^{13}C Nuclear Magnetic Resonance Studies of Some Fluorinated and Trifluoromethylated Aromatic Compounds. Studies on ^{13}C–^{19}F Coupling Constants

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Carbon-13 n.m.r. spectra of a wide variety of carbocyclic and heterocyclic fluoro-, difluoro-, trifluoromethyl-, and fluoro-trifluoromethyl-substituted aromatic compounds have been examined and assigned. Substituent effects on the ^{13}C chemical shifts and one-bond and long range ^{13}C–^{19}F scalar coupling constants have been extracted. Experimental coupling constant data are compared with representative calculated results using INDO semi-empirical molecular orbital theory. The poorest agreement is for geminal and long range ^{13}C–^{19}F coupling, which can only be partially attributable to the neglect of orbital and spin dipolar mechanisms. By means of a valence-bond bond-order formulation for coupling constants, an expression is derived for the relationship between ^{13}C–^{19}F and ^{1}H–^{19}F coupling constants. The previously used proportionality is shown to be an over-simplification. Systematic trends of the great variety of experimental ^{13}C–^{19}F coupling constant data with structural and electronic factors are discussed qualitatively. The substituent effect of the trifluoromethyl group on the ^{13}C chemical shifts in benzene and naphthalene is discussed and it is proposed that field effects are important in explaining the chemical shift trends.

THE ease of interpretation of proton-decoupled ^{13}C spectra has resulted in an upsurge of interest in one-bond and long range ^{13}C–X (X=heteroatom, metal atom, *etc.*) scalar couplings and in recent publications[1] we have demonstrated the structural utility of such investigations. Whereas ^{13}C–^{13}C couplings may be understood in terms of Fermi contact interactions and good correspondence is usually obtained between experimental and theoretical

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[1] D. Doddrell, M. Bullpitt, C. Moore, C. Fong, W. Kitching, W. Adcock, and B. Gupta, *Tetrahedron Letters*, 1973, 665; D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, E. J. Mynott, J. L. Considine, H. J. Kuivilla, and R. H. Sarma, *J. Amer. Chem. Soc.*, 1974, **96**, 1640; F. A. L. Anet, J. Krane, W. Kitching, D. Doddrell, and D. Praeger, *Tetrahedron Letters*, 1974, 3255; W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *ibid.*, 1975, 759.

couplings by use of the INDO finite perturbation method,[2] ^{13}C–^{19}F couplings are less well understood.[3] Previous investigations by Blizzard and Santry[4] and others[5] on ^{19}F–^{19}F coupling suggest that Fermi contact interactions are not solely responsible for the transmission of nuclear spin information between pairs of interacting nuclei and other processes, particularly orbital (OB) and spin dipolar (SD), need to be considered. It is therefore likely that other mechanisms besides Fermi contact are also important in controlling ^{13}C–^{19}F couplings.

TABLE 1

^{13}C Chemical shifts[a] and C–F coupling constants[b] for some selected fluoro- and trifluoromethyl-substituted aromatic compounds

Compound		C-1	C-2	C-3	C-4	C-5	C-6					CF_3
Fluorobenzene	σ	163.2	115.5	130.2	124.2	130.2	115.5					
	J_{CF}	245.6	21.0	7.9	3.2	7.9	21.0					
		(−245.3)^{c}	(+21.0)^{c}	(+7.7)^{c}	(+3.3)^{c}	(+7.7)^{c}	(+21.0)^{c}					
Trifluoromethylbenzene	σ	130.8	125.4	128.9	131.9	128.9	125.4					124.5
	J_{CF_3}	32.2	3.9	0.0	1.3	0.0	3.9					272.1
		(32.3)^{d}	(3.9)^{d}		(1.3)^{d}							(271.7)^{d}
1,3-Bis(trifluoromethyl)benzene	σ	132.4	122.9	132.4	129.1	130.1	129.1					124.1
	J_{CF_3}	33.3	3.9	0.0	1.2	0.0	3.8					270
	J_{CF_3}'	0.0	3.9	33.3	3.8	0.0	1.2					*g*
1,4-Bis(trifluoromethyl)benzene	σ	134.5	126.0	126.0	134.5	126.0	126.0					123.7
	J_{CF_3}	33.8	4.0	*g*	~1	*g*	4.0					272.1
	J_{CF_3}'	~1	*g*	4.0	33.8	4.0	*g*					*g*
								C-α	C-β			
2-Fluorostyrene	σ	124.6	160.0	114.4	126.3^{e}	123.1^{e}	128.1	128.6	115.3			
	J_{CF}	12.4	252.4	21.3	3.6	3.5	9.0	4.7	5.3			
3-Fluorostyrene	σ	140.2	112.3^{e}	163.4	114.0	129.5	121.8	135.9	114.1			
	J_{CF}	8.3	21.8	248.2	21.3	8.3	2.6	2.4	*g*			
4-Fluorostyrene	σ	133.3	127.0	114.4	162.0	114.4	127.0	135.2	112.3			
	J_{CF}	3.3	8.1	21.1	249.7	21.1	8.1	*g*	1.9			
								C-7	C-8	C-40	C-8a	
1-Fluoronaphthalene	σ	159.9	109.0	125.3	123.5	125.9^{e}	126.6	127.4^{e}	120.2	123.9	135.2	
	J_{CF}	254.7	19.6	8.9	4.5	1.2	*g*	3.3	5.6	16.4	4.7	
2-Fluoronaphthalene	σ	115.9	160.6	109.2	130.3	130.6	126.3	127.8	126.7	134.5	127.2	
	J_{CF}	25.9	248.8	21.0	10.1	*g*	2.8	1.2	*g*	9.9	5.1	
1-Trifluoromethylnaphthalene	σ	*f*	124.6	124.1	133.0	129.0	126.7	127.9	124.6	129.7	134.6	
	J_{CF}	*f*	*f*	*f*	*f*	*f*	*f*	*f*	*f*	*f*	*f*	*f*
2-Trifluoromethylnaphthalene	σ	126.0	*f*	121.7	127.4	128.3	129.1	128.1	129.2	132.5	134.9	124.9
	J_{CF}	4.5	*f*	3.2	*g*	*g*	*g*	*g*	*g*	*g*	~0.7	272.1

[a] In p.p.m. to high frequency of tetramethylsilane. [b] In Hz. [c] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 2361. [d] L. F. Johnson and W. C. Jankowski, ' Carbon-13 N.M.R. Spectra,' Wiley, New York, 1972. [e] Tentative assignment. [f] Poor spectral quality precluded determination of these quantities. [g] Unresolved or negligible splitting.

The difference between ^{13}C–^{19}F and other ^{13}C–X couplings is readily illustrated by considerations of results for monosubstituted phenyl derivatives.[6,7] For $X = {}^{1}H$, $^{11}B^-$, $^{31}P^+$, ^{119}Sn, ^{199}Hg, ^{205}Tl, and ^{207}Pb it has been shown experimentally that the magnitudes of the intra-ring coupling constants are such that $J_{C_m\text{-}X} > J_{C_o\text{-}X} > J_{C_p\text{-}X}$ whereas for ^{19}F (and ^{31}P)[6] the order is $J_{C_o\text{-}X} > J_{C_m\text{-}X} > J_{C_p\text{-}X}$. Although this feature of ^{13}C–^{19}F and C–X coupling has been well documented, no rationale has as yet been put forward.

In other studies we have demonstrated the utility of fluorine substituent effects and ^{13}C–^{19}F coupling constants in the assignment of the ^{13}C spectra of substituted aromatic compounds.[8] This method has been extremely useful as a means of spectral assignment in our studies of substituent effects by ^{13}C n.m.r. spectroscopy.[9]

In order to define further the factors controlling ^{13}C–^{19}F couplings and exemplify some of the important features of fluorine substituent effects on ^{13}C chemical shifts we have studied the ^{13}C spectra of some mono- and di-fluorinated, trifluoromethylated, and fluoro-trifluoromethylated aromatic compounds. We have also determined the substituent effect of the CF_3 group. Part of this work has been published in preliminary form.[10]

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[2] D. Doddrell, I. Burfitt, J. Grutzner, and M. Barfield, *J. Amer. Chem. Soc.*, 1974, **96**, 1241; M. Barfield, I. Burfitt, and D. Doddrell, *ibid.*, 1975, **97**, 000; G. E. Maciel, J. W. McIver, jun., N. S. Ostlund, and J. A. Pople, *ibid.*, 1970, **92**, 11.

