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(8) Because the vapor pressure of bromobenzene is low (~4 Torr at room temperature), small changes in the initial weight of bromobenzene result in negligible changes in pressure. Hence initial conditions are expressed in terms of the pressure of ICl and the molar ratio $[ICl]/[C_6H_5Br]$.
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Fluorine-19 NMR Studies of Fluoroaromatic Systems with Complete Proton Decoupling. The Signs and Magnitudes of Certain F···F and ^{13}C···F Spin-Spin Couplings[1a]

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Abstract: Using complete proton decoupling, the fluorine-19 NMR spectra of the ^{13}C satellites of a particular isotopomer of each of the difluorobenzenes and 1,8-difluoronaphthalene and two isotopomers of 2-fluorotrifluoromethylbenzene have been studied in $^{19}F[^{19}F]$ and $^{19}F[^{13}C]$ experiments. Based on the sign of the ^{13}C–F spin-spin coupling as negative, the signs and magnitudes of various F···F and ^{13}C···F couplings have been determined. These results are compared with other available pertinent spin-spin coupling information. Also, it was noted that the directly bonded ^{13}C-fluorine isotope chemical shift in the trifluoromethyl group is larger (11.1 Hz upfield) than observed in the case of fluorine bonded to sp^2 carbon (all about 8 Hz upfield). A significant result emerges relative to the sign of ^{13}C–C–C–F coupling, at least for molecular fragments involving sp^2 carbon. The stereochemical disposition of the spin coupled nuclei appears to matter very little and the observed sign must depend in a complicated manner on substituent effects. This conclusion stands in contrast to all previous observations on other types of vicinal couplings where stereochemical orientation has been demonstrated to be much more important than electronic substituent effects and can be determined from the coupling magnitude with some reliability.

Substantial interest in the NMR parameters of fluoroaromatic molecules has persisted for some years as various difficulties have accompanied the unequivocal establishment of the signs of the various F···F and F···H coupling constants. Originally this state of affairs no doubt arose because of the complexities of the observed ^{19}F and ^{1}H spectra. Perhaps another aspect of the problem has been that the observed trends of F···F coupling constants in many cases defy comparison with the intuition that the vast body of H···H couplings has instilled in chemists. Thus, some types of the H···F and F···F couplings in these systems have been shown to possess either positive or negative sign.[2-4] The observation of large-magnitude coupling constants between spatially proximate fluorine nuclei, which are separated by four or more bonds, has been another puzzling aspect of the problem of understanding F···F couplings.[5-10] The recent increased facility with which high-resolution ^{13}C spectral data can be obtained means that the various F···^{13}C couplings are potentially new indicators of the details of electronic structure of aromatic molecules.[2,11,12] Theoretical approaches for calculation of F···F and F···^{13}C couplings as yet have not always given satisfying explanations of experimental coupling constant results, especially when coupling constant sign information is available.[8,9,11-16]

The work described here was carried out to provide the signs of various F···X coupling constants (X = ^{19}F or ^{13}C) in some aromatic molecules possessing a minimum of halogen atoms or other substituents. Results for molecules possessing a minimum of substituents are particularly important because such systems are probably more amenable to theoretical treatments at the present time. The specific objectives were to establish unequivocally the signs of several F···F and F···^{13}C coupling constants in each of the difluorobenzenes and the sign of a large F-C-C-C-F coupling constant in an aromatic system less heavily fluorinated than all other molecules in which the sign of this coupling has been previously established.[5,9,10,17,18] We were also interested in obtaining information concerning the stereochemical specificity of the F-C-C-^{13}C coupling constant in sp^2 fragments. As yet systematic and complete studies of the magnitudes and signs of H···H, F···^1H, ^{13}C···H, F···F, and F···^{13}C coupling constants in any particular aromatic molecule are few[2,19] in spite of the great ease with which ^{13}C spectral data can now be obtained and the potential of such data for revealing very subtle aspects of aromatic molecular electronic structure. In the experiments reported here, ^{13}C spectra were not observed, but the approach was the use of ^{19}F proton decoupled spectra where either $^{19}F[^{19}F]$ or $^{19}F[^{13}C]$ experiments were utilized to obtain the coupling constant signs and, in some cases, magnitude information.

Experimental Section

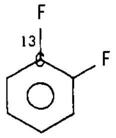
The difluorobenzenes and 2-fluorotrifluoromethylbenzene were commercial samples which proved to possess no major impurities from their ^1H and ^{19}F NMR spectra and gas chromatographic analyses; they were used without further purification. The sample of 1,8-difluoronaphthalene was that used in previous work.[20,21] All samples were studied at ambient probe temperatures (28-32 °C) and in 5-mm o.d. precision sample tubes. Two of the difluorobenzenes were studied as 50 v/v % solutions in CCl_4 while the 1,3 compound was studied in the latter solvent and as a 50 v/v % solution in acetone; the naphthalene was a 40 v/v % solution in acetone; the fluorotrifluoromethylbenzene was a 50 v/v % solution in $CDCl_3$. To each sample about 5 v/v % C_6F_6 was added to provide a locking signal. Samples were degassed for 30 s by a fine stream of purified nitrogen and capped by a plastic top before study. There was sufficient signal to noise from most samples that only single scans needed to be recorded except in the selective decoupling experiment with the two isotopomers of 2-fluorotrifluorobenzene where spectra were averaged with a HP-5480 averager.

