

PERTURBATIONS OF ${}^6\text{J}(\text{F},\text{CH}_3)$ BY RING SUBSTITUENTS IN
4-FLUOROTOLUENE DERIVATIVES. CONFORMATIONAL
IMPLICATIONS.

by

 Potlaki F. Tseki

A thesis submitted to
the Faculty of Graduate Studies
of the University of Manitoba in
partial fulfillment of the degree
Master of Science

Winnipeg, Manitoba,
July, 1988.

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I think that a lot of things happen by chance but within that element of chance there is an apparent order.

I wish to dedicate this thesis to the people who unselfishly and through their love made my education possible: my late father Peiso Stanford Tseki, my late friend and medical practitioner Dr. Carl vanAswagen and last but not least my late foster mother and friend Shirley Elizabeth Morgan.

Love like God is beyond the perception of any human being, and yet, its so true, pure and beautiful.

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Abstract

The six-bond long-range spin-spin coupling constant between methyl protons and the fluorine nucleus in derivatives of parafluorotoluene can be described by a σ - π interaction mechanism which is formulated as

$${}^6J_{H,F} = {}^6J_{90} \langle \sin^2\theta \rangle .$$

In order to study the substituent perturbations of the mechanism of ${}^6J_{H,F}$, the angle dependent $\langle \sin^2\theta \rangle$ term is kept constant at 0.5 by making use of the three-fold symmetry of the methyl group. In this way, any variations in ${}^6J_{H,F}$ must be due to intrinsic perturbations of the coupling mechanism and not due to conformational changes in the side chain. The experimental procedure involves preparation of samples for high resolution nuclear magnetic resonance spectroscopy using a variety of compounds covering a fair range of frequently encountered substituents. In most cases commercially available compounds are used. The spectra are obtained from the 300 MHz Bruker nmr spectrometer and analysed using the programme NUMARIT. The results suggest a variation of 10% in ${}^6J_{H,F}$ due to substituent perturbations and a negligible solvent effect. The errors in the twofold rotational barrier heights are estimated as 10% and 30% for benzylidene and benzyl derivatives of 4-fluorotoluenes, respectively. Therefore provided these errors are built into the analysis, this coupling constant can be used to determine approximate rotational barrier heights and conformational preferences in benzyl and benzylidene derivatives of 4-fluorotoluenes even in the presence of ring substituents. Similar variations for the other long-range spin-spin coupling constants are observed. However, ${}^5J_{C,F}$ is found to be exceptionally sensitive to intrinsic substituent perturbations, thus precluding its use in conformational work.

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INTRODUCTION

The long-range spin-spin coupling constant involving the methyl proton and the para ring proton in toluene arises from a σ - π transmission¹ mechanism. The σ - π spin-spin interaction mechanism assumes that the σ - π component of the long-range coupling constant for the coupled nuclei is simply proportional to the respective hyperfine interaction constants involving the π electrons and the adjacent σ orbitals as in [1]. In other words, the π framework is an efficient

$$J^\pi \propto Q_N Q_{N'} \quad [1]$$

transmitter of nuclear spin state information. For toluene the latter equation is explicitly written as in [2]. Q_{CH} is negative, Q_{CCH} is positive² and proportional to $\sin^2\theta$ as in figure 1.

$${}^6J^{H,H} \propto Q_{CCH} Q_{CH} \quad [2]$$

In a similar way, Schaefer and Wasylshen have shown that the six-bond coupling constant between the methyl protons and the fluorine nucleus in 4-fluorotoluene follows a σ - π spin-spin transmission mechanism, and is dominated by the σ - π component. The possibility of a small σ component is not ruled out¹. Therefore the analogous coupling in 4-fluorotoluene can similarly be expressed as in [3] below. Unlike its counterpart in toluene, Q_{CF} is positive in sign and is larger

$${}^6J^{H,F} \propto Q_{CCH} Q_{CF} \quad [3]$$

in magnitude² than Q_{CH} . A schematic representation of the σ - π spin-spin transmission mechanism for 4-fluorotoluene is depicted in figure 2.

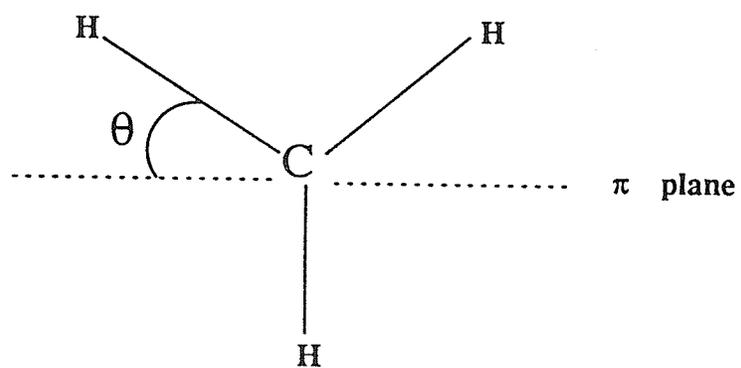
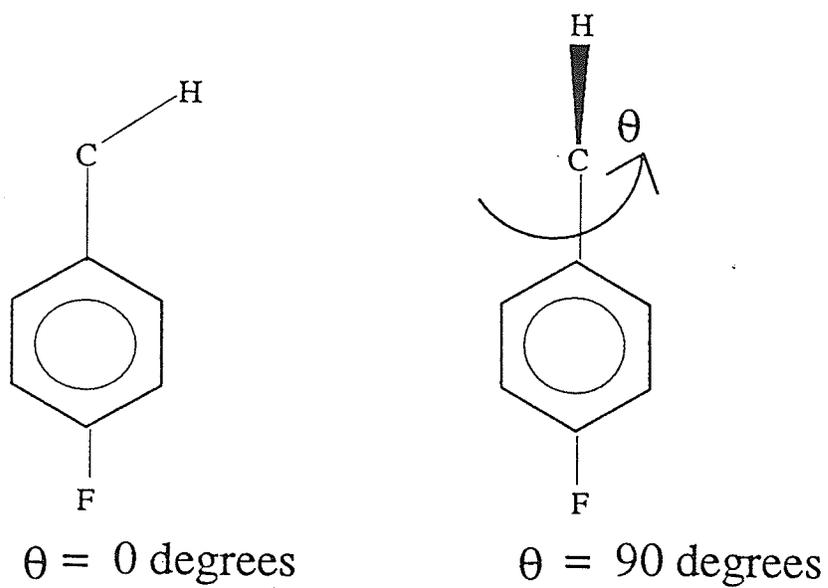


Figure 1.