[3] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 2361; N. Muller and D. J. Carr, *J. Phys. Chem.*, 1963, **67**, 112; R. K. Harris, *J. Mol. Spectroscopy*, 1963, **10**, 309; G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1962, **84**, 3972; S. Mohanty and P. Venkateswarlu, *Mol. Phys.*, 1966, **11**, 329; G. Miyajima, H. Akiyama, and K. Nishimoto, *Org. Magnetic Resonance*, 1972, **4**, 811; G. A. Olah, R. J. Spear, and D. Forsyth, *J. Amer. Chem. Soc.*, in the press.

[4] A. C. Blizzard and D. P. Santry, *Chem. Comm.*, 1970, 1085; *J. Chem. Phys.*, 1971, **55**, 950; A. D. C. Towl and K. Schaumburg, *Mol. Phys.*, 1971, **22**, 49; H. Jensen and K. Schaumburg, *ibid.*, p. 1041.

[5] K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1972, **94**, 4018; K. Hirao, H. Nakatsuji, and H. Kato, *ibid.*, 1973, **95**, 31.

[6] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 4940.

[7] D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Kitching, and W. Adcock, *Austral. J. Chem.*, 1974, **27**, 417; W. Kitching, D. Praeger, C. J. Moore, D. Doddrell, and W. Adcock, *J. Organometallic Chem.*, 1974, **70**, 339; unpublished results.

[8] S. P. A. Rizvi, B. D. Gupta, W. Adcock, D. Doddrell, and W. Kitching, *J. Organometallic Chem.*, 1973, **63**, 67; W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, D. Jordan, and W. Kitching, *J. Amer. Chem. Soc.*, 1974, **96**, 1595.

[9] D. Doddrell and P. R. Wells, *J.C.S. Perkin II*, 1973, 1333; W. Kitching, M. Bullpitt, D. Doddrell, and W. Adcock, *Org. Magnetic Resonance*, 1974, **6**, 289; W. Adcock, M. Aurangzeb, W. Kitching, N. Smith, and D. Doddrell, *Austral. J. Chem.*, 1974, **27**, 1817.

[10] D. Doddrell, D. Jordan, N. V. Riggs, and P. R. Wells, *J.C.S. Chem. Comm.*, 1972, 1158.

RESULTS

Chemical shift and coupling constant data for some selected monofluoro- and trifluoro-methylated aromatic compounds are listed in Table 1.

The spectral assignments for fluorobenzene are those of Weigert and Roberts [3] which are based on general considerations of substituent effects on ^{13}C chemical shifts in aromatic compounds. The assignments for the fluorostyrenes are less straightforward and are based mainly on chemical shift considerations and the expected magnitude of $^{13}C-^{19}F$ coupling constants available from Weigert and Roberts' extensive study on monosubstituted fluorobenzenes.[3] However, the assignment for C-β- in 4-fluorostyrene is quite certain, the chemical shift being consistent with a vinyl CH_2 group.[11] This carbon is coupled to the fluorine six bonds away, J_{CF} 1.9 Hz. We have discussed previously the assignments for trifluoromethylbenzene [1] and pointed out that the correct assignments are different from those put forward by Weigert and Roberts.[3] Our results demonstrate conclusively ^{19}F coupling to C-4 and no coupling to C-3 and -5. The spectra of 1,3- and 1,4-bistrifluoromethylbenzenes were readily assigned.

TABLE 2

^{13}C Chemical shifts [a] and C–F coupling constants [b] for some fluoropyridines

Compound		C-2	C-3	C-4	C-5	C-6
Pyridine [c]	σ	150.1	123.8	135.8	123.8	150.1
Pyridinium ion [c]	σ	142.3	127.9	148.1	127.9	142.3
2-Fluoropyridine	σ	164.1	109.7	141.3	121.4	147.9
	J_{CF}	238.3	37.8	8.0	3.8	15.5
2-Fluoropyridinium [d]	σ	163.7	110.9	144.4	122.5	146.0
	J_{CF}	250.8	32.6	8.9	4.4	10.0
3-Fluoropyridine	σ	138.3	159.9	122.1	124.2	145.6
	J_{CF}	23.3	258.8	18.2	3.8	3.6
3-Fluoropyridinium	σ	131.1	160.1	132.7	128.3	138.6
ion [d]	J_{CF}	34.4	257.2	18.2	7.1	3.6

[a] In p.p.m. downfield from tetramethylsilane. [b] In Hz. [c] Data from R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, 1968, **90**, 697, 4232. [d] Protonation affected by running the spectrum with CF_3CO_2H as solvent.

TABLE 3

^{13}C Chemical shifts [a] and C–F coupling constants [b] for some fluoroquinolines

Compound		C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
Quinoline [c]	σ	150.2	120.8	135.4	127.6	126.1	129.0	129.4	148.3	128.0
3-Fluoroquinoline	σ	142.0	160.3	118.2	127.8 [d]	127.9 [d]	128.8 [d]	130.2 [d]	146.3	128.9
	J_{CF}	27.0	257.0	16.1	3.6	*f*	*f*	*f*	1.7	5.3
5-Fluoroquinoline	σ	151.8	129.2	126.4	159.0 [e]	110.4	129.3	121.8	149.9	119.4
	J_{CF}	*f*	3.5	4.7	250 [e]	19.2	9.1	2.4	2.5	16.4
6-Fluoroquinoline	σ	144.4	120.5	134.2	109.8 [d]	159.3	118.3 [d]	130.8	148.4	127.7
	J_{CF}	*f*	*f*	5.3	21.8	250.1	26.5	9.1	2.3	10.0
8-Fluoroquinoline	σ	151.1	122.7	136.2	124.2	126.8	113.9	158.9	139.3	130.6
	J_{CF}	*f*	*f*	2.7	4.8	7.5	19.3	259.9	11.9	2.3

[a] In p.p.m. downfield from tetramethylsilane. [b] In Hz. [c] Data from R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.*, 1969, **91**, 6381. [d] Assignment is tentative. [e] Not precisely determined owing to partial overlap with C-4a signal. [f] Unresolved or negligible splitting.

The assignments given for 1-fluoronaphthalene are the same as those of Weigert and Roberts [3] except that in recent studies we have suggested that the assignments for C-5 and -7 may need to be reversed.[12] The assignments for 2-fluoronaphthalene are based on, among other evidence, results for 2-fluoro-6-methylnaphthalene [10] and show conclusively ^{19}F coupling to C-6. Weigert and Roberts proposed [3] that the fluorine was coupled only to carbons in the fluorinated ring.

The spectral assignments for the trifluoromethylated napthalenes are less certain particularly for the unsubstituted ring; nevertheless, the substituent effects derived for these compounds follow the same patterns as those found from the fluoro-trifluoromethylated derivatives where $^{13}C-^{19}F$ coupling constants can be used as a guide in making the assignments (see Discussion section).

^{13}C Chemical shift and $^{13}C-^{19}F$ coupling constant data for 2- and 3-fluoropyridine and their protonated forms are listed in Table 2. The spectral assignments for these compounds is quite straightforward based mainly on the expected chemical changes on protonation.[13]

Table 3 lists ^{13}C chemical shifts and $^{13}C-^{19}F$ coupling constants for some fluoroquinolines. In general, reasonable assignments can be made based on the chemical shift in quinoline [14] and data for the fluoropyridines and the expected magnitude of $^{13}C-^{19}F$ coupling constants. In a few cases the assignments must be considered to be tentative. Poor spectral signal-to-noise precluded investigations of the effects of protonation for these compounds.

Table 4 lists data for a series of difluorinated naphthalenes. For the majority of the unsymmetrical substituted compounds the spectra were sufficiently simple to yield complete analysis and chemical shift data and the two $^{13}C-^{19}F$ coupling constants could be readily extracted. As Weigert and Roberts [3] have pointed out, the ^{13}C in the symmetrically substituted cases forms the X part of an ABX spin system. The spectra obtained for these compounds showed appreciable second-order splittings, often the ^{13}C resonances appearing as 'apparent' 1 : 2 : 1 triplets. In these cases, as Weigert and Roberts have shown, insufficient data are available for a complete analysis.[3,15] For 2,6-difluoronaphthalene the spectral quality was sufficient for an analysis to be attempted. Considering C-3 and-7 and C-1 and -5 if it is reasonable to assume that the cross-ring coupling is small (*ca.* 0 Hz) then it is found that J_{FF} 7 Hz.