The spectra were recorded essentially with the modified HA-100 spectrometer which has been described previously.[20] However, the double tuned 94.1/100 MHz probe system was further modified by provisions for tickling experiments at the ^{13}C frequency. This was accomplished by winding a coil tuned to 25.1 MHz on a "Teflon" former around the probe insert.[22] The ^{13}C frequency to this coil was derived from a HP 5100A synthesizer through an rf attenuator. In most experiments the audio sweep frequency, the 25.1 MHz and the 94.1 MHz or 100 MHz were all derived from synthesizers and the same 1 MHz source. The V-4354A manual oscillator frequency was used for the lock modulation and was found to drift very little (less than 0.2 Hz/h) when the room temperature was constant. Line position measurements determined with this system are believed to be accurate to at least ±0.2 Hz. In a few experiments four synthesizers were available so that the 94.1 MHz center band could be stabilized too. Because of the high concentrations of the samples studied, the chemical shifts reported in Table I relative to the frequency of the C_6F_6 lock are not regarded as particularly significant and are not discussed further. They are tabulated here mainly as an aid to others who subsequently might wish to perform similar experiments on related molecules. Some ^{19}F measurements were checked using a normal HA-100 lock and sweep system (spectrometer at the Universität Köln) but with a normal V-4333 probe transmitter coil tuned to accept mainly 100 MHz. Proton CW decoupling power in these experiments was provided by a second V-4311 rf unit which was fed a 16.6-MHz signal from a synthesizer.

Results

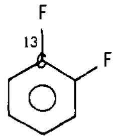
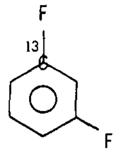
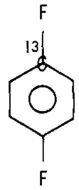
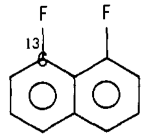
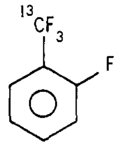
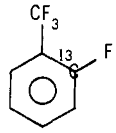
To set up the spectrometer for performing the multiple resonance experiments reported here, the following procedure was followed. The C_6F_6 signal of a 25 v/v % fluorobenzene solution in acetone was used to lock the spectrometer (high field modulation sideband of about 2000 Hz was chosen so that the fluorobenzene signal fell in the center of a 100 Hz sweep width). Next the fluorobenzene signals were monitored while either a high-level, noise-modulated (noise bandwidth 15-500 Hz), 100-MHz signal from the multiplier-mixed device described previously[20] was varied in frequency or a noise-modulated 100-MHz signal from the usual crystal controlled V-4311 unit was applied to the probe transmitter coil. In the former case a 100-MHz frequency lying in the center of the range that gave collapse of the proton line structure was selected. In the latter case, the 94.1-MHz center-band frequency of the fluorine-19 observing unit was varied and a frequency selected that gave complete collapse of proton fine structure. The procedure used depended on whether three or four frequency synthesizers were available. The triple resonance experiments which were performed varied somewhat from molecule to molecule and only in one case was more than one isotopomer studied. The coupling constant magnitudes that are reported are corrected for second-order effects as has been discussed previously;[20] this was not necessary in the case of the isotopomers of the fluorotrifluoromethylbenzene.

1,2-Difluorobenzene (1). Collapse of the proton couplings was achieved and the fluorine-19 ^{12}C signal for this molecule was set up to fall midrange on a 100-Hz sweep width with a locking modulation of 2070.00 Hz and a center-band frequency of 94 076 382.00 Hz. The spectral regions of interest, low-field ^{13}C-F satellites, ^{12}C region, and high-field ^{13}C-F satellites, which needed to be swept by the Barry Research LSC-7A digital sweep unit, as described before,[20] were from 4499.99 to 4400.00 Hz, 4399.99 to 4300.00 Hz, and 4299.99 to 4200.00 Hz, respectively. Example digital swept spectra of these three regions obtained with sweep width range switching, as described previously,[20] are shown in Figure 1d. Seven satellite lines of the possible eight for the isotopomer



were observed (seventh line of ^{13}C-C-F satellite not visible in the particular spectrum shown in Figure 1b). Measurements of these signals provided first-order estimates of ^{13}C-F and ^{13}C-C-F couplings and two ^{19}F-isotope chemical shifts, a one-bond one of 7.82 Hz and a two-bond one of 2.30 Hz (both upfield). One of the low-field (high-frequency) satellite members was monitored while the 25.1-MHz frequency was varied until splitting was noted. A systematic set of experiments was performed wherein various ^{13}C-satellite lines were mon-