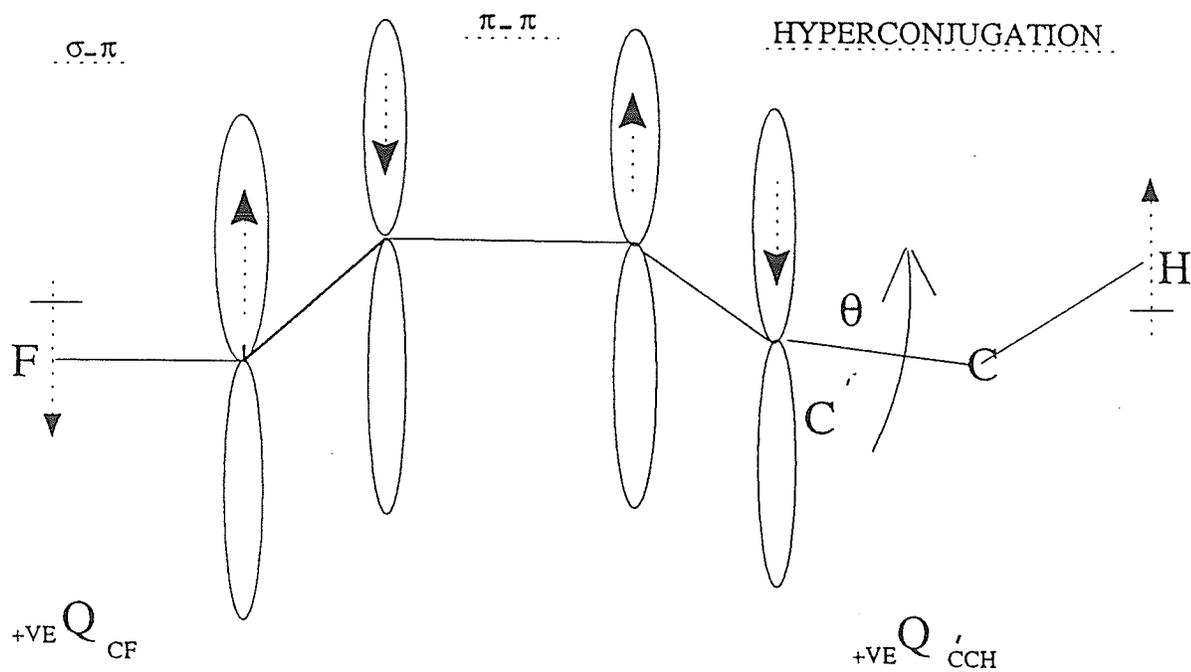


Figure 2.

A comparison of equations [2] and [3] prompts one to perform a calibration of equation [4] as follows.

$${}^6J_{H,F} = \frac{Q_{CF}}{Q_{CH}} {}^6J_{H,H} \quad [4]$$

Using the measured values^{2,3} for the parameters on the right of equation [4], ${}^6J_{H,H} = -0.602(2)$ Hz, $Q_{CH} = -22.5$ G and $Q_{CF} = 47.2$ G, ${}^6J_{H,F}$ is predicted to be 1.26(2) Hz. The measured values are 1.153(1) and 1.15(2) Hz in carbon disulfide and acetone- d_6 solutions, respectively⁴. This supports the view that ${}^6J_{H,F}$ is dominated by a σ - π electron contribution in 4-fluorotoluene.

In particular, the six-bond coupling constant in toluene is known to be insensitive to intrinsic substituent perturbations on the ring^{5,6}. Schaefer and Parr⁶ have shown that ${}^6J_{H,H}$ for benzyldene and benzyl derivatives of toluene depends on the conformation at the side chain as described by [5]. Here ${}^6J_{90}$ is the value of

$${}^6J_P^{H,H} = {}^6J_{90} \langle \sin^2\theta \rangle \quad [5]$$

${}^6J_{H,H}$ when θ is 90 degrees and θ is the angle by which the C-H bond of the group in the side chain twists out of the ring plane (see figure 1). The angular brackets denote the quantum mechanical expectation value of $\sin^2\theta$ taken over the hindered rotor states, at a given temperature. By equations [2] and [3] an equation similar to [5] can be written for 4-fluorotoluene. Here the variables have the same meaning

$${}^6J_{H,F} = {}^6J_{90} \langle \sin^2\theta \rangle \quad [6]$$

as for equation [5]. Because of the dependence of this coupling constant on the expectation value of $\sin^2\theta$, ${}^6J_{H,F}$ is used to determine ground state conformational preferences for benzyldene and benzyl derivatives of 4-fluorotoluene, and the corresponding small twofold⁸ barriers to internal rotation (≤ 13 kJ) about the exocyclic C_{sp^2} - C_{sp^3} bond.

It turns out that both quantum and classical averaging procedures of $\sin^2\theta$ give the same values for the range of V_2 values that can be studied by the J method. The classical averaging procedure for $\sin^2\theta$ for a barrier⁸, $V(\theta)$, follows in equation [7].

$$\langle \sin^2\theta \rangle = \frac{\int_{-\pi}^{\pi} \sin^2\theta \exp\left\{-\frac{V(\theta)}{RT}\right\} d\theta}{\int_{-\pi}^{\pi} \exp\left\{-\frac{V(\theta)}{RT}\right\} d\theta} \quad [7]$$

A computer program written in this laboratory⁹ accepts as input the functional form of the potential and the temperature T . Numerical integration is performed to give the expectation values of $\sin^2\theta$.

The expectation value of $\sin^2\theta$ can be obtained from [6]. The numerical value of $\langle \sin^2\theta \rangle$ indicates both the magnitude of the internal barrier to rotation and the preferred conformation for the side chain group of an α -substituted toluene or 4-fluorotoluene derivative. As already pointed out, the six-bond coupling constant in toluene is insensitive to intrinsic electronic ring substituent perturbations. However, ${}^6J_{H,F}$ in ring substituted derivatives of parafluorotoluenes may be sensitive to intrinsic substituent perturbations. The primary aim of this piece of work is to find out if this is so, and perhaps attempt to seek an explanation for the existence and nature of such a perturbation.

Note that since $\langle \sin^2\theta \rangle$ is always 0.5 for 4-fluorotoluene and derivatives (because of the three-fold symmetry of the methyl group), any variation in ${}^6J^{H,F}$ cannot be due to conformational changes in the side-chain, but must be due to intrinsic electronic perturbations of the coupling mechanism by the ring substituents.

High resolution proton, carbon-13 and fluorine-19 nmr spectra of selected compounds covering a fair range of substituents, namely, amino, halogen, alkyl and nitro in the two and three positions of 4-fluorotoluenes, are analysed in carbon disulfide, and for some also in acetone- d_6 solutions, to give the various nmr parameters. For the present study the intrinsic electronic substituent perturbations of the mechanism for the six-bond coupling constant, and the application of ${}^6J^{H,F}$ as a measure of the twofold barrier heights in benzylidene and benzyl derivatives of 4-fluorotoluene, is of immediate interest. The other exocyclic coupling constants, ${}^5J^{H,H}$, ${}^4J^{H,H}$, ${}^5J^{C,F}$ and ${}^1J^{C,F}$ will also be considered in the general context of intrinsic electronic ring substituent perturbations.

Experimental data show variation of ${}^6J^{H,F}$ of about 10% as a direct result of substituent perturbations of the coupling mechanism. Maximum values occur for the 3-fluoro and 3-nitro derivatives and minimum values are observed for the amino and the methyl derivatives. A negligible solvent effect is observed for this set of coupling constants (3% maximum). The perturbations of ${}^6J^{H,F}$ lead to an

estimated error in V_2 of about 10% for benzylidene derivatives of 4-fluorotoluenes, and 30% for the corresponding benzyl derivatives. It is concluded that these findings indicate that the errors due to substituents perturbations have to be built into the analysis for an accurate assessment of the twofold rotational barrier heights through ${}^6J^{H,F}$ by the J method.