Table 5 lists data for some fluoro-trifluoromethyl substituted naphthalenes. For these compounds reasonable assignments could be made on the basis of the expected magnitude of $^{13}C-^{19}F$ coupling expected from the CF_3 group

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[11] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972.

[12] P. R. Wells, D. P. Arnold, and D. Doddrell, *J.C.S. Perkin II*, 1974, 1745.

[13] R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, 1968, **90**, 697, 4232.

[14] R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, *J. Amer. Chem. Soc.*, 1969, **91**, 6381.

[15] J. D. Roberts, 'An Introduction to Spin–Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra,' Benjamin, New York, 1961.

TABLE 4

^{13}C Chemical shifts[a] and C–F coupling constants[b] for some difluoronaphthalenes

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
1,2-F_2	σ	144.8[c]	146.5[c]	116.2	119.7	m	m	m	124.2	124.9	131.1
	$J_{\mathrm{CF-1}}$	252.2	11.5	*h*	4.8				7.3	12.9	3.5
	$J_{\mathrm{CF-2}}$	12.1	247.9	20.4	6.7				4.9	2.1	1.3
1,3-F_2	σ	159.9[c]	100.8	159.4[c]	106.5	127.8[c]	125.1[c]	m	m	126.9	134.5
	$J_{\mathrm{CF-1}}$	248.1	24.2	13.2	5.1	*h*	1.7			6.7	10.9
	$J_{\mathrm{CF-3}}$	12.6	29.5	256.7	20.9	*h*	*h*			4.8	5.8
1,4-F_2	σ	155.4	108.4[e]	108.4[e]	155.4	120.4[e]	126.9	126.9	120.4[e]	124.4[e]	124.1[e]
	$J_{\mathrm{CF-1}}$	254.0	16.0		5.9	3.0	*h*	*h*	3.0	11.7	
	$J_{\mathrm{CF-4}}$	5.9		16.0	254.0		*h*	*h*			11.7
1,5-F_2	σ	158.8	110.3[d]	125.9[e]	116.4[e]	158.8	110.3[d]	125.9[e]	116.4[e]	m	m
	$J_{\mathrm{CF-1}}$	254.5		4.8	4.8	254.5		4.8	4.8		
	$J_{\mathrm{CF-5}}$	5.6				5.6					
1,6-F_2	σ	159.2[c]	107.5[c]	120.9	126.9	116.2	161.7[c]	108.9[e]	m	m	136.5
	$J_{\mathrm{CF-1}}$	256.9	20.0	17.7	8.3	*h*	*h*	2.3			9.4[c]
	$J_{\mathrm{CF-6}}$	*h*	2.6	*h*	*h*	26.2	252.3	21.0			4.4[c]
1,7-F_2	σ	161.0	109.9	129.8	123.3	132.1	116.9	158.6	104.0	124.5	124.4
	$J_{\mathrm{CF-1}}$	250.7	19.6	9.1	4.1	*h*	*h*	6.1	6.0	16.7	8.8[c]
	$J_{\mathrm{CF-7}}$	*h*	*h*	3.0	*h*	4.9	25.6	255.3	18.2	9.1	3.0[c]
2,3-F_2	σ	113.4	150.1	150.1	113.4[e]	127.3	126.2	126.2	127.3	130.5[e]	130.5[e]
	$J_{\mathrm{CF-2}}$	7.0	255.2	17.7		*h*	*h*	*h*	*h*	3.8	
	$J_{\mathrm{CF-3}}$		17.7	255.2	7.0	*h*	*h*	*h*	*h*		3.8
2,6-F_2	σ	117.3	160.3	110.9	129.6[e]	117.3	160.3	110.9	129.6[e]	131.3[e]	131.3[e]
	$J_{\mathrm{CF-2}}$	25.4[f]	246.9	19.9[f]	6.1	*h*[f]	3.1	*h*[f]	6.1	4.2	4.2
	$J_{\mathrm{CF-3}}$	*h*[f]	3.1	*h*[f]		25.4	246.9	19.9[f]			
2,7-F_2	σ	115.3	162.0	110.3	130.4	130.4	110.3	162.0	115.3	135.5	127.6
	$J_{\mathrm{CF-2}}$	25.6[g]	258.8	21.6[g]	9.7	*h*	5.2[g]	*h*	2.4[g]	10.0	*h*
	$J_{\mathrm{CF-7}}$	2.4[g]	*h*	5.2[g]	*h*	9.7	21.6[g]	258.8	25.6[g]	10.0	*h*

[a] In p.p.m. downfield from tetramethylsilane. [b] In Hz. [c] Assignment could be reserved. [d] X part of ABX but poor spectral quality precluded a complete analysis. [e] Apparent triplet; coupling quoted is the observed splitting (see text). [f] From an analysis of the ABX pattern, $J_{\mathrm{FF}} = 7 \pm 1$ Hz. [g] Apparent splittings. [h] Unresolved. m = Multiplet.

TABLE 5

^{13}C Chemical shifts[a] and C–F coupling constants[b] for some fluoro-trifluoromethyl-substituted napthalenes

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a	CF_3
1-Fluoro-4-trifluoromethylnaphthalene	σ	161.3	109.0	125.6	*c*	124.4	128.9	127.1	121.5	*c*	*c*	124.7
	J_{CF}	248.5	21.2	10.0	*c*	2.5	<0.5	1.9	6.3	*c*	*c*	*d*
	$J_{\mathrm{CF_3}}$	*d*	*d*	6.2	*c*	2.5	*d*	*d*	*d*	*c*	*c*	272.7
1-Fluoro-5-trifluoromethylnaphthalene	σ	161.3	111.4	127.8	120.6	*c*	125.8	124.8	125.4	*c*	*c*	124.8
	J_{CF}	256.2	19.8	8.1	4.4	*c*	5.9	2.2	5.1	*c*	*c*	<0.5
	$J_{\mathrm{CF_3}}$	*d*	*d*	*d*	2.9	*c*	<0.5	*d*	~1	*c*	*c*	271.4
1-Fluoro-7-trifluoromethylnaphthalene	σ	159.4	111.1	128.4	123.9	128.9	122.5	128.4	119.0	122.8	136.0	124.4
	J_{CF}	254.0	19.5	8.4	4.3	3.1	~1	*d*	4.6	~15	~3	*d*
	$J_{\mathrm{CF_3}}$	*d*	*d*	*d*	*d*	*d*	2.9	32.0	5.3	*d*	~1.5	272.1
2-Fluoro-6-trifluoromethylnaphthalene	σ	117.9	162.1	111.4	131.6	125.9	*c*	122.7	128.6	135.8	*c*	*c*
	J_{CF}	25.7	249.2	21.2	9.5	1.2	*c*	0.9	5.9	9.6	*c*	*c*
		d	*d*	*d*	*d*	3.4	*c*	3.1	*d*	*d*	*c*	*c*
2-Fluoro-7-trifluoromethylnaphthalene	σ	118.8	161.5	112.2	130.6	129.2	121.1	*c*	125.2	133.4	126.0	124.8
	J_{CF}	25.3	248.6	21.1	9.1	1.2	3.2	*c*	5.7	9.5	~6	*d*
	$J_{\mathrm{CF_3}}$	*d*	*d*	*d*	*d*	*d*	2.9	*c*	4.8	*d*	*d*	273.5
2-Fluoro-8-trifluoromethylnaphthalene	σ	108.7	161.8	117.9	131.5	132.8	123.8	125.9	*c*	*c*	*c*	124.9
	J_{CF}	23.4	248.5	25.5	9.6	*d*	2.5	~0.5	*c*	*c*	*c*	*d*
	$J_{\mathrm{CF_3}}$	2.5	*d*	*d*	*d*	~1	*d*	5.9	*c*	*c*	*c*	273.2

[a] In p.p.m. to high frequency of tetramethylsilane. [b] In Hz. [c] Spectral complexity and/or long relaxation times precluded determination of these quantities. [d] Unresolved or negligible splitting.

and the fluorine from considerations of our data listed in Table 1. In many cases the resonances arising from C-4a and -8a could not be observed. This is probably the result of the expected long relaxation time of these carbons and their ' saturation ' resulting from the reasonably fast recycle times that needed to be employed. We have noted, however, that addition of small (a few mg) amounts of iron(III) acetylacetonate often helped in obtaining spectra because of the resultant shorter relaxation times under these conditions.