Table I. Summary of Spectral Data[a]

	Isotopomer	$^{1}J_{^{13}C-F}$[b]	$J_{^{13}C\cdots F}$[b]	$J_{F\cdots F}$[b]	$\phi_{^{19}F}$[c]	$\phi_{^{13}C}$[c]	$\Delta\phi_{^{19}F(^{13}C-C^{12})}$
1		−247.1	+12.5	−20.5	94 080 736.3 (+24.281 ppm)	25 148 778.6	+8.0 (1 bond) +2.3 (2 bond)
2		−246.8[d]	+11.8[d]	+ 6.6[d]	94 082 502.3 (+43.052 ppm)	25 148 975.6	+8.0 (1 bond) +0.6 (3 bond)
3		−241.2	+2.5	+17.8	94 083 346.1 (+52.021 ppm)	25 148 761.0	+7.9 (1 bond)
4		−255.4	−1.6	+58.8	94 082 881.8 (+47.086 ppm)	25 148 936.3	+8.1 (1 bond)
5a		−271.8	−1.0	+12.8	94 082 980.7 (+48.137 ppm) (aromatic)	25 148 056.2	+11.1 (1 bond) +0.7 (3 bond)
					94 087 984.9 (+101.329 ppm) (trifluoromethyl)		
5b		−255.5	+2.6	+12.8			+8.8 (1 bond) +0.35 (3 bond)

[a] All measurements expressed in Hz unless indicated otherwise. [b] Corrected for second-order effects where necessary. [c] Adjusted to C_6F_6 resonance frequency of 94 078 452.00 Hz and 0.000 ppm. [d] For 50 v/v % CCl_4.

itored while the optimum ^{13}C tickling frequency was determined that gave a doublet splitting. In this way all four of the ^{13}C lines were located. Some typical results are shown in Figures 1a and 1c. Irradiation of the low-frequency ^{13}C line at 25 148 647.25 Hz and observation of the outer ^{13}C–F satellites establishes the relative signs of the ^{13}C–C–F and F–C–C–F couplings. Observation of the inner or ^{13}C–C–F satellites establishes the relative signs of ^{13}C–F and F–C–C–F. The results of these experiments can be interpreted in terms of the corresponding spin states of the irradiated line and the lines which exhibit doublet splittings. Thus, the experiment described above with the lowest frequency ^{13}C line perturbed both high-frequency members of the doublet ^{13}C–F satellites so that the signs of the ^{13}C–C–F and F–C–C–F couplings are opposite. With the inner ^{13}C–C–F satellites, the two lower frequency lines were perturbed (see Figure 1a where the change in the lowest frequency satellites is shown) so that the signs of the ^{13}C–F and F–C–C–F couplings are the same. Three additional ^{13}C tickling experiments at 25 148 661.35, 25 148 895.85, and 25 148 909.99 Hz were performed, and the observed spectral perturbations of the various lines were consistent with the first experiment. With no ^{13}C irradiation, $^{19}F[^{19}F]$ experiments were performed where the inner ^{19}F satellites were irradiated. When the lowest frequency member was irradiated (modulation 4336.20 Hz; observed Bloch-Siegert shift of about 0.4 Hz on the lock signal was observed), both high-frequency members of the ^{13}C–F satellites were split. This shows that the ^{13}C–F and ^{13}C–C–F coupling are opposite sign. A similar experiment on the eighth, unobserved ^{13}C–C–F satellite signal (4356.70-Hz frequency) confirmed this result. As has been discussed previously,[20] the observed first-order couplings for such ABC systems sometimes need to be refined to yield the true coupling constants. From the observed spacings and signs established above of −248.62, +14.12, and −20.50, iteration with LAOCOON III[23] yielded ^{13}C–F of −247.01, ^{13}C–C–F of +12.52, and F–C–C–F of −20.50 Hz with an rms error of 0.031 Hz. The experiments with **1** have been described in considerable detail so those with the other molecules studied here will be covered more briefly.

1,3-Difluorobenzene (2). In the case of this molecule, the proton noise decoupled ^{19}F spectrum has been exhibited before.[20] All four of the ^{13}C lines were located and the changes observed for the ^{13}C–F satellites and the two outer ^{13}C–C–C–F satellites were noted. In this case irradiation of the lowest frequency ^{13}C line produced changes in the lower frequency members of the ^{13}C–F satellites which showed that the ^{19}F–C–C–C–F and ^{13}C–C–C–F coupling signs are similar. This result was verified by irradiation experiments on the other three ^{13}C lines. Changes of the ^{13}C–C–C–F satellites were not sought in the case of this molecule. $^{19}F[^{19}F]$ experiments, where the