Unpublished work in this laboratory, concerning standard INDO MO FPT computations of ${}^6J^{H,F}$ as a function of the angle θ by which the C-H bond of the methyl group twists out of the ring plane, indicates that this coupling constant may still be described by a $\sin^2\theta$ relationship even in the presence of ring substituent perturbations.

The nature of the intrinsic substituent perturbations of the mechanism of ${}^6J^{H,F}$ appears to be rather complex. However, the observed variation of ${}^6J^{H,F}$ in the presence of various ring substituents seems to be linearly correlated with the substituent induced electronic changes that are observed at the C-F bond. Specifically, the σ_{ST}^{10} for meta substituents correlate well with $({}^6J^{H,F} - {}^6J^{H,F}_{PFT}) \equiv \Delta^6J$, which appears as evidence in support of the hypothesis that the intrinsic electronic substituent perturbations of the coupling mechanism are dominated by the electronic changes occurring at the carbon-fluorine bond.

The second half of this presentation concerns the intrinsic perturbations of ${}^4J_{\text{H,H}}$ and ${}^5J_{\text{H,H}}$ by ring substituents. The spin-spin transmission mechanisms^{11,12} for these long-range coupling constants are very well established. The present data seem to indicate a similar variation in magnitude of these long-range proton-proton coupling constants as observed for ${}^6J_{\text{H,F}}$. Strong correlations exist among some of the proton-proton couplings and weak or no correlations with the ${}^6J_{\text{H,F}}$. Correlations are also observed for ${}^4J(\text{CH}_3, \text{H}_6)$ with the squares of the π bond orders along the respective coupling path, and for ${}^5J(\text{CH}_3, \text{H}_5)$ with the sum of the squares of the π bond orders for the intervening ring C-C bonds.

The final part of this work deals with the one-bond carbon-fluorine spin-spin coupling constant, ${}^1J_{\text{C,F}}$, and also with ${}^5J_{\text{C,F}}$. ${}^1J_{\text{C,F}}$ is negative¹³ and about 245 Hz in magnitude for most of the ring substituted derivatives of parafluorotoluenes. It is interesting to note that ${}^1J_{\text{C,F}}$ is linearly correlated with ${}^6J_{\text{H,F}}$ and therefore linearly correlated with the same electronic parameters determined at the C-F bond or fluorine atom as for ${}^6J_{\text{H,F}}$.

The long-range spin-spin coupling interactions involving the methyl carbon-13 and the fluorine-19 nuclei in 4-fluorotoluene derivatives, ${}^5J_{\text{C,F}}$, is comparatively easy to extract from a carbon-13 broad-band ${}^1\text{H}$ decoupled spectrum. However, its high sensitivity to intrinsic electronic substituent perturbations and marked dependence on solvent, in sharp contrast to the other long-range spin-spin coupling constants (${}^6J_{\text{H,F}}$ and ${}^6J_{\text{H,H}}$), renders it unsuitable as a reliable conformational indicator.

EXPERIMENTAL

Sample preparation

Most of the compounds studied were of commercial origin.

4-Fluoro-2-iodotoluene, 4-fluoro-3-nitrotoluene, 4-fluoro-2-nitrotoluene, 5-fluoro-2-methylaniline, 2-fluoro-5-methylaniline, 2-chloro-4-fluorotoluene and 4-fluorotoluene were all obtained from Aldrich Chemical Company. 3-Bromo-4-fluorotoluene and 3,4-dimethylfluorobenzene came from Pierce Chemical Company, 2,4-difluorotoluene came from Fairfield Chemical Company, and 2-bromo-4-fluorotoluene from Fluorochem. Fluorobenzene came from J. T. Baker Chemical Company. All the other 3-halogen substituted parafluorotoluenes and the 3-methyl-4-fluorotoluene were prepared by standard methods from the 3-amino derivative.

1.5g of 2.5 mole percent solutions of each compound were prepared in both carbon disulfide and acetone- d_6 solutions. Deuterated cyclohexane (10.0 mol%) was used as the internal lock for compounds prepared in carbon disulfide solution. Both tetramethylsilane and hexafluorobenzene (0.25 mol%) were used as internal references for proton and fluorine nuclei, respectively. 5mm od nmr tubes containing the compound in the appropriate solvent were flame-sealed after degassing several times by the freeze-pump-thaw procedure. For carbon-13 nmr, 1.5 g of 10 mole percent samples were prepared in both acetone- d_6 and carbon disulfide. The 5mm od tubes were flame-sealed.

Spectroscopic data

The ^1H nmr spectra for the samples were run on the Bruker AM 300 spectrometer at a probe temperature of 300 K. The proton nmr spectra were stored on both disk and hard copy. Several free induction decays (8-32) were accumulated for sweep widths ranging from 200-250 Hz for the benzene ring and 50-100 Hz for the methyl group. Adequate data regions were used to give acquisition times of about 40 s. Gaussian multiplication of the fids, with zero filling to twice the original size, was routinely done for all experiments.

The carbon-13 nmr spectra were obtained in a very similar manner. However, larger spectral widths of over 3500 Hz for some sections of the ring carbon atoms required larger data regions of about 128 K, and for such cases, zero filling before transforming the fids was not performed. Acquisition times for the ring sections of the molecules were generally greater than 20 s and were 40 s for the methyl carbons. The linewidths at half height ranged from 0.05 Hz to 0.08 Hz for the proton spectra and 0.075 to 1.00 Hz for the carbon-13 spectra.

Computational procedure

INDO molecular orbital theory with finite perturbation introduced at the fluorine atom (INDO MO FPT), and using standard geometries¹⁴, was employed to compute the spin-spin coupling constants from the fluorine in the para position to the methyl protons. Both INDO and CNDO bond orders and density matrices were simultaneously computed for all the molecules amenable to this computational procedure. The theoretical dependence of the coupling constant on the C-F bondlength was investigated by varying the C-F bondlength from 1.00 Å to 1.50 Å in steps of 0.01 Å and simultaneously computing ${}^6J^{H,F}$ for a θ value of 60° .

Spectral analysis

All proton nmr spectra were analysed using the programme NUMARIT¹⁵. The ensuing optimized parameters formed the input for the non-iterative calculation mode of the programme to generate the simulated spectra, that could be compared with the experimental. The fluorine spectra were not always run, as all the parameters of interest could be obtained without such information. The maximum error in the parameters¹⁶ is estimated to be twice the standard deviation. For carbon-13 nmr all spectra were visually analysed on a first order basis. The estimated error in the parameters is taken to be twice the digital resolution (number of Hertz per point). For those cases where the coupling (usually $^5J_{C,F}$) is not fully resolved, a first order correction was performed following the procedure of Jackman and Sternhell¹⁷.

RESULTS.

TABLE 1 . Spectral parameters^{a,b}for 2,4-difluorotoluene in CS₂ and acetone-d₆ at 300 K.