DISCUSSION

Coupling Constants

At an early stage in this investigation it was thought that certain aspects of the factors determining the signs and magnitudes of these coupling constants, especially the long-range ones, could be interpreted in terms of the Fermi contact (FC) coupling mechanism. In section (A) we compare the experimental results with the calculated Fermi contact contribution to the coupling using semi-empirical molecular orbital theory.[16] In section (B) a valence-bond bond order formulation,[17] which makes use of the relationship of coupling constants to Penney–Dirac bond orders, is used to relate the ^{13}C–^{19}F coupling constants to ^{1}H–^{19}F coupling constants, while in section (C) the individual types of coupling in the various compounds are examined, especially with a view to correlating

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[16] J. A. Pople, J. W. McIver, jun., and N. S. Ostlund, *J. Chem. Phys.*, 1968, **49**, 2960, 2965.

[17] M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, 1967, **91**, 1.

the data with such salient features as bond lengths and substituent effects.

(A) *Comparison of Calculated INDO–FPT* ^{13}C–^{19}F *Coupling Constant Results with Experimental Values.*— Calculated INDO–FPT (intermediate neglect of differential overlap approximation of finite perturbation theory) results for ^{13}C–^{19}F coupling constant in a series of fluoro-substituted aromatic compounds are compared with the experimental data in Table 6. Standard bond lengths and bond angles [18] were used for fluorobenzene and the fluoronaphthalenes, whereas representative experimental values [19] of structural data for the unsubstituted pyridine and quinoline were used for the other fluoroaromatic compounds in Table 6. In view of the extreme sensitivity of the calculated results to the assumed molecular geometry, the severity of this initial assumption should not be minimized. Indeed, one knows that there are substantial changes of the C–C bond lengths in naphthalene from the assumed value of 1.40 Å, and that the effects of fluorine substitution on the calculated π-bond orders suggest that this will also produce non-negligible changes in bond lengths and angles.

Substitution of the fluorine at C-1 of napththalene or C-8 of quinoline will produce additional steric effects on the geometry.[20] However, correspondence between calculated and experimental results in Table 6 is sufficiently inadequate that we can relegate the problem of poor structural data to that of a second-order effect. However, it is very apt to be a major factor in the apparent inconsistencies in the experimental coupling constant data in Tables 1—5.

TABLE 6

Calculated INDO–FPT results for Fermi contact coupling in a series of fluoro-substituted aromatic compounds compared with experimental results from Tables 1—5 [a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a	N-1 [b]
Fluorobenzene											
(calc)	−213.0	−1.7	12.4	−0.9	12.4	−1.7					
	(−207) [c]	(4.5) [c]	(9.6) [c]	(−0.8) [c]	(9.6) [c]	(4.5) [c]					
(exp) [d]	−245.3	+21.0	+7.7	+3.2	+7.7	+21.0					
1-Fluoronaphthalene											
(calc)	−204.4	−3.4	16.0	−0.6	2.4	−0.8	1.1	14.5	−3.2	8.7	
(exp)	−254.7	+19.6	+8.9	+4.5	±1.2	*f*	±3.3	±5.5	+16.4	+4.7	
2-Fluoronaphthalene											
(calc)	−5.1	−209.2	−1.4	10.0	0.8	1.3	−0.1	2.4	17.0	−1.7	
(exp)	+25.9	−248.8	+21.0	+10.1	nr	±2.8	±1.2	nr	+9.9	±5.1	
2-Fluoropyridine											
(calc)		−186.2	12.5	11.2	−0.5	16.1					38.7
(exp)		−238.3	+37.8	+8.0	±3.8	+15.5					(35—38) [e]
3-Fluoropyridine											
(calc)		−3.0	−222.6	−2.7	9.0	−0.9					−5.4
(exp)		+23.3	−258.8	+18.2	±3.8	±3.6					
5-Fluoroquinoline											
(calc)		−1.5	1.8	13.9	−206.0	−2.7	16.6	0.4	8.4	−5.1	−0.7
(exp)		*f*	±3.5	±4.7	−250.0	+19.2	+9.1	±2.4	±2.5	+16.4	
8-Fluoroquinoline											
(calc)		1.3	−1.8	3.8	0.2	14.8	−4.2	−230.0	−3.8	9.2	1.0
(exp)		*f*	*f*	±2.7	±4.8	+7.5	+19.3	−259.9	+11.9	±2.3	

[a] All values in Hz. [b] ^{14}N–^{19}F Coupling constants. [c] Extended Hückel results from ref. 3. [d] Signs from ref. 3. Coupling over 1—3 bonds in other compounds assumed the same. [e] T. Alger and H. S. Gutowsky, *J. Chem. Phys.*, 1968, **48**, 4625. [f] Unresolved splitting.

From the results of a very large number of calculations of coupling constants with different computational schemes and wavefunctions [21] for the FC term it is reasonable to expect that the best correspondence should be with the directly bonded and vicinal (one- and three-bond) and the worst would be for the geminal (two-bond) coupling constants. Indeed, the data for coupling over 1—3 bonds in Table 6 is consistent with this observation. The calculated directly bonded ^{13}C–^{19}F coupling constants are smaller in magnitude but of the correct sign. Since the *s*-orbital densities at carbon and fluorine are empirical values, which are greater than the Hartree–Fock values, we must not be overly impressed with quantitative agreement here. The calculated three-bond ^{13}C–^{19}F coupling constants are typically twice the experimental values in Table 6 and invariably positive in sign in conformity with the sign inferred for coupling over this many bonds in fluorobenzene.[3] The reasonable correspondence of several values in Table 6 must be fortuitous. On the basis of our failure to obtain agreement for these two types of coupling (as opposed to geminal C–F coupling), one is tempted to say that the quantitative inadequacy is due to our failure to include the OB and SD terms.

The calculated INDO–FPT results for Fermi contact coupling over two bonds in this series of compounds are invariably too small in magnitude and probably of the wrong sign as inferred from the value in fluorobenzene.[3] Clearly, the problems of integral cancellation, which

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[18] J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4353.

[19] L. E. Sutton, ed., *Chem. Soc. Special Publ.* No. 11, 1958; No. 18, 1965.

[20] M. A. Cooper, H. E. Weber, and S. L. Manatt, *J. Amer. Chem. Soc.*, 1971, **93**, 2369; S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *ibid.*, 1973, **95**, 975.

[21] M. Barfield and D. M. Grant, *Adv. Magnetic Resonance*, 1965, **1**, 149; J. N. Murrell, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 1; R. Grinter in 'Nuclear Magnetic Resonance,' ed. R. K. Harris, The Chemical Society, London, 1972, vol. 1; 1973, vol. 2; 1974, vol. 3.

caused serious difficulties in adequate descriptions of geminal H–H coupling,[21] have not disappeared in going to the more complex situation of coupling between carbon and fluorine. In general, it has been noted that geminal coupling constants are much more sensitive to the effects of changes in geometry,[22] substituents,[23] and solvents [24] than other types of coupling constants. Hence, some of the variations in the calculated and experimental results reflect these kinds of effects and are discussed in section (C). The extended Hückel MO [25] result for fluorobenzene (in parentheses in Table 6), which was obtained by Weigert and Roberts,[3] is of the correct sign. However, the sign of the geminal H–H coupling in the extended Hückel coupling constant treatment of Fahey *et al.*[26] is clearly related to the integral parameterization so that it is not possible to conclude that this is a superior computational scheme.

The failure of the calculated results to reproduce the experimental values of long range ^{13}C–^{19}F coupling constants in Table 6 would appear to provide further evidence that the Fermi contact mechanism does not dominate this type of coupling. This conclusion follows from the observation that the INDO–FPT scheme provides a generally adequate description of most types of H–H,[27] C–H,[28] C–C,[2] and H–F [29] coupling constants. The major question raised by poor agreement of the calculated INDO–FPT results in Table 6 is to what extent is the major inadequacy due to the wavefunctions [30,31] rather than the neglect of OB and SD terms? Existing theoretical treatments,[4,5] which include all three types of terms, have not provided an answer to this question. Not only does the inclusion of OB and SD terms introduce at least one more adjustable parameter, but it does not appear feasible to find a consistent set of scaling factors, which are applicable to more than a few items of ^{13}C–^{19}F coupling constant data. Therefore, the inclusion of the other terms as well as configuration interaction (CI) in the triplet manifold does not remove questions of the inadequacies of the molecular wavefunctions and/or molecular geometries.