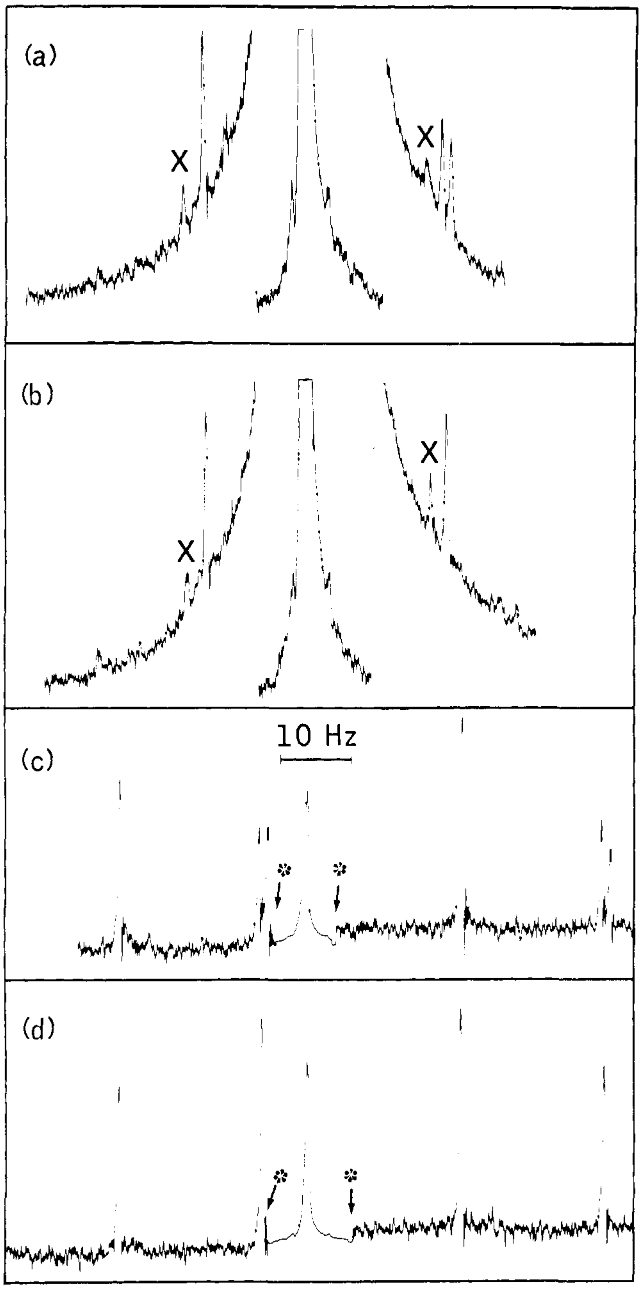
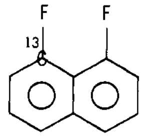


Figure 1. The ^{19}F spectrum of 1,2-difluorobenzene at 94.1 MHz in a 50 v/v % solution in CCl_4. Spectrometer was locked on C_6F_6 at 94 078 452.00 Hz; (X) denotes signals possibly from other isotopomers; (*) denotes digital sweep frequency range changes. Spectra (a) and (b) show two of the inner ^{13}C-satellite lines: (a) shows the result when the high-frequency (low-field) member of the low-frequency (high field) doublet in the ^{13}C spectrum is irradiated at 25 148 661.35 Hz. This result shows that the ^{13}C-F and F-C-C-F are of the same sign. Spectra (c) and (d) show the outer ^{13}C satellites and the center band at reduced gain: (c) shows the result of the ^{13}C irradiation experiment described above. This result shows that the ^{13}C-C-F and F-C-C-F are of opposite sign. Perturbation of the other three carbon transitions at 25 148 909.99, 25 148 895.85, and 25 148 647.25 Hz confirmed the above results.

various ^{13}C-C-C-F satellites were irradiated, gave results indicating that the ^{13}C-C-C-F and ^{13}C-F couplings are different signs and a three-bond isotope shift of 0.6 Hz upfield.

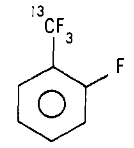
1,4-Difluorobenzene (3). For this molecule the four ^{13}C lines were located and irradiated in separate experiments. The changes in the ^{13}C-F satellites only were sought. These results indicated that the ^{13}C-C-C-C-F and F-C-C-C-C-F couplings were the same sign. ^{19}F-[^{19}F] experiments where the ^{13}C-C-C-C-F satellites were irradiated and the ^{13}C-F ones observed demonstrated that the signs of the ^{13}C-C-C-C-F and ^{13}C-F couplings were different.

1,8-Difluoronaphthalene (4). For this molecule the two pairs of ^{13}C-F satellite lines for the isotopomer below were easily observed.