	CS ₂	Acetone-d ₆
$\nu(\text{CH}_3)^c$	= 659.012(1)	665.667(1)
$\nu(\text{F}_2)^d$	= 32908.398(1)	14139.683(1)
$\nu(\text{H}_3)$	= 1985.528(1)	2074.412(1)
$\nu(\text{F}_4)$	= 32725.085(1)	13846.573(1)
$\nu(\text{H}_5)$	= 1998.080(1)	2065.395(1)
$\nu(\text{H}_6)$	= 2109.837(1)	2185.230(1)
$^4J(\text{CH}_3, \text{F}_2)$	= 2.080(1)	2.117(1)
$^5J(\text{CH}_3, \text{H}_3)$	= 0.418(1)	0.419(1)
$^6J(\text{CH}_3, \text{F}_4)$	= 1.218(1)	1.211(1)
$^5J(\text{CH}_3, \text{H}_5)$	= 0.350(1)	0.357(1)
$^4J(\text{CH}_3, \text{H}_6)$	= -0.789(2)	-0.800(1)
$^3J(\text{F}_2, \text{H}_3)$	= 9.721(1)	10.165(1)
$^4J(\text{F}_2, \text{F}_4)$	= 6.395(1)	6.232(1)
$^5J(\text{F}_2, \text{H}_5)$	= -1.164(1)	-0.903(1)
$^4J(\text{F}_2, \text{H}_6)$	= 8.645(1)	8.896(1)
$^3J(\text{H}_3, \text{F}_4)$	= 8.725(1)	9.217(1)
$^4J(\text{H}_3, \text{H}_5)$	= 2.587(1)	2.627(1)
$^5J(\text{H}_3, \text{H}_6)$	= 0.314(1)	0.329(1)
$^3J(\text{F}_4, \text{H}_5)$	= 7.927(1)	8.440(1)

$^4J(\text{F}_4, \text{H}_6)$	= 6.395(1)	6.579(1)
$^3J(\text{H}_3, \text{H}_6)$	= 8.451(1)	8.519(1)
Trans.calcd.	= 647	644
Trans.assnd.	= 514	514
Peaks.obsvd.	= 247	258
rms dev.	= 0.001	0.007
largest.diff.	= 0.019	0.021

Footnotes

^aNo significant correlations among the parameters in both CS_2 and acetone- d_6 .

^bNumbers in parentheses are the standard deviations in the last significant digit as calculated by NUMARIT¹⁵

^cin Hz at 300.135₂MHz to high frequency of internal TMS.

^dIn Hz at 282.361₂MHz to high frequency of internal C_6F_6 .

TABLE 2. Spectral parameters^{a,b} for 2-chloro-4-fluorotoluene in CS₂ at 300 K.

	CS ₂
$\nu(\text{CH}_3)^c$	= 689.630(1)
$\nu(\text{H}_3)$	= 2088.802(1)
$\nu(\text{H}_5)$	= 2032.898(1)
$\nu(\text{H}_6)$	= 2125.611(1)
${}^5\text{J}(\text{CH}_3, \text{H}_3)$	= 0.385(1)
${}^6\text{J}(\text{CH}_3, \text{F}_4)$	= 1.223(2)
${}^5\text{J}(\text{CH}_3, \text{H}_5)$	= 0.367(1)
${}^4\text{J}(\text{CH}_3, \text{H}_6)$	= -0.734(1)
${}^5\text{J}(\text{H}_3, \text{F}_4)$	= 8.331(2)
${}^4\text{J}(\text{H}_3, \text{H}_5)$	= 2.659(2)
${}^5\text{J}(\text{H}_3, \text{H}_6)$	= 0.312(2)
${}^3\text{J}(\text{F}_4, \text{H}_5)$	= 7.870(3)
${}^4\text{J}(\text{F}_4, \text{H}_6)$	= 6.020(2)
${}^3\text{J}(\text{H}_5, \text{H}_6)$	= 8.467(2)
Trans.calcd.	= 208
Trans.assnd.	= 200
Peaks.obsvd.	= 94
rms dev.	= 0.007
largest.diff.	= 0.016

Footnotes

^a $^5J(\text{CH}_3, \text{H}_3)$ and $^5J(\text{H}_3, \text{H}_6)$ are correlated by -0.197.

^b Numbers in parentheses are the standard deviations in the last significant digit as calculated by NUMARIT¹⁵.

^c In Hz at 300.135₂ MHz to high frequency of internal TMS.

TABLE 3. Spectral parameters^{a,b} for 2-bromo-4-fluorotoluene in CS₂ at 300 K.

	CS ₂
$\nu(\text{CH}_3)^c$	= 694.414(1)
$\nu(\text{H}_3)$	= 2145.884(1)
$\nu(\text{H}_5)$	= 2047.335(1)
$\nu(\text{H}_6)$	= 2129.450(1)
$^5\text{J}(\text{CH}_3, \text{H}_3)$	= 0.367(2)
$^6\text{J}(\text{CH}_3, \text{F}_4)$	= 1.214(2)
$^5\text{J}(\text{CH}_3, \text{H}_5)$	= 0.361(1)
$^4\text{J}(\text{CH}_3, \text{H}_6)$	= -0.713(1)
$^5\text{J}(\text{H}_3, \text{F}_4)$	= 8.048(3)
$^4\text{J}(\text{H}_3, \text{H}_5)$	= 2.660(2)
$^5\text{J}(\text{H}_3, \text{H}_6)$	= 0.286(2)
$^3\text{J}(\text{F}_4, \text{H}_5)$	= 7.863(3)
$^4\text{J}(\text{F}_4, \text{H}_6)$	= 5.935(3)
$^3\text{J}(\text{H}_5, \text{H}_6)$	= 8.458(2)
Trans.calcd.	= 208
Trans.assnd.	= 183
Peaks.obsvd.	= 89
rms dev.	= 0.009
largest.diff.	= 0.027

Footnotes

^a $\nu(\text{H}_3)$ and ⁵ $J(\text{H}_3, \text{H}_6)$ are correlated by 0.214

^bThe numbers in parentheses are the standard deviations in the last significant digit as calculated by NUMARIT.

^cIn Hz at 300.135₂MHz to high frequency of internal TMS.

TABLE 4. Spectral parameters^{a,b} for 2-iodo-4-fluorotoluene in CS₂ and acetone-d₆ at 300 K.

	CS ₂	Acetone-d ₆
$\nu(\text{CH}_3)^c$	= 710.709(1)	716.599(1)
$\nu(\text{H}_3)$	= 2225.271(1) ^d	2280.359(2)
$\nu(\text{H}_5)$	= 2058.838(1)	2130.038(2)
$\nu(\text{H}_6)$	= 2128.897(1)	2202.157(1)
$^5\text{J}(\text{CH}_3, \text{H}_3)$	= 0.346(1)	0.343(2)
$^6\text{J}(\text{CH}_3, \text{F}_4)$	= 1.194(2)	1.187(3)
$^5\text{J}(\text{CH}_3, \text{H}_5)$	= 0.356(1)	0.361(1)
$^4\text{J}(\text{CH}_3, \text{H}_6)$	= -0.686(1)	-0.694(1)
$^3\text{J}(\text{H}_3, \text{F}_4)$	= 7.855(2)	8.826(4)
$^4\text{J}(\text{H}_3, \text{H}_5)$	= 2.679(1)	2.722(2)
$^5\text{J}(\text{H}_3, \text{H}_6)$	= 0.256(1)	0.265(2)
$^3\text{J}(\text{F}_4, \text{H}_5)$	= 7.909(2)	8.495(3)
$^4\text{J}(\text{F}_4, \text{H}_6)$	= 5.809(2)	5.980(3)
$^3\text{J}(\text{H}_5, \text{H}_6)$	= 8.443(1)	8.501(2)
Trans.calcd.	= 208	208
Trans.assnd.	= 169	191
Peaks.obsvd.	= 94	89
rms dev.	= 0.005	0.010
largest diff.	= 0.013	0.028

Footnotes

^aIn CS₂ $\nu(\text{H}_3)$ and $^5\text{J}(\text{CH}_3, \text{H}_5)$ are correlated by as much as -0.20 ,
 $^5\text{J}(\text{CH}_3, \text{H}_3)$ and $^5\text{J}(\text{H}_3, \text{H}_6)$ by 0.19. ^bIn acetone-d₆ $\nu(\text{H}_3)$ and
 $^5\text{J}(\text{H}_3, \text{H}_6)$ are correlated by -0.199 ; $^5\text{J}(\text{CH}_3, \text{H}_3)$ and $^5\text{J}(\text{H}_3, \text{H}_6)$ by
-0.306.