(B) *Valence-bond Bond Order Formulation for* ^{13}C–^{19}F *Coupling.*—In the absence, therefore, of any suitable quantitative model for discussing ^{13}C–^{19}F coupling in these fluoroaromatic systems, consider the simple VB model which relates coupling constants to Penney–Dirac bond orders.[17] This model can be used to relate one type of coupling to another [32] without explicitly calculating any type of wavefunction, hopefully avoiding some of the drastic approximations described above. For molecular systems in which there are only small deviations from a localized bond description, coupling constants are related to the non-local bond orders of four electron fragments. These assumptions would certainly not be applicable to the highly delocalized π-electron contributions as would be present in the fluoroaromatic compounds described in this paper. Therefore, we are restricting ourselves to the question of C–F coupling, which is transmitted *via* the σ-electron system. It seems quite likely that the large magnitudes for coupling over 2—4 bonds is due to the dominance of effects taking place in the σ-electron system. However, the formulation in terms of VB bond orders could compensate for some aspects of σ–π exchange effects.

We will not review the theoretical formulation of ref. 17, but simply generalize the results [equation (25) of ref. 17] to the case in which there is more than one atomic orbital on each of the coupled nuclei [equation (1) where

$$J(\mathrm{C,F}) = K(\Delta E)^{-1}\Big[\sum_{i,j} p^0(c_i,f_j) + (3/2)\sum_{i,j,k} p^0(c_i,\sigma_j)p^0(\sigma_j,f_k)\Big] \quad (1)$$

K is a constant which is dependent on the magnetogyric ratios of the coupled nuclei, the *s*-orbital densities, and physical constants which do not depend on the type of nuclei involved, and ΔE is the so-called ‘ average excitation energy ’]. The $p^0(c_i,f_j)$ parameters are the bond orders based on four electron fragments associated with bonds i and j on the coupled carbon and fluorine atoms, respectively. The first sum in equation (1) corresponds to the previous definition [17] of *direct* (electron-mediated) coupling. The second summation in equation (1) corresponds to *indirect* mechanisms and involved summations over bonds associated with the atomic orbital σ_j, which are not associated with bonds to the coupled nuclei. An expression (2), analogous to equation (1), can be written for the situation of ^{1}H–^{19}F coupling by considering only the single 1*s* atomic orbital on hydrogen. The various

$$J(\mathrm{H,F}) = K'(\Delta E)^{-1}\Big[\sum_{j} p^0(h,f_j) + (3/2)\sum_{j,k} p^0(h,\sigma_j)p^0(\sigma_j,f_k)\Big] \quad (2)$$

terms of equation (2) have definitions which are completely analogous to those given for equation (1). It also follows from equation (20) of ref. 17 that (3) and (4) apply where $n_i = 0$ or 1 if h_i replaces c_i (see examples

$$p^0(c_i,f_j) = (-1)^{n_i}p^0(h_i,f_j) \quad (3)$$

$$p^0(c_i,\sigma_j) = (-1)^{n_i}p^0(h_j,\sigma_i) \quad (4)$$

described below), or if orbital c_j is directed toward orbital h_i, respectively.

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[22] G. E. Maciel, J. W. McIver, jun., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4151.

[23] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899; J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.

[24] M. Barfield and M. D. Johnston, jun., *Chem. Rev.*, 1973, **73**, 53.

[25] R. Hoffman *J. Chem. Phys.* 1963, **39**, 1397.

[26] R. C. Fahey, G. C. Graham, and R. L. Piccioni, *J. Amer. Chem. Soc.*, 1966, **88**, 193.

[27] G. E. Maciel, J. W. McIver, jun., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4497, 4506; M. Barfield, *ibid.*, 1971, **93**, 1066.

[28] G. E. Maciel, J. W. McIver, jun., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 1.

[29] R. E. Wasylishen and M. Barfield, *J. Amer. Chem. Soc.*, in the press.

[30] M. Barfield, A. M. Dean, C. J. Fallick, R. J. Spear, S. Sternhell, and P. W. Westerman, *J. Amer. Chem. Soc.*, 1975, **97**, 1482.

[31] E. Hiroike, *J. Phys. Soc. Japan*, 1967, **22**, 379.

[32] S. Karplus and M. Karplus, *Proc. Nat. Acad. Sci. U.S.A.*, 1967, **69**, 3204.

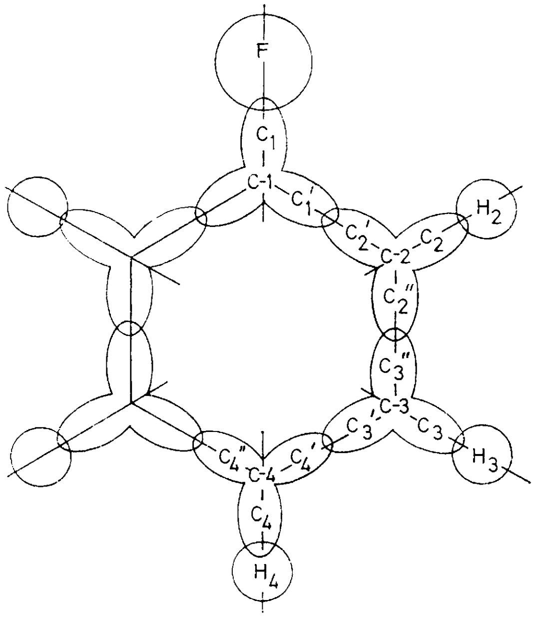
Substituting equations (3) and (4) into (1), and pulling the sum over i outside the brackets, the ^{13}C–^{19}F coupling constants are related to the fragment bond orders by equations (5). Substituting from equation (2) into (5),

$$J(\mathrm{C,F}) = K(\Delta E)^{-1}\sum_{i}(-1)^{n_i}[\sum_{i}p^0(h_i,f_j) + 3/2\sum_{j,k}p^0(h_i,\sigma_j)p^0(\sigma_j,f_k)] \quad (5)$$

we obtain a very simple result in which the ^{13}C–^{19}F coupling constants are related to the ^{1}H–^{19}F coupling constants and the troublesome ' average excitation energy ' fortunately cancels in the process [equation (6)].

$$J(\mathrm{C,F}) = (K/K')\sum_{i}(-1)^{n_i}J(\mathrm{H}_i,\mathrm{F}) \quad (6)$$

The summation in equation (6) is over all the bonds centred on the carbon atom and directed toward the protons H_i. For the case of sp^2 hybridization at the carbon atom the summation i will extend over the three hybrid orbitals, and for the case of SCF atomic orbital densities,[33] the coefficient in equation (6) is given by (7).



$$K/K' = \gamma_{\mathrm{C}}\phi^2_{2s}(\mathrm{C})/\gamma_{\mathrm{H}}\phi^2_{1s}(\mathrm{H}) = 0.422 \quad (7)$$

First, consider the case of ^{13}C–^{19}F coupling over two bonds. In the fragment depicted in the Figure there are three orbitals directed from C-2, but only one of these (c_2) is directed toward a hydrogen for which the coupling in fluorobenzene is known. The other two will have to be estimated from the best analogous H–F coupling situation which can be inferred. From equations (6) and (7) it follows that the two bond C–F coupling is given by (8)

$$J(\mathrm{C\text{-}2,F}) = 0.42\,[{}^2J(\mathrm{H_2',F}) - {}^3J(\mathrm{H_2,F}) - {}^3J(\mathrm{H_3'',F})] \quad (8)$$

where the first term in brackets is the geminal coupling constant which would be obtained on replacing the c_2' hybrid orbital on C-2 by the 1s atomic orbital of a hydrogen atom. The plus sign is used for this term in equation (8) because the orbital replaces the one on the carbon so that $n = 0$. Geminal H–F coupling constants in unsaturated molecules are typically *ca.* +85 Hz.[34] The second term in brackets in equation (8) is simply the *ortho*-H–F coupling in fluorobenzene, which has a value of +8.91 Hz.[3,35] The minus sign in equation (8) arises because the c_2 orbital is directed toward H_2. The remaining coupling constant in equation (8) is also not directly obtainable. If it is assumed that the *trans* : *cis* vicinal H–F coupling constant ratio[34] of 2.60 can be combined with the *ortho*-H–F coupling in fluorobenzene to give a reasonable value for *trans* aromatic H–F coupling, the value obtained is ${}^2J(\mathrm{H'',F}) + 23.2$ Hz. Substitution of these three values of the H–F coupling constants into equation (8) yields a ' calculated ' value of J(C-2,F) of +22.2 Hz to be compared with the experimental value of +21.0 Hz in Table 1.