They exhibited first-order F-C-C-C-F and ^{13}C-F coupling magnitudes of 58.8 and 268.1 Hz respectively with a one-bond isotope shift of +8.1 Hz. A number of troublesome spinning sidebands, perhaps impurity peaks and peaks from other isotopomers than the one shown above, were observed where the ^{13}C-C-C-F satellites were expected. The first experiments performed were ^{19}F-[^{19}F] ones to establish the first-order ^{13}C-C-C-F spacing, the lines belonging to the ^{13}C-C-C-F satellites and the signs of the ^{13}C-F and ^{13}C-C-C-F couplings. All four of the ^{13}C-C-C-F satellite lines were located and yielded a first-order spacing of 11.3 Hz and the conclusion that the first-order ^{13}C-F and ^{13}C-C-C-F couplings are of opposite sign. Four ^{13}C irradiation experiments were performed and led to the conclusion that first-order F-C-C-C-F and ^{13}C-C-C-F couplings are the same sign from the ^{13}C-F satellites and F-C-C-C-F and the first-order ^{13}C-F couplings are the opposite signs from the ^{13}C-C-C-F satellites. The first-order spacings in the ^{13}C spectra were 268.7 and 11.4 Hz for the ^{13}C-F and ^{13}C-C-C-F couplings. Application of LAOCOON III[23] to the line position measurements and assignment above, however, resulted in a ^{13}C-F coupling of −255.4, a ^{13}C-C-C-F coupling of −1.65, and a F-C-C-F coupling of +58.8 Hz with a rms error of 0.09 Hz. Thus, this spectrum is a case where two of the apparent first-order coupling constants are substantially different from the spacings exhibited in the experimental spectrum. Also, double resonance experiments interpreted in terms of a first-order spectrum lead to the incorrect sign for one of the couplings.

2-Fluorotrifluoromethylbenzene (5). Experiments were carried out on two isotopomers of this molecule. For the isotopomer shown below, **5a**, four ^{13}C irradiation experiments

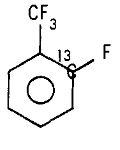


5a

were performed where the center four lines of the doublet of 1:3:3:1 quartets of the carbon spectrum were irradiated while the fluorine lines of the ^{13}C-F satellites were monitored. A first-order ^{13}C-C-C-F coupling of 1.0 Hz and a ^{13}C-F one of 271.8 Hz were measured. The perturbations of the $^{13}CF_3$ satellite lines (split into triplets) indicated that the F-C-C-C-F and ^{13}C-C-C-F couplings have opposite signs. From the ^{19}F spectrum a ^{13}C-F spacing of 271.5 Hz and an upfield isotope chemical shift of 11.1 Hz were observed. Two types of F-[^{19}F] experiments were carried out on this isotopomer. The $^{13}CF_3$ satellites were quite easy to observe so that they were utilized in four INDOR experiments[24] where the ^{13}C-C-C-F satellite region was swept while each of the four $^{13}CF_3$-C-C-F lines were monitored in turn. These experiments indicated that the signs of the ^{13}C-F and ^{13}C-C-C-F couplings are the same.

Selective decoupling experiments were also performed where both high-field members of the $^{13}CF_3$ satellite doublets were monitored while an irradiation field was applied in the vicinity of the high-field intense line of the ^{12}C-F quartet. The changes in the ^{12}CF$_3$ spectrum were first observed when the irradiating field was on the latter line. The results for such an experiment with an A_3X system have been described previously[25] and are that each member of the A_3 doublet should split into three lines. This was observed and the nature of the splitting pattern was observed to be quite sensitive (±0.1 Hz) to the position of the irradiating field. Next the corresponding ^{13}CF$_3$ satellites were monitored. It was noted that the low-field one exhibited an appearance qualitatively but not exactly similar to that of the ^{12}CF$_3$ spectrum. Setting the irradiating field 0.2 Hz lower in frequency yielded a spectrum for the former satellite lines which was identical with that of the ^{12}CF$_3$ spectrum for the irradiating field on resonance for the ^{12}C-F line. It was necessary to sweep at a rate of 0.2 Hz/s and to average 8 scans to obtain a good comparison between the ^{13}CF$_3$ satellite signals and a single scan of the ^{12}CF$_3$ line. In a similar manner, but monitoring the high-field ^{13}CF$_3$ satellite, the other member of the ^{13}C-F doublet was found to be 1.0 Hz to higher field of its partner. These results show a ^{13}C-C-C-F isotope shift of +0.7 Hz and first-order ^{13}C-C-C-F coupling of -1.0 Hz (sign same as the ^{13}C-F one).