^cThe numbers in parentheses are the standard deviations in the last
significant digit as calculated by NUMARIT¹⁵.

^dIn Hz at 300.135₂MHz to high frequency of internal TMS.

TABLE 5. Spectral parameters^{a,b} for 2-methyl-4-fluorotoluene in CS₂ at 300 K.

	CS ₂
$\nu(\text{CH}_3)^c$	= 649.980(1)
$\nu(\text{CH}_3)$	= 658.048(1)
$\nu(\text{H}_3)$	= 2004.473(1)
$\nu(\text{H}_5)$	= 1988.353(1)
$\nu(\text{H}_6)$	= 2077.698(1)
${}^5\text{J}(\text{CH}_3, \text{CH}_3)$	= 0.398(1)
${}^5\text{J}(\text{CH}_3, \text{H}_3)$	= 0.407(1)
${}^6\text{J}(\text{CH}_3, \text{F}_4)$	= 1.192(2)
${}^5\text{J}(\text{CH}_3, \text{H}_5)$	= 0.370(2)
${}^4\text{J}(\text{CH}_3, \text{H}_6)$	= -0.760(1)
${}^5\text{J}(\text{CH}_3, \text{H}_3)$	= -0.716(1)
${}^5\text{J}(\text{CH}_3, \text{F}_4)$	= -0.185(2)
${}^6\text{J}(\text{CH}_3, \text{H}_5)$	= -0.606(1)
${}^5\text{J}(\text{CH}_3, \text{H}_6)$	= 0.380(1)
${}^3\text{J}(\text{H}_3, \text{F}_4)$	= 9.383(3)
${}^4\text{J}(\text{H}_3, \text{H}_5)$	= 2.760(2)
${}^5\text{J}(\text{H}_3, \text{H}_6)$	= 0.333(2)
${}^3\text{J}(\text{F}_4, \text{H}_5)$	= 8.263(3)
${}^4\text{J}(\text{F}_4, \text{H}_6)$	= 5.829(2)
${}^3\text{J}(\text{H}_5, \text{H}_6)$	= 8.323(2)

Trans.calcd.	= 1632
Trans.assnd.	= 1221
Peaks.obsvd.	= 148
rms dev.	= 0.020
largest diff.	= 0.567

Footnotes

^aNo significant correlations among the parameters.

^bThe numbers in parentheses are the standard deviations in the last significant digit as calculated by NUMARIT¹⁵.

^cIn Hz at 300.135₂MHz to high frequency of internal TMS.

TABLE 6. Spectral parameters^{a,b} for 2-amino-4-fluorotoluene in CS₂ and acetone-d₆ at 300 K.

	CS ₂	Acetone-d ₆
$\nu(\text{CH}_3)^c$	= 606.008(2)	622.946(1)
$\nu(\text{H}_3)$	= 1841.098(2)	1927.969(1)
$\nu(\text{F}_4)^d$	= 13071.454(2)	
$\nu(\text{H}_5)$	= 1873.602(1)	1873.602(1)
$\nu(\text{H}_6)$	= 2076.382(1)	2076.382(1)
$^5J(\text{CH}_3, \text{H}_3)$	= 0.409(2)	0.404(1)
$^6J(\text{CH}_3, \text{F}_4)$	= 1.111(2)	1.091(2)
$^5J(\text{CH}_3, \text{H}_5)$	= 0.336(2)	0.328(1)
$^4J(\text{CH}_3, \text{H}_6)$	= -0.779(2)	-0.786(1)
$^4J(\text{H}_2, \text{F}_4)$	= 10.284(3)	11.283(2)
$^4J(\text{H}_3, \text{H}_5)$	= 2.558(3)	2.654(2)
$^5J(\text{H}_3, \text{H}_6)$	= 0.312(3)	0.295(2)
$^3J(\text{F}_4, \text{H}_5)$	= 8.371(3)	8.825(2)
$^4J(\text{F}_4, \text{H}_6)$	= 6.347(3)	6.634(2)
$^3J(\text{H}_5, \text{H}_6)$	= 8.262(2)	8.255(2)
Trans.calcd.	= 256	256
Trans.assnd.	= 221	174
Peaks.obsvd.	= 125	91
rms dev.	= 0.0114	0.00748
largest.diff.	= 0.057	0.021

Footnotes

^aIn acetone- d_6 $\nu(H_6)$ and ${}^4J(H_6, F_4)$ are correlated by -0.199 .

In CS_2 ${}^5J(CH_3, H_3)$ and ${}^5J(H_3, H_6)$ are correlated by -0.184.

^bThe numbers in parentheses are the standard deviations in the last significant digit.

^cIn Hz at 300.135₂MHz to high frequency of internal TMS.

^dIn Hz at 282.361₂MHz to high frequency of internal C_6F_6 .

TABLE 7. Spectral parameters^{a,b} for 3-amino-4-fluorotoluene in CS₂ and acetone-d₆ at 300 K.

	CS ₂	Acetone-d ₆
$\nu(\text{CH}_3)^c$	= 648.713(2)	649.407(1)
$\nu(\text{H}_2)$	= 1910.175(2)	1992.831(1)
$\nu(\text{H}_5)$	= 1999.626(2)	2039.462(1)
$\nu(\text{H}_6)$	= 1896.243(2)	1912.706(1)
$^4J(\text{CH}_3, \text{H}_2)$	= 0.696(2)	0.696(2)
$^6J(\text{CH}_3, \text{F}_4)$	= 1.118(2)	1.092(2)
$^5J(\text{CH}_3, \text{H}_5)$	= 0.312(2)	0.311(1)
$^4J(\text{CH}_3, \text{H}_6)$	= -0.718(2)	-0.705(1)
$^4J(\text{H}_2, \text{F}_4)$	= 8.577(3)	8.812(2)
$^5J(\text{H}_2, \text{H}_5)$	= 0.278(3)	0.203(2)
$^4J(\text{H}_2, \text{H}_6)$	= 2.165(3)	2.208(1)
$^3J(\text{F}_4, \text{H}_5)$	= 10.928(3)	11.492(2)
$^4J(\text{F}_4, \text{H}_6)$	= 4.488(3)	4.442(2)
$^3J(\text{H}_5, \text{H}_6)$	= 8.210(3)	8.206(1)
Trans.calcd.	= 208	208
Trans.assnd.	= 226	164
Peaks.obsvd.	= 115	80
rms dev.	= 0.015	0.008
largest diff.	= 0.045	0.025

Footnotes

^aIn CS₂, ⁵J(CH₃,H₅) and ⁵J(H₂,H₅) are correlated by as much as -0.16.