For the case of ^{13}C–^{19}F coupling over three bonds equations (6) and (7) give the result (9) where the first

$$J(\mathrm{C\text{-}3,F}) = 0.42[{}^3J(\mathrm{H_3'',F}) - {}^4J(\mathrm{H_3,F}) - {}^4J(\mathrm{H_4',F})] \quad (9)$$

term in brackets corresponds to the previously deduced value of +23.2 Hz, and the second term is simply the experimental *meta*-H–F coupling constant of +5.70 Hz.[36] The last term in brackets in equation (9), which is a four-bond coupling, again has no experimental counterpart. Since it corresponds (see Figure) to a change from a *trans–trans*(*t–t*) or W arrangement to a *trans–cis*(*t–c*) or ' dipper ' arrangement, we again make the simplifying assumption of multiplying the *meta*-H–F coupling constant (5.70 Hz) by the vicinal H–F coupling *cis* : *trans* ratio (0.384)[34] and obtain a value of ${}^4J(\mathrm{H_4',F})$ of +2.19 Hz. This value is probably in the correct range as four-bond H–F coupling constants in 2-fluoroprene (2-fluorobuta-1,3-diene) are +0.41 and +1.19 Hz.[36] If fluoroprene was assumed to be planar, then the latter value would not be an unreasonable one to use. Substitution of the three values of the H–F coupling constants into equation (9) yields a value of J(C-3,F) of +6.4 Hz to be compared with the experimental value of +7.7 Hz in Table 1.

Coupling between ^{13}C and ^{19}F over the dual four bond path in the Figure is given from equations (6) and (7) as (10) where by symmetry the first two terms in brackets

$$J(\mathrm{C\text{-}4,F}) = 0.42[{}^4J(\mathrm{H_4'',F}) + {}^4J(\mathrm{H_4'',F}) - {}^5J(\mathrm{H,F})] \quad (10)$$

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[33] J. R. Morton, J. R. Rowlands, and D. H. Whiffen, National Phys. Lab. Report BPR 13, 1962, cited as footnote 36 in ref. 21.

[34] G. W. Flynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, 1963, **38**, 2295; R. A. Beaudet and J. D. Baldeschwieler, *J. Mol. Spectroscopy*, 1962, **9**, 30.

[35] L. C. Snyder, *J. Chem. Phys.*, 1965, **43**, 4041; T. F. Page, jun., *Mol. Phys.*, 1967, **13**, 523; S. Castellano, R. Kostelnik, and C. Sun., *Tetrahedron Letters*, 1967, 4635.

[36] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, 1965, **87**, 3445.

are identical, and equal to the value estimated above. The last term is simply the five-bond *para* H–F coupling constant of +0.22 Hz.[35] Coupling over the dual path suggests that some additional five-bond coupling constants should be included in equation (10). However, these must be so small that their inclusion would make little difference in this crude empirical scheme. Substitution of the values into equation (10) yields *J*(C-4,F) +1.8 Hz to be compared with the experimental value of +3.2 Hz from Table 1.

The results obtained here for coupling over two, three, and four bonds are certainly in much better correspondence with the experimental data than the theoretical results in Table 6. On this basis one is tempted to try extending the VB bond-order technique to some of the longer range coupling situations for which there is experimental data in the Tables. However, it was noted at the outset that the treatment was applicable to *localized systems*, *i.e.* systems for which deviations from perfect pairing are small. Clearly, the coupling transmitted *via* the π-electron systems of these aromatic molecules would be the worst possible case for applications of such a formulation.[37]

In concluding this section it should be noted that several groups [3,38] have suggested a relation of the form $^nJ(\mathrm{C,F}) = A\,^nJ(\mathrm{H,F})$, where $n = 1$—3 and $A = 0.4$—0.5. Clearly, this expression is a special case of equation (6) in which only that term corresponding to coupling over the same number of bonds is retained. For the case of the relationship of C–H to H–H coupling constants this appears to be a reasonable approximation,[39] but for the C–F coupling constants the use of only the first term in equation (8) gives 36 Hz for the two-bond ^{13}C–^{19}F coupling constant. The suggestion [3] of the importance of OB and SD mechanisms may be correct, but (as is so often the case in comparing calculated and experimental results) the over-estimation here was a manifestation of the use of only one term in the sun. Some concern might be expressed about the use of the ' average energy approximation ' in deriving equation (6) since this leads to results which are usually only of qualitative significance.[17] However, with the simplifying assumptions that were made in obtaining equation (1) it can be shown (Appendix of ref. 17) that the VB sum-over-triplet states [40] result differs from the simpler expression by a constant value, which would cancel in taking the ratio of two coupling constants. The mathematical details could be carried out, but would be cumbersome.

(C) *Systematic Correlations with Structural and Other Factors*.—(i) *Directly bonded coupling constants*. The directly bonded (aromatic C) ^{13}C–^{19}F coupling constants reported in Tables 1—5 range from a maximum absolute value of 259.9 Hz in 8-fluoroquinoline to a minimum absolute value of 238.3 Hz in 2-fluoropyridine. The calculated INDO–FPT results in Table 6 provide no help in sorting out the various factors which might be responsible for the observed 20 Hz variation. Nishimoto *et al.*[3] observed variations in the directly bonded C–F coupling constants by this amount in the series of *para*-substituted fluorobenzenes and found a reasonable correlation with C–F π-bond orders based on semi-empirical molecular orbital methods. In another study of ^{19}F n.m.r. of fluorobenzenes and fluoronaphthalenes, Manatt and his co-workers [20] found directly bonded ^{13}C–^{19}F coupling constants which ranged from 241.8 to 254.6 Hz. The latter value was obtained for the 1,8-difluoronaphthalene and it was assumed that the larger absolute value could be attributed to molecular distortion arising from juxtaposition of the two *peri*-fluorine atoms.

As an alternative to the proposal that enhanced ^{13}C–^{19}F coupling constants are due to distortions by *peri*-atoms, it is proposed that the variations observed in the series of molecules studied here are due to differences in the interactions of the C–F bonds with vicinal C–H bonds, lone-pairs, and vicinal C–N bonds. This is the type of term which occurs in equation (1) as the product of bond orders involving interactions with other bonds or orbitals in the molecule. For example, this type of term is responsible for the enhancement of geminal H–H coupling by adjacent π-bonds.[23]

Directly bonded ^{13}C–^{19}F coupling in the trifluoromethyl groups in Tables 1 and 5 are within experimental error of the value |272.1| Hz which occurs four times, and would be as good a value as any to adopt for this coupling.

(ii) *Geminal* ^{13}C–^{19}F *coupling constants*. The major factors affecting ^{13}C–^{19}F coupling constants over two bonds in fluorobenzene were reasonably well described by means of the valence-bond bond order formulation in section (B). Inspection of the experimental data in the Tables indicates that structural and substituent effects can produce substantial changes in the magnitudes of this type of coupling. For example, experimental values $^2J(\text{C-3,F}) = 37.8$ and 32.6 Hz in 2-fluoropyridine and its protonated analogue, respectively. This is probably due to the fact that an electronegative substituent, which produces a positive shift of geminal H–H couplings, has an analogous effect on $^2J(\mathrm{C,F})$. On the other hand, the 9 Hz increase of $^2J(\text{C-2,F})$ in 3-fluoropyridine on protonation compared with no change in $^2J(\text{C-4,F})$ has no obvious explanation.

The interpretation of two-bond ^{13}C–^{19}F coupling constants in terms of Penney–Dirac bond orders in section (B) tacitly assumed that this type of coupling would be determined primarily by the σ-electron framework. Indeed, there is little, if any, correlation of the $^2J(\mathrm{C,F})$ data in the Tables with the calculated C–C π-bond orders. However, in 1-fluoronaphthalene *J*(C-2,F) 19.6, *J*(C-4a,F) 16.4 Hz and the respective INDO π-bond orders are 0.762 and 0.494. However, the effect may be determined more by steric rather than

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[37] M. Barfield, C. J. Macdonald, I. R. Peat, and W. F. Reynolds, *J. Amer. Chem. Soc.*, 1971, **93**, 4195.

[38] A. De Marco and G. Gatti, *Spectrochimica Acta*, 1972, **28A**, 2295.

[39] G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, 1962, **84**, 37; F. J. Weigert and J. D. Roberts, *ibid.*, 1967, **89**, 2967.

[40] M. Barfield, *J. Chem. Phys.*, 1967, **46**, 811; 1969, **48**, 4458.