No ^{13}C irradiation experiments were performed on the isotopomer **5b.** The sign of the F-C-C-C-F coupling relative to ^{13}C-F one follows from the experiments on **5a.** With **5b** the ^{13}C-C-C-F magnitude and sign were determined in ^{19}F[^{19}F] selective irradiation experiments. To accomplish this the ^{12}C high-field intense line of the 1:3:3:1 quartet was monitored while an irradiating modulation was set on the high-field line of the A_3 doublet. This split the ^{12}C-F line into a 1:3:3:1 quartet as has been described previously.[25] Next the corresponding ^{13}C-F satellite lines were observed. It required about 16 scans at a 1 Hz/s sweep rate to determine the degree of symmetry of the two central members of these double resonance quartets. An irradiating frequency 1.0 Hz higher than that for the high-field ^{12}CF$_3$ line yielded a symmetrical doublet for the high-field ^{13}C-F satellite line that was monitored. Similarly the other member of the ^{13}C-C-CF$_3$ satellite was found to be 1.6 Hz to lower frequency from the ^{12}CF$_3$ line by monitoring the corresponding low-field ^{13}C-F satellite line. The other two ^{13}C-C-CF$_3$ satellite lines were located in a similar manner. These results show that the ^{13}C-C-CF$_3$ coupling is +2.6 Hz and the corresponding isotope shift is +0.35 Hz in this isotopomer.



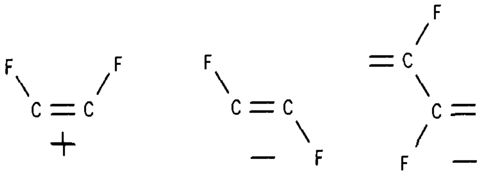
5b

Discussion

The coupling constant magnitude and sign results obtained here for **1–5** are summarized in Table I. These have been corrected where necessary for second-order effects. All the signs reported here are related to the sign of the ^{13}C-F coupling as negative.[26] This seems to be a well-established experimental fact, and the theoretical reasons for this now seem to be recognized.[27]

F···F Couplings. There are two classes of F···F couplings to which the results reported here relate. First, there are the F-C-C-F, F-C-C-C-F, and F-C-C-C-C-F couplings existing in **1–3.** Second, there are the F-C-C-C-F couplings in **4** and **5** which are believed to arise by a "through-space" mode of spin-spin coupling.[5-10,17,18]

There has been some debate concerning the sign of $^3J_{FF}$ in various types of molecular fragments. This coupling was determined to vary in sign in a number of olefin[28-31] and diene[32] systems as shown below.



The results for *cis*-1,2-difluoroethylene for a long time were believed to fit this pattern provided that the H-C-C-H in this molecule was negative.[33-37] The latter was considered to be a distinct possibility. Some theoretical calculations supported this possibility of *cis*-F—C═C—F as positive.[14,15] However, consideration of substituent effects[38] and more recent work[39,40] suggests that this opinion is wrong and the F-C-C-F coupling is negative for this olefin. The debate over this problem was reflected in the concern regarding the analyses of the NMR spectra of fluorinated aromatics,[2-4,41-43] but it would seem that the rather limited range of magnitude of this coupling in aromatic molecules[3,41] and the liquid crystal determination[44] of this coupling constant as negative in C_6F_6 should have settled the matter some time ago. The negative sign for this coupling obtained in **1** in the present work should further clinch the case for aromatic systems.

The positive sign results obtained here for the F-C-C-C-F and F-C-C-C-C-F couplings in **2** and **3,** respectively, should remove any doubts and are consistent with the various detailed substituent treatments of these couplings.[2,45] Such treatments have shown that these couplings can lie in the ranges of -20 to $+20$ Hz and 0 to $+18$ Hz, respectively, so that due consideration of substituent effects is required in interpretation of any observed couplings of these types.

The observation of very large coupling between fluorine nuclei separated by four and five bonds has been a very interesting facet of fluorine NMR parameters. That the sign of these large $^4J_{FF}$'s and $^5J_{FF}$'s might be positive was foreshadowed by the early observations that $^4J_{FF}$ in molecules like $CF_3CF_2CF_2X$ (where X was Br, Cl, and H) is positive.[29,30,46] This impression was supported by the first sign determinations of these couplings in some perfluorinated or nearly perfluorinated aromatic molecules[18] where they are very large. However, initially there were no reasons to believe that their signs would be positive in less fluorinated derivatives because, for example, the $^4J_{FF}$ couplings in aromatic systems exhibit substantial substituent effects which give rise to variation over a range of 40 Hz and couplings of both signs.[3,45] Concern that the possibility of a sign inversion for the $^4J_{FF}$ in **4** and **5** must be settled stemmed from certain theoretical calculations which suggested that this coupling was very distance dependent and in some cases might be negative.[14,15] We were particularly interested in **5** because results of some double resonance experiments on perfluorotoluene were interpreted as indicating that the CF$_3$-C-C-F coupling in that molecule was negative.[47] In some of our earlier work on solvent effects on F···F coupling, we tentatively suggested that this coupling should be positive.[48] The positive sign results found here for the $^4J_{FF}$ couplings in **4** and **5** indicate that perhaps the theoretical calculations alluded to above need to be amended to give only positive signs for this coupling, at least in systems like **4** and **5.** Also, the present results lend support to our previous solvent effect approach for finding F···F coupling sign information.[48] Further support of the sign result in **5** comes from a recent reinvestigation of perfluorotoluene where the CF$_3$-C-C-F coupling has been found to be positive[5] in contrast to earlier results.[47]