^bThe numbers in parentheses are the standard deviations in the last digit as calculated by NUMARIT¹⁵.

^cIn Hz at 300.135₂MHz to high frequency of internal TMS.

TABLE 8. Spectral parameters^{a,b} for 3-bromo-4-fluorotoluene in CS₂ at 300 K.

	CS ₂
$\nu(\text{CH}_3)^c$	= 684.118(1)
$\nu(\text{H}_3)$	= 2175.358(1)
$\nu(\text{H}_5)$	= 2060.243(1)
$\nu(\text{H}_6)$	= 2091.179(1)
${}^4\text{J}(\text{CH}_3, \text{H}_3)$	= -0.719(1)
${}^6\text{J}(\text{CH}_3, \text{F}_4)$	= 1.242(2)
${}^5\text{J}(\text{CH}_3, \text{H}_5)$	= 0.315(1)
${}^4\text{J}(\text{CH}_3, \text{H}_6)$	= -0.718(1)
${}^4\text{J}(\text{H}_3, \text{F}_4)$	= 6.520(2)
${}^5\text{J}(\text{H}_2, \text{H}_5)$	= 0.264(1)
${}^4\text{J}(\text{H}_2, \text{H}_6)$	= 2.209(1)
${}^3\text{J}(\text{F}_4, \text{H}_5)$	= 8.293(2)
${}^4\text{J}(\text{F}_4, \text{H}_6)$	= 4.571(2)
${}^3\text{J}(\text{H}_5, \text{H}_6)$	= 8.352(1)
Trans.calcd.	= 208
Trans.assnd.	= 186
Peaks.obsvd.	= 92
rms dev.	= 0.006
largest diff.	= -0.017

Footnotes

^a No significant correlations among the parameters.

^bThe numbers in parentheses are the standard deviations in the last significant figures.

^cIn Hz at 300.135₂MHz to high frequency of internal TMS.

TABLE 9. Spectral parameters^{a,b} for 3-nitro-4-fluorotoluene in CS₂ and acetone-d₆ at 300 K.

	CS ₂	Acetone-d ₆
$\nu(\text{CH}_3)^c$	= 725.481(3)	731.991(2)
$\nu(\text{H}_2)$	= 2322.138(4)	2377.374(5)
$\nu(\text{F}_4)^d$	= 11161.373(4)	
$\nu(\text{H}_5)$	= 2123.594(4)	2209.006(3)
$\nu(\text{H}_6)$	= 2210.183(4)	2286.460(3)
${}^4J(\text{CH}_3, \text{H}_2)$	= -0.760(4)	-0.738(4)
${}^6J(\text{CH}_3, \text{F}_4)$	= 1.254(5)	1.219(3)
${}^5J(\text{CH}_3, \text{H}_5)$	= 0.329(3)	0.330(2)
${}^4J(\text{CH}_3, \text{H}_6)$	= -0.701(3)	-0.715(2)
${}^4J(\text{H}_2, \text{F}_4)$	= 4.201(6)	7.168(5)
${}^5J(\text{H}_2, \text{H}_5)$	= 0.306(6)	0.304(5)
${}^4J(\text{H}_2, \text{H}_6)$	= 2.338(6)	2.313(5)
${}^3J(\text{F}_4, \text{H}_5)$	= 10.489(6)	11.226(4)
${}^4J(\text{F}_4, \text{H}_6)$	= 4.201(6)	4.350(4)
${}^3J(\text{H}_5, \text{H}_6)$	= 8.478(5)	8.550(4)
Trans.calcd.	= 256	256
Trans.assnd.	= 211	215
Peaks.obsvd.	= 107	96
rms dev.	= 0.025	0.019

largest diff. = 0.085 0.057

Footnotes

^aNo significant correlations among the parameters in acetone-d₆. In CS₂, ⁴J(CH₃,H₂) and ⁴J(H₂,H₆) are correlated by 0.18.

^bThe numbers in parentheses are the standard deviations in the last significant digit as calculated by NUMARIT¹⁵.

^cIn Hz at 300.135₂MHz to high frequency of internal TMS.

^dIn Hz at 282.361₂MHz to high frequency of internal C₆F₆.

TABLE 10. ^{13}C nmr spectral parameters^a for
4-fluorotoluene in acetone- d_6 at 300 k.

# ^{13}C	$\delta(\text{ppm})^{\text{b}}$	$J(^{13}\text{C}, ^{19}\text{F})\text{Hz.}$
1	134.27(2)	3.21(7)
2	131.20(2)	7.78(7)
3	115.46(2)	21.18(7)
4	161.84(2)	-241.05(7)
5	115.46(2)	21.18(7)
6	131.20(2)	7.78(7)
7	20.47(1)	-0.73(3)

Footnotes

^aThe numbers in parentheses are the estimated errors in
the last significant digits.

^bAt 75.477 MHz.

TABLE 11. ^{13}C nmr spectral parameters^{a,b} for 2,4-difluorotoluene in both CS_2 and acetone- d_6 at 300 K.

# ^{13}C	Acetone- d_6	CS_2	Acetone- d_6	CS_2
1	121.30(2) ^c	120.25(2)	3.8(1)	3.7(4)
1	-----	-----	17.1(1)	17.2(4)
2	161.88(1)	161.44(2)	11.80(4)	21.0(5)
2	-----	-----	-246.61(4)	-247.3(4)
3	103.81(2)	103.37(2)	25.5(1)	26.0(4)
3	-----	-----	25.5(1)	26.0(4)
4	162.14(1)	160.97(2)	11.83(4)	20.9(5)
4	-----	-----	-244.07(4)	-247.4(4)
5	111.53(2)	110.68(2)	3.8(1)	3.9(4)
5	-----	-----	21.0(1)	20.8(4)
6	132.90(2)	131.61(2)	9.4(1)	9.1(4)
6	-----	-----	9.4(1)	9.1(4)
7	13.736(5)	13.84(2)	0.06(2)	-----
7	-----	-----	3.39(2)	3.26(4)

Footnotes

^aThe numbers in parentheses are the estimated errors in the last significant digit.

^bThe first two columns are the δ values and the last two columns are the $J(^{13}\text{C},\text{F})$ in Hz.

^cAt 75.477 MHz.

TABLE 12. ^{13}C nmr spectral parameters^{a,b} for 2-chloro-4-fluorotoluene in both CS_2 and acetone- d_6 at 300 k.

# ^{13}C	Acetone- d_6	CS_2	Acetone- d_6	CS_2
1	132.59(2) ^c	131.50(2)	3.55(6)	3.6(2)
2	-----	135.03(2)	-----	9.9(2)
3	116.68(2)	116.37(2)	24.82(6)	24.4(2)
4	161.73(1)	161.03(2)	-245.31(5)	-248.1(2)
5	114.54(2)	113.55(2)	20.89(6)	20.7(2)
6	132.73(2)	131.35(2)	8.50(6)	8.2(2)
7	19.110(5)	20.49(2)	-0.13(2)	-0.14(3)

Footnotes

^aThe numbers in parentheses are the estimated errors in the last significant digit.