π-bond factors since the two-bond C–F coupling J(C-6,F) 12.4, J(C-3,F) 21.4 Hz in 2-fluorostyrene in Table 1. The bond orders for the C-1–C-2 and C-2–C-3 bonds in styrene are 0.638 and 0.678, respectively.

Possibly, a better correlation of the two-bond C–F coupling constant data is with the total electronic charge at the coupled carbon atom, which should be related to the ^{13}C chemical shift data. A plot of the geminal C–F coupling constant data *versus* ^{13}C chemical shift data from the Tables does show such a crude correlation. For example, in 1,2-difluoronaphthalene in Table 4 the values of ^2J(C-1,F-2) 12.1 and ^2J(C-2, F-1) 11.5 Hz correspond to δ(C-1) 144.8 and δ(C-2) 146.5 p.p.m. from tetramethylsilane, corresponding to substantial deshielding by the bonded fluorine atoms. The other extreme is noted for 24.2 Hz coupling to C-2 of 1,3-difluoronaphthalene (this corresponds to the most shielded carbon in the entire series) with δ(C-2) 100.8 p.p.m. However, note that the coupling to C-4a is only 12.9 Hz, and the chemical shift is intermediate (124.9 p.p.m.).

(iii) *Vicinal* ^{13}C–^{19}F *coupling constants*. As noted previously, the INDO–FPT results for ^{13}C–^{19}F coupling over three bonds were not as bad as those for ^2J(C,F). In most cases the values were of the correct sign, but about half the experimental magnitudes. An exception is 2-fluoropyridine, where the calculated results appear to be in fortuitously good agreement for this type of coupling. Furthermore, the VB bond-order formulation result for fluorobenzene was in reasonable agreement with the experimental value. Vicinal coupling constants have been generally better understood because the FC mechanism leading to most types of vicinal coupling is dominated by a single term, *i.e.* the interaction term between the hybrid orbitals directed to the coupled atoms, which has the mathematical form (11)

$$^3J(\phi) = A\cos^2\phi + B\cos\phi + C \qquad (11)$$

where ϕ is the dihedral angle measured about the C–C bond, and A—C are constants. For many types of coupling B is of opposite sign to A so that the *trans*-coupling is of greater absolute magnitude than the *cis*. In the case of vicinal H–H coupling the relationship of the constants in equation (11) to substituents[41] and bond orders[42] has been discussed extensively. The combination of conformation, substituent, and bond order effects must be responsible for the three-bond ^{13}C–^{19}F coupling constants of 8.9 to C-3, 4.7 to C-8a, and 5.6 Hz to C-8 in 1-fluoronaphthalene. The first two of these have *trans*-orientations of the coupled atoms, whereas the last conforms to a *cis*-arrangement. Comparable data for coupling over this many bonds in 5-fluoroquinoline are 9.1, 2.5, and 4.7 to C-7, C-4a, and C-4, respectively.

An interesting bond-order dependence, which parallels that noted for geminal coupling in 2-fluoronapthalene, is noted for the vicinal C–F coupling of ^3J(C-1,F) 4.5 and ^3J(C-3,F) 3.2 Hz in 2-trifluoromethylnaphthalene in Table 1. The INDO π-bond orders for the C-1–C-2 and C-2–C-3 bonds of trifluoromethylnaphthalene are 0.765 and 0.516, respectively. The same trends are noted for example in the three-bond couplings in the 1-fluoro- and 2-fluoro-7-trifluoromethylnaphthalenes in Table 5.

(iv) *Long-range* ^{13}C–^{19}F *coupling constants* (LRCFC). By analogy to the situation which obtains for long range H–H coupling constants, π-electronic effects on C–F coupling probably dominate when the number of bonds exceeds four. It was noted in section (B) that at least part of the coupling to the *para*-carbon in fluorobenzene could be accounted for in terms of the VB bond-order formulation. A most interesting result in the series of trifluoromethyl compounds in Tables 1—5 is the vanishing of the four bond ^{13}C–^{19}F coupling to the *meta*-carbon, and may be taken as diagnostic of a carbon in such a position. This coupling must be very small indeed, as no discernible broadening of the C-2 signal was noted for the 1,3-bis(trifluoromethyl)benzene. It is proposed that the vanishing of this four-bond coupling is due to some type of cancellation of the contributions arising from the σ- and π-electronic systems. The non-vanishing of the five-bond C–CF_3 coupling constants in this series of compounds also suggests that the σ-electron mechanism is effectively attenuated over this many bonds and that the π-electron transmission is the primary factor. The appearance of four-bond C–CF_3 coupling of magnitude 2.5 Hz between the 4-trifluoromethyl group and C-5 and 2.9 Hz between the 5-trifluoromethyl group and C-4 of the first two entries of Table 5 is indicative of a direct mechanism or possibly an unfavourable arrangement for transmission of coupling in the σ-electron framework.

Inter-ring coupling over four bonds occurs for the **W** or all-*trans*-arrangement of the bonds and ranges from 1.2 to 2.7 Hz in 1-fluoro(trifluoromethyl)naphthalenes, 3.3 Hz in 1-fluoronaphthalene, and 5.7 to 5.9 Hz in 2-fluoro-6(7)-trifluoromethylnaphthalenes. The larger values seem to be associated with transmission along the periphery of the molecule rather than through the C-4a–C-8a bond. For 1-fluoronaphthalene, the INDO–FPT results for **W** type coupling to C-5 and -8 are +2.4 and +1.1 Hz, respectively. Inter-ring LRCFC over four bonds is also observed for the dipper arrangement of the bonds connecting carbon and fluorine atoms and ranges from 1.9 to 2.2 Hz in 1-fluoro-4(5)-trifluoromethylnaphthalenes up to 3.5 Hz in 8-fluoroquinoline. Note, however, in the latter compound that coupling over a similar path involving the nitrogen gives no resolvable LRCFC. It is interesting to note that the calculated INDO–FPT result in Table 6 for this type of coupling is 2.4 Hz even though this type of coupling was not resolved in the ^{13}C n.m.r. spectrum of 2-fluoronaphthalene.

As noted above intra-ring C–CF_3 LRCFC is normally observed and falls in the range 0.7—1.3 Hz. However, inter-ring C–CF_3 coupling was not observed in any of the compounds studied. There are a number of possible geometrical (*cis*, *c*, or *trans*, *t*) arrangements about the three C–C bonds connecting the coupling nuclei. For

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[41] A. A. Bothner-By, *Adv. Magnetic Resonance*, 1965, **1**, 195.

[42] M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 1969, **91**, 6325.

example, values of 1.2 and 5.3 Hz are noted for the all-*trans* (*ttt*) arrangements which occur respectively in 2-fluoronaphthalene and 6-fluoroquinoline. LRCFC of 2.7 and 3.5 Hz were noted in the dual path (*ttc,ctc*) arrangements in 8- and 5-fluoroquinoline, respectively, but were not observed for this arrangement in 1-fluoronaphthalene. Furthermore, no LFCFC over five bonds was observed for the dual path (*tct,tct*) arrangement to C-5 in 2-fluoronaphthalene. Generally, the all-*trans* (*ttt*) arrangement is favoured if σ-electron mechanisms are dominant, but in aromatic systems in which the dominant effects are transmission in the π-electronic framework, one is more apt to observe sign alternation, rather than attenuation. The observation of 16 ^{13}C–^{19}F coupling constants in 1-fluoropyrene[43] clearly bears out this observation.

TABLE 7

^{19}F SCS[a] (p.p.m.) of *o*-fluoro-substituted 1- and 2-fluoronaphthalene and fluorobenzene

Compound		Solvent: Benzene	Solvent: Dimethylformamide
1,2-Difluoronaphthalene	(2α)[b]	−26.98	−27.35
1,2-Difluoronaphthalene	(1β)[b]	−26.96	−27.28
2,3-Difluoronaphthalene	(3β)[b]	−22.90	−23.67
1,2-Difluorobenzene	(*ortho*)	−25.9[c]	

[a] Defined as the difference between the chemical shift of the unsubstituted fluoroardmatic and the substituted fluoroardmatic compound. A negative sign implies shielding. [b] Refers to disposition. The Greek letter indicates the position of the fluorine atom, the numeral that of the other substituent. [c] H. S. Gutoursky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, 1952, **74**, 4809.