F···^{13}C Couplings. The ^{13}C-F coupling was originally shown to be of negative sign in a methane derivative,[26] and in view of its large magnitude (158–377 Hz)[49] there is little doubt that its sign is anything but negative. As mentioned before, it is this coupling to which all others in this study have been referred. Discussion of the ortho, meta, and para substituent effects[11,50,51] and steric effects[21,51] on this coupling have appeared elsewhere. Certainly substituent effects account for the variations observed in **1, 2,** and **3.** The difference in the value for ^{13}C–F observed in **4** (−255.4 Hz) from that in fluorobenzene (**6**) probably arises from two effects. The magnitude of one of these effects may be estimated by comparing the ^{13}C–F couplings in **6** (−245.8 Hz in 50 v/v % CCl_4)[20] and **2.** The fluorines in these two molecules are separated by the same number of bonds in these aromatic systems so perhaps the substituent effect of one fluorine atom on the other might be about the same or an effect of about −1.2 Hz. That the rest of the observed difference between the coupling in 2-fluoronaphthalene (**7**) (−244.7 Hz in 50 v/v % acetone)[20] and that in **4** arises from a steric effect of about −9.4 Hz has been discussed before.[21,51] The $^{13}CF_3$ coupling of 271.8 Hz in **5a** is about the same as that reported for benzotrifluoride (−272.1 Hz);[51] even though there is a sparcity of data on this coupling in the trifluoromethyl aromatic groups at this time, it appears that this coupling may be little affected by ring substituents.[51]

The ^{13}C–F coupling of −255.2 Hz in **5b** is substantially larger than that in **6.** Part of this may arise from steric origins and part from substituent effects of the adjacent CF_3 group. A rough estimate of the relative importance of these two effects can be made. In 2-fluorotoluene the ^{13}C–F coupling is −250.5 Hz.[52] The CF_3 group should be somewhat larger but not too different in steric size than the CH_3 group. Thus, roughly a −5 Hz steric contribution may exist in **5** which suggests that a similar magnitude substituent effect is present.

It was first recognized that the ^{13}C–F coupling was a different sign than the ^{13}C–C–F coupling in a number of fluorinated two-carbon molecules.[53-56] The magnitudes of this latter coupling lie over a rather large range (6 to 103 Hz);[11,12,39,53-56] the smallest value, 5.9 Hz, which occurs in *cis*-difluoroethylene, has been shown to be positive.[39] Thus, the ^{13}C–C–F coupling, as has been observed for the geminal F–C–F and H–C–F couplings,[57] appears always to be positive. This is in contrast to the signs of other geminal couplings, such as those in the H–C–H,[58] ^{13}C–C–H,[59] H–P–H,[60] P–C–H,[61] P–C–F,[62] and N–C–H[63] fragments which can be either sign. The magnitude of ^{13}C–C–F in **6** of about +21.0 Hz[11,19] compared with the value in **1** of +12.5 Hz indicates a substantial substituent effect. From the available ^{13}C–C–F data for a number of substituted fluorobenzenes[11] and 1,2-difluorobenzenes,[50,51] substituent contribution estimations have been derived[50] which suggest that in ortho derivatives an electronegative group reduces substantially the magnitude of this coupling to the substituted carbon.

Values of ^{13}C–C–C–F couplings in a number of aromatic systems have been reported but these have been for the situation where the dihedral angle between the ^{13}C–C–C and C–C–F planes is 180°.[2,11,12,51] Thus, the results for **4** and **5** represent two of the few examples where this angle is 0° and the first sign determinations for this orientation. In some work in which it was implied that most of the sign relationships between the various couplings in **6** could be derived from iterative analyses of the coupled ^{19}F and ^{13}C spectra,[19] this coupling has been given as +7.7 Hz. This stands in contrast to the results for **1** derived by matching of calculated ^{13}C spectra for various choices of the ^{13}C–C–C–F coupling to the observed spectrum for a different isotopomer than studied here. The observed ^{13}C spectrum was only consistent with a ^{13}C–C–C–F coupling of −3.0 Hz.[11] Data in this same work for a number of other ortho-substituted fluorobenzenes indicate that this coupling in the fragment $=FC=CX=^{13}C$ is always small and can be zero, a situation in which sign inversion could easily exist. In the same molecules, the other ^{13}C–C–C–F coupling in the fragment that involves the 5-carbon atom is about twice as large and does not exhibit substantial variation with change of substituent at carbon-2.[11] The ^{13}C spectrum of a different isotopomer of **4** than studied here[11] and extensive work on 1,3,5-trifluorobenzene (**8**)[2] found couplings of this type of +8.5 and +15.39 Hz, respectively. Thus, the results of a +2.5 Hz in **3,** −1.6 Hz in **4,** and −1.0 and +2.6 Hz in **5** reported here along with the other data discussed here suggest that the stereochemical dependence of this coupling is outweighed by various electronic substituent effects. Theoretical estimates of this coupling will have to be regarded with some caution until more experimental data are available.