^bThe first two columns are the δ values and the last two columns are the $J(^{13}\text{C},\text{F})$ in Hz. The dashed lines indicate the shift and the coupling that were not observed or resolved.

^cAt 75.477 MHz.

TABLE 13. ^{13}C nmr spectral parameters^a for
2-bromo-4-fluorotoluene in CS_2 at 300 K.

# ^{13}C	$\delta(\text{ppm})^b$	$J(^{13}\text{C}, ^{19}\text{F})\text{Hz.}$
1	133.21(2)	3.6(1)
2	125.00(2)	9.1(1)
3	119.41(2)	24.1(1)
4	160.66(2)	-249.5(1)
5	114.02(2)	20.6(1)
6	131.00(2)	7.9(1)
7	23.00(1)	0.15(6)

Footnotes :

^aThe numbers in parentheses are the estimated errors in
the last significant digit.

^bAt 75.477 MHz.

TABLE 14. ^{13}C nmr spectral parameters^a for
2-amino-4-fluorotoluene in acetone- d_6 at 300 k.

# ^{13}C	$\delta(\text{ppm})^{\text{b}}$	$J(^{13}\text{C}, ^{19}\text{F})\text{Hz}$.
1	117.92(2)	2.57(9)
2	----- ^c .	
3	101.27(2)	24.29(9)
4	163.089(5)	-237.97(5)
5	103.38(2)	21.22(9)
6	131.52(2)	10.02(9)
7	16.712(5)	0.37(2)

Footnotes

^aNumbers in parentheses are the estimated errors in the last significant digit.

^bAt 75.477 MHz.

^cThe dashed line indicates a shift that was not observed .

TABLE 15. ^{13}C nmr spectral parameters^{a,b} for 2-methyl-4-fluorotoluene in both CS_2 and acetone- d_6 at 300 K.

# ^{13}C	Acetone- d_6	CS_2	Acetone- d_6	CS_2
1	132.77(2) ^c	131.44(2)	3.06(8)	3.1(1)
2	139.35(2)	138.08(2)	7.58(8)	7.4(1)
3	112.67(2)	116.13(2)	20.71(8)	20.9(1)
4	161.93(2)	161.31(2)	-240.78(4)	-243.9(1)
5	116.63(2)	112.36(2)	21.09(8)	20.6(1)
6	131.43(2)	130.65(2)	8.04(8)	7.8(1)
7	18.804(5)	18.89(1)	-0.53(1)	-0.47(5)
8	19.715(5)	19.76(1)	1.64(1)	1.64(5)

Footnotes

^aThe numbers in parentheses are the estimated errors in the last significant digit.

^bThe first two columns are the δ values and the last two columns are the $J(^{13}\text{C},\text{F})$ in Hz.

^cAt 75.477 MHz.

REPRESENTATIVE SPECTRA

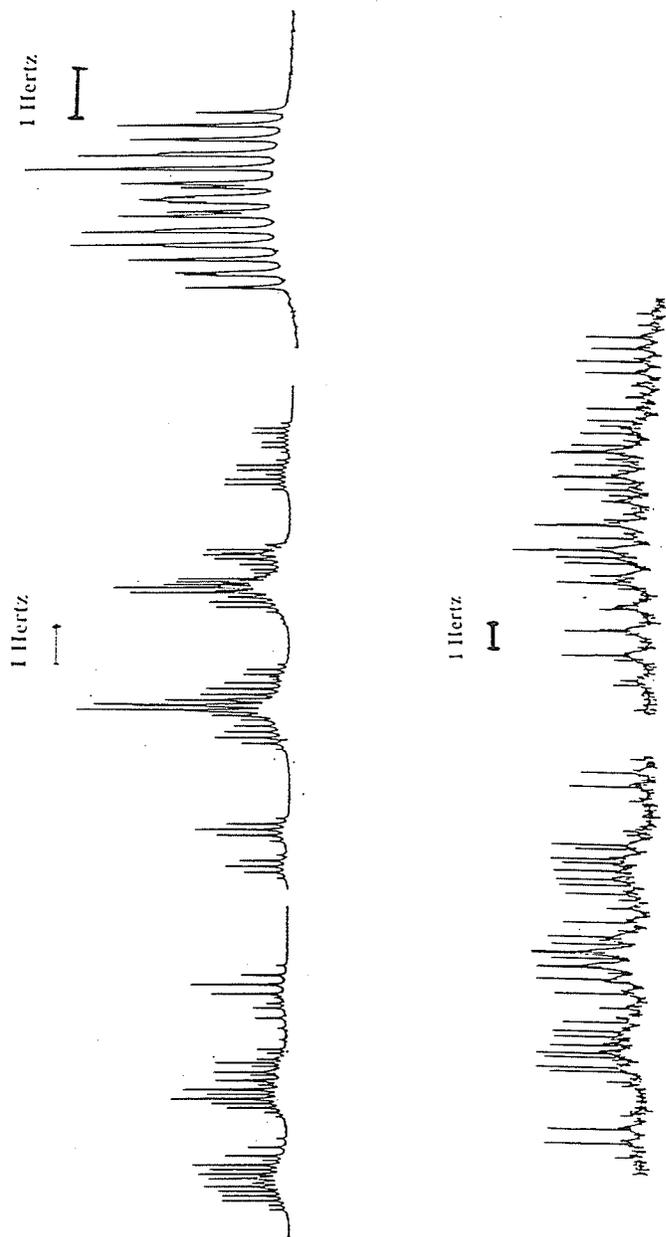


Figure 3

Figure 3.

Full ^1H (upper) and ^{19}F (lower) nmr spectrum for 2,4-difluorotoluene in acetone- d_6 solution, at 300 MHz and $T = 300$ K. The methyl spectral region is to the extreme upper right, and to the left that of ring protons. Fluorine attached to the ortho carbon is to the bottom right. Downfield is towards the left of the methyl spectral region at the top, and to the left of the ortho fluorine spectral region at the bottom.

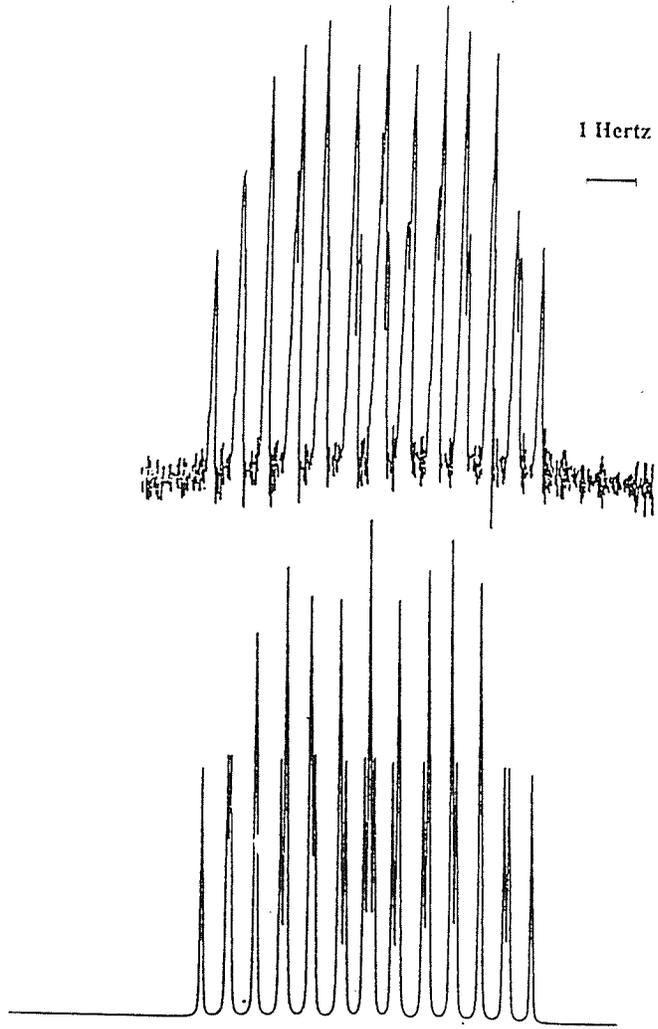


Figure 4

Figure 4.