TABLE 8

^{13}C SCS[a] (p.p.m.) of *ortho*-disposed carbons in 1- and 2-fluoronaphthalene and fluorobenzene

Compound		SCS
1-Fluoronaphthalene	(1β)[b]	−16.9
2-Fluoronaphthalene	(2α)	−12.1
2-Fluoronaphthalene	(3β)	−15.2
Fluorobenzene	(*ortho*)	−14.1[c]

[a] Defined as the difference between the ^{13}C chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon. A negative sign implies shielding. [b] The Greek letter indicates the position of the carbon atom, the numeral that of the substituent. [c] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

TABLE 9

^{13}C SCS[a] of the carbons in 1- and 2-trifluoromethylnaphthalene and trifluorobenzene

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
1-Trifluoromethylnaphthalene	*b*	−1.2	−1.7	+5.0	+1.0	+0.9	+1.9	−3.4	−4.2	+0.7
2-Trifluoromethylnaphthalene	−2.0	*b*	−4.1	−0.6	+0.3	+3.3	+2.3	+1.2	−1.4	+1.0
Trifluoromethylbenzene	+2.4	−3.0	+0.5	+3.5	+0.5	−3.0				

[a] Defined as the difference between the ^{13}C chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon. A negative sign implies shielding. [b] Not determined, see Table 1.

LRCFC over six bonds of magnitude 1.9 Hz is observed to C-8 in 4-fluorostyrene, and of magnitude 2.8 Hz to C-6 in 2-fluoronaphthalene. The calculated INDO–FPT result for this type of coupling in Table 6 is 1.3 Hz. It will be interesting to see if improvements in the Fermi contact formulation will bring these long-range C–F coupling constants into correspondence, or whether the other terms in the Hamiltonian are essential The experimental data presented here provide a tremendously diverse source for further theoretical investigation.

Substituent Effects

In a previous study[44] the relative magnitude of the ^{19}F SCS (substituent chemical shift) for the cyano-substituent in the *ortho*-positions of 1- and 2-fluoronaphthalene and fluorobenzene ($1\beta \simeq 2\alpha >$ *ortho* $> 3\beta$)* was interpreted qualitatively in terms of partial bond-fixation in naphthalene. This was based essentially on the reasonable assumption that spatial 'proximity' factors should be the same in all three compounds and that differences in SCS reflect variances in through-bond interactions. It is of interest to note that the ^{19}F SCS for the fluorine substituent (Table 7) in the same orientations are also in accord with expectations based on this simple model. However, it should be noted that the order of the corresponding ^{13}C SCS ($1\beta > 3\beta >$ *ortho* $> 2\alpha$; Table 8) is quite different to that displayed by the fluorine nucleus. We can offer no rationale for this behaviour at present except to *note* that these effects may originate from the different responses of the ^{13}C and ^{19}F nuclei to field effects.[45]

^{13}C SCS values for the various carbons of 1-trifluoromethyl- and 2-trifluoromethyl-naphthalene and trifluoromethylbenzene are listed in Table 9. It is readily apparent that in 1-trifluoromethylnaphthalene the CF_3 group strongly deshields C-4, the effect being larger than for the corresponding position of trifluoromethylbenzene. We have noted and discussed in detail this feature of ^{13}C SCS values.[9] One other interesting feature which emerges from an inspection of the data is that there are large chemical shift charges induced in the unsubstituted ring, C-6 and -7 in 2-trifluoromethylnaphthalene being deshielded to about the same extent. This result alone implies that the CF_3 exerts a strong π-inductive effect as well as a field effect on ^{13}C chemical shifts. A similar deshielding effect operative at C-6 and -7 has been observed in the corresponding 2-nitro-compound.[12]

Except for cases where there are clearly likely to be

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* See footnote *b* to Table 7.

[43] A. Berg, P. E. Hansen, and H. J. Jakobsen, *Acta Chem. Scand.*, 1972, **26**, 2159.

[44] W. Adcock and S. Q. A. Rizvi, *Austral. J. Chem.*, 1973, **26**, 2659.

[45] W. Adock, M. J. S. Dewar, and B. D. Gupta, *J. Amer. Chem. Soc.*, 1973, **95**, 7353.

distortions of the molecular geometry because of through-space interactions between substituent groups the ^{13}C SCS induced by fluorine atom and/or trifluoromethyl group substitution appear to be quite additive and in most cases the carbon chemical shift can be predicted with a reasonable degree of confidence. This observation is quite consistent with our recent study of the ^{13}C chemical shifts in a variety of substituted naphthalenes.[12] The importance of this observation cannot be too strongly stressed. In previous studies,[8] we have often had to resort to fluorine substituent effects on ^{13}C chemical shifts and values of long range $^{13}C-^{19}F$ coupling constants in order to assign the ^{13}C spectra of aromatic hydrocarbons. The results reported in this study give support to this approach as a general method for ^{13}C chemical shift assignment.

The ^{13}C chemical shift changes induced in 2-fluoro- and 3-fluoro-pyridine on protonation should be noted (Table 2). In comparing the data to that given for pyridine and its protonated analogue it is readily apparent that the fluorine atom produces a large variation in the response of the ^{13}C chemical shift to introduction of the positive charge. For example, for pyridine, the chemical shift change at C-2 on protonation is —7.8 p.p.m. (shielding) whereas in 2-fluoropyridine it is —0.4 p.p.m. The other carbon positions show far less response than the corresponding positions in pyridine and this behaviour can readily be ascribed to the weaker base strength of 2-fluoropyridine compared with pyridine. However, the only position in 3-fluoropyridine that does not show the expected behaviour on protonation compared with pyridine is C-3. We can offer no rationale for this result at present.

EXPERIMENTAL

Spectra of some of the compounds in Tables 1 and 5 were obtained on a Bruker WH-90 Fourier transform n.m.r. spectrometer operating at 22.63 MHz. Spectra were recorded at 3 012 and 600.1 Hz spectral widths with 8K or 4K data points. Samples were prepared in deuteriochloroform with CS_2 as internal reference. In all cases maximum concentrations of the available materials were used. A modified [46] Varian HA60IL spectrometer was used to record the spectra of the remaining compounds. Cyclohexane or 1,4-dioxan was used as internal reference. All chemical shifts have been converted to the tetramethylsilane scale by use of the appropriate conversion factors.

Except for 1,2- and 2,3-difluoronaphthalene, all the difluoronaphthalenes and the trifluoromethyl-substituted fluoronaphthalenes were available from another investigation.[47] 1- and 2-Trifluoromethylnaphthalene were prepared according to a known procedure.[48]

1,2-*Difluoronaphthalene*.—1-Fluoronaphthalene (11.05 g, 0.076 mol) in tetrahydrofuran (50 ml) and ether (50 ml) was lithiated with t-butyl-lithium according to the method outlined by Kinstle and Beckner.[49] After 5 h at −60°, perchloryl fluoride gas [50] (10 g, 0.09 mol) was passed into the reaction mixture. Stirring was continued for a further 30 min at −60° and the mixture then allowed to come to room temperature. The excess perchloryl fluoride was removed by bubbling nitrogen through the mixture. The mixture was then poured into water and extracted with ether. The residue, after removing the solvent, distilled as an oil (7.5 g, 60%), b.p. 34—36° at 0.1 mmHg, n_D^{18} 1.575 (Found: C, 74.0; H, 3.75%; *m/e*, 164. Calc. for $C_{10}H_6F_2$:C, 73.15; H, 3.7%; *M*, 164). The compound was slightly contaminated with 1-fluoronaphthalene.

2,3-*Difluoronaphthalene*.—2-Fluoronaphthalene (11.05 g) was converted to a mixture of 1,2- and 2,3-difluoronaphthalene according to the method described above. Recrystallization from ethanol followed by sublimation afforded glistening crystals of 2,3-difluoronaphthalene (2.2 g), m.p. 62—64° (Found: C, 72.3; H, 3.88%; *m/e*, 164). The compound was slightly contaminated with 2-fluoronaphthalene.

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[46] D. Doddrell, F. B. Hanson, A. Marker, R. J. Kenny, and N. V. Riggs, *Austral. J. Chem.*, 1974, **27**, 2175.

[47] W. Adcock, J. Alste, S. Q. A. Rizvi, and M. Aurangzeb, unpublished results.

[48] T. E. Bull and J. Jonas, *J. Chem. Phys.*, 1970, **52**, 1978.

[49] T. H. Kinstle and J. P. Beckner, *J. Organometallic Chem.*, 1970, **22**, 497.

[50] F. L. Hedberg and H. Rosenberg, *J. Organometallic Chem.*, 1971, **28**, C14.