The positive sign for ^{13}C–C–C–C–F in **3** is consistent with the only other sign determinations now available for this coupling. In **2** for a different isotopomer than studied here it was found to be +3.6 Hz;[11] in **6** it is reported as +3.22 Hz[19] and in **8** as +4.34 Hz.[2] Substituent effects on this coupling do not seem to be significant[11] so perhaps this coupling is always small (1.6–4.0 Hz) and positive.

Isotope Effects. The one-bond ^{13}C-fluorine isotope chemical shifts observed here in the case of aromatic fluorine (all about 8 Hz upfield) are consistent with what has been reported before.[2,20] In the case of **5,** the shift for the $^{13}CF_3$ group is rather larger (11.1 Hz upfield). The two-bond ^{13}C-fluorine isotope shift in **1** (2.3 Hz upfield) is similar to that observed in **8.**[2] The three-bond isotope shifts of 0.6 Hz upfield observed in **2** and 0.7 Hz in **5a** are close to that observed in **8** (0.65 Hz).[2] However, the 0.35 Hz upfield shift observed in **5b** is about half that observed in **2, 5a,** and **8.** This particular effect, however, involves a $^{13}CF_3$ group and not a ^{13}C–F situation so perhaps some difference is to be expected.

Conclusion

Another application of completely proton decoupled ^{19}F NMR spectroscopy to obtain ^{13}C spectral data has been demonstrated here. The signs of the F···F couplings in the three difluorobenzenes have been conclusively determined by relation to the sign of the ^{13}C–F coupling through a series of triple resonance experiments. The sign results for the large $^4J_{FF}$ in lightly fluorinated **4** should dispel any doubts that this coupling derived by strong "through space" fluorine–fluorine interactions can be anything but positive. The ABX spectrum of **4** represents a classical example of a rather simple spectrum where double resonance experiments interpreted in terms of the first-order spectrum would yield the incorrect sign for the ^{13}C–C–C–F coupling. Thus, the correct magnitude and sign for this coupling only emerges upon computer analysis of the spectrum. Also, the signs of some other ^{13}C···F couplings have been established in four other aromatic molecules. These results and other available results for the ^{13}C–C–C–F spin–spin coupling are significant. They demonstrate that it can have either sign even in one particular stereochemical disposition. Whether this is a peculiarity of the particular aromatic molecules for which sign information is presently available or a general complexity of this vicinal fluorine–carbon coupling remains to be seen. This problem certainly warrants further study. The results discussed here should provoke a challenge and due caution in dealing with this particular coupling constant. The use of this particular vicinal coupling to make stereochemical assignments thus appears not to be useful relative to the rather extensive use of other vicinal coupling constants for this purpose. It has been observed that the vicinal F–C–C–F coupling in saturated fragments also exhibits sign changes but these changes seem to be of a more predictable nature.[64] It remains to be seen whether the sign of vicinal ^{13}C–C–C–F couplings in nonaromatic systems exhibits the complicated changes observed and discussed here.

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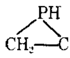

one of the P–C–H couplings is negative and the other positive (unpublished work of S. L. Manatt, M. T. Bowers, and H. Goldwhite). The P–C–H couplings of opposite sign in the same molecule have also been observed in other phosphorus(III) compounds (see, for example, D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, **819** (1967), and J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.* 40 (1969)).

(62) See A. H. Cowley and M. W. Taylor, *J. Am. Chem. Soc.*, **91**, 1026 (1969).

(63) For example, in $CH_3CH_2N{\equiv}C$ and $(CH_3)_2CHN{\equiv}C$ it is negative from a combination of $^1H\{^1H\}$, $^1H\{^{14}N\}$, and $^{15}N\{^1H\}$ experiments (unpublished work of S. L. Manatt, D. D. Elleman, and J. Casanova, Jr.; see also J. P. Maher, *J. Chem. Soc.*, 1855 (1966), for similar results on the former compound and W. McFarlane, *J. Chem. Soc. A*, 1660 (1967), for similar results on both). In contrast, in quaternary ammonium salts such as $CH_2{=}CHN(CH_3)_3$ and in the isonitrile $CH_2{=}CHN{\equiv}C$ this coupling is positive (S. L. Manatt and D. D. Elleman, unpublished work, and also for the former compound see M. Ohtsuru, K. Tori, J. Lehn, and R. Seher, *J. Am. Chem. Soc.*, **91**, 1187 (1969), and W. McFarlane, *J. Chem. Soc. A*, 1660 (1967)).

(64) See, for example, R. R. Ernst, *Mol. Phys.*, **16**, 241 (1969), and L. D. Hall, R. N. Johnson, J. Adamson, and A. B. Foster, *Chem. Commun.*, 463 (1970).