Experimental nmr spectrum(top) and calculated (bottom) showing the methyl ^1H spectral region for 2,4-difluorotoluene in CS_2 solution at 300 MHz and $T = 300 \text{ K}$. The linewidths at half-height are 0.08 Hz.

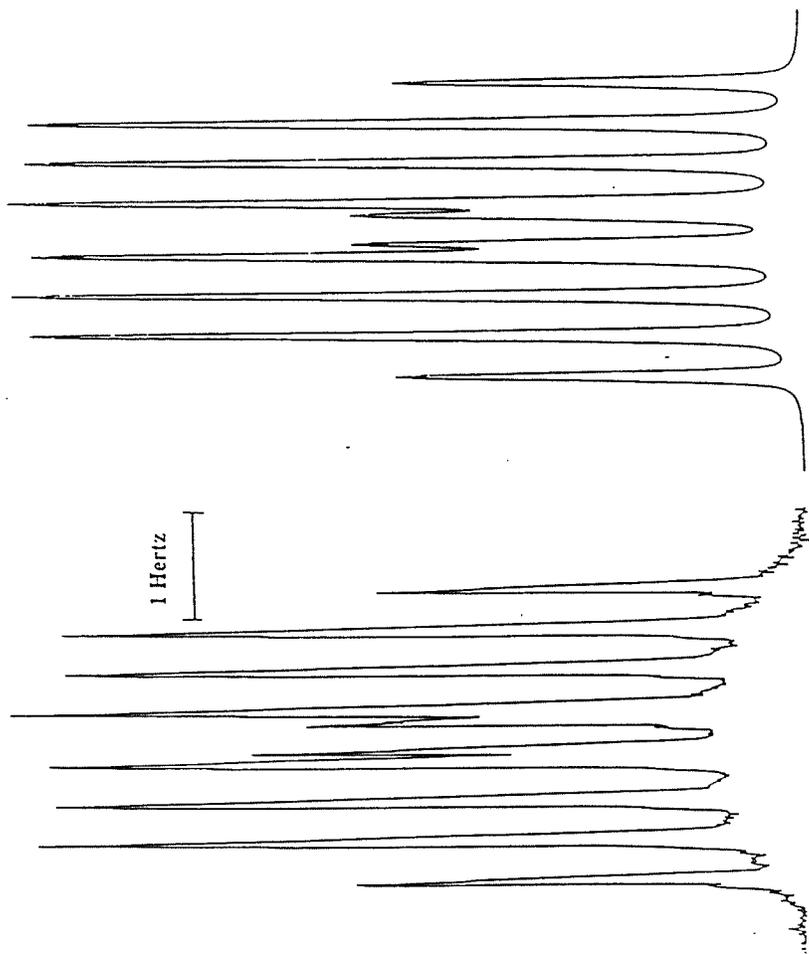


Figure 5

Figure 5.

The observed (right) and calculated (left) methyl proton nmr spectrum at 300 MHz and 300 k for a 2.5 mol% CS₂ solution of 2-chloro-4-fluorotoluene. The linewidths at half-height are 0.08 Hz.

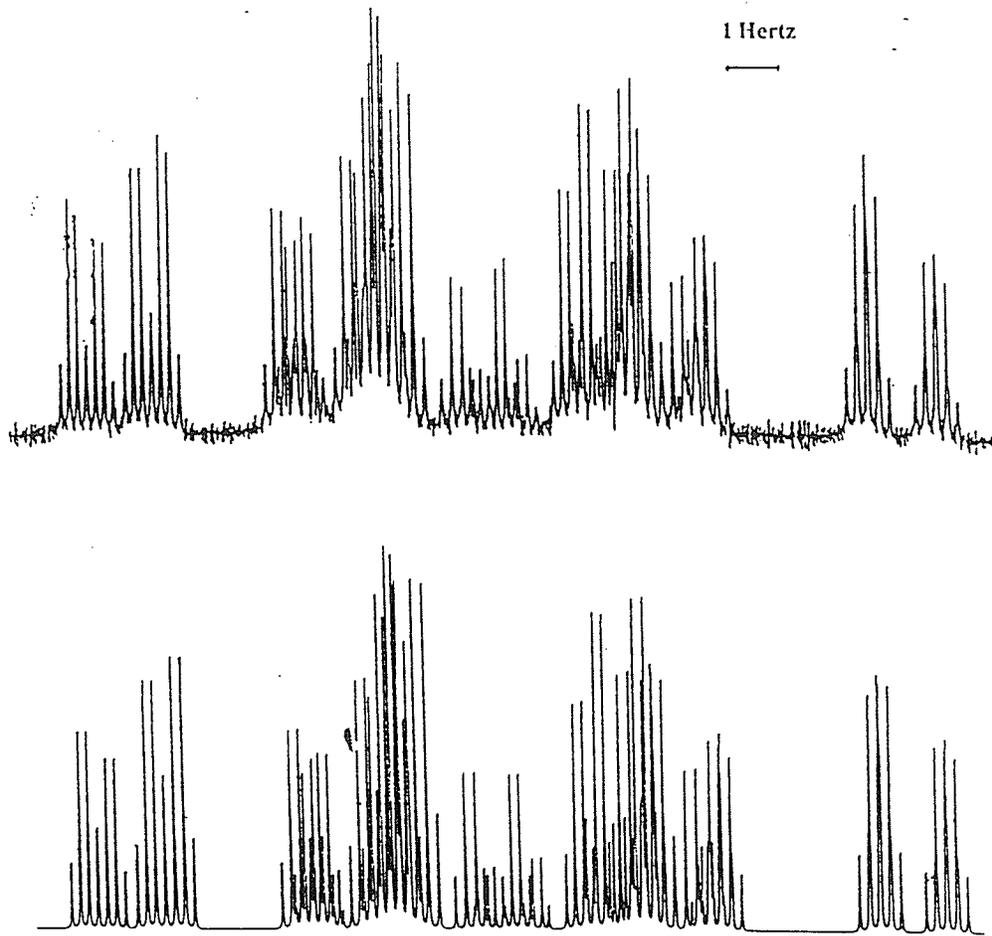


Figure 6

Figure 6.

The observed (top) and calculated (bottom) proton nmr spectrum for the meta protons (H_3 and H_5) in a 2.5 mol% CS