973).
- (10) W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, D. Jordan, and W. Kitching, *J. Am. Chem. Soc.*, **96**, 1595 (1974).
- (11) D. Doddrell, M. Barfield, W. Adcock, M. Aurangzeb, and D. Jordan, *J. Chem. Soc., Perkin Trans. 2*, submitted for publication. We thank Professor Barfield for a preprint.
- (12) D. Doddrell, D. Jordan, and N. V. Riggs, *J. Chem. Soc., Chem. Commun.*, 1158 (1972).
- (13) R. L. Lichter and R. E. Wasylshen, *J. Am. Chem. Soc.*, **97**, 1808 (1975).
- (14) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975).
- (15) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).
- (16) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 1 (1970).
- (17) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 11 (1970).
- (18) J. M. Schulman and M. D. Newton, *J. Am. Chem. Soc.*, **96**, 6295 (1974).
- (19) A. C. Blizzard and D. P. Santry, *Chem. Commun.*, 1085 (1970).
- (20) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).
- (21) K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Am. Chem. Soc.*, **94**, 4078 (1972).
- (22) I. Brown and D. W. Davies, *Chem. Commun.*, 939 (1972).
- (23) C. Haigh and S. Sykes, *Chem. Phys. Lett.*, **19**, 571 (1973).
- (24) See ref 3, Chapter 5, for a discussion of substituent influences on C-13 shifts.
- (25) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967).
- (26) H. Schneider and V. Hoppen, *Tetrahedron Lett.*, 579 (1974).
- (27) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973).
- (28) E. L. Eliel et al., *J. Am. Chem. Soc.*, **97**, 322 (1975).
- (29) The additional shielding of C(2) by the γ -substituent in **15**, **16**, **18**, and **19** leaves no doubt about the assignment relative to C(6).
- (30) Such a shielded position requires that C(2) be subject to shielding by both the neighboring fluorine and a γ -substituent effect from the hydroxyl; cf. C(2) in **15** (Table II).
- (31) R. Jost, J. M. Sommer, and T. Drakenberg, *J. Chem. Soc., Perkin Trans. 2*, in press. We thank Dr. Sommer for a preprint.
- (32) For a discussion on the magnitude of this γ -substituent effect in 1-fluoronaphthalene, see ref 6.
- (33) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).
- (34) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960), and references therein.
- (35) J. W. Timberlake, J. A. Thompson, and R. W. Taft, *J. Am. Chem. Soc.*, **93**, 274 (1971), and references therein.
- (36) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94**, 3089 (1972).
- (37) P. C. Lauterbur, *Tetrahedron Lett.*, 274 (1961).
- (38) See, for example, W. Adcock and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 379 (1967).
- (39) D. A. Forsyth, R. J. Spear, and G. A. Olah, *J. Am. Chem. Soc.*, submitted for publication.
- (40) G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, **39**, 2394 (1974).
- (41) Although the sign of $^2J_{CF}$ has not been determined for any fluorobenzene, the sign in **1–19** can be assumed to be positive by analogy with the sign determination in 1,2-dichloro-1,2-difluoroethene; G. V. D. Tiers and P. C. Lauterbur, *J. Chem. Phys.*, **36**, 1110 (1962), and examples in ref 3.
- (42) From ref 4. We have also determined the carbon-fluorine couplings from the ^{13}C NMR spectrum: $^1J_{CF}$, 344.7 Hz; $^2J_{CF}$, 60.1 Hz; $^3J_{CF}$, 4.2 Hz; $^4J_{CF}$, 1.2 Hz; $^5J_{CF}$, <1 Hz, in SO_2 at $-40^\circ C$.
- (43) D. J. Chadwick, *Tetrahedron Lett.*, 679 (1975).
- (44) For a discussion of these effects in vicinal proton-proton coupling, see L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon, London, 1969, pp 283–284.
- (45) (a) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 7107 (1970); (b) D. Doddrell, C. Charrier, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 1649 (1970).
- (46) W. Kitching, M. Bullpitt, D. Doddrell, and W. Adcock, *Org. Magn. Reson.*, **6**, 289 (1974).
- (47) G. A. Olah, R. D. Porter, C. L. Jewell, and A. M. White, *J. Am. Chem. Soc.*, **94**, 2044 (1972).
- (48) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 2686 (1973).
- (49) Based on signs of J_{CF} suggested by Roberts for fluorobenzene in ref 6.
- (50) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).
- (51) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).
- (52) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
- (53) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4151 (1970).
- (54) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).
- (55) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).
- (56) M. Barfield and M. D. Johnston, Jr., *Chem. Rev.*, **73**, 53 (1973).
- (57) D. A. Tomalia, *J. Org. Chem.*, **34**, 2583 (1969).
- (58) G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 3706 (1973).
- (59) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 3212 (1973).
- (60) G. A. Olah, G. D. Mateescu, and Y. K. Mo, *J. Am. Chem. Soc.*, **95**, 1865 (1973).
- (61) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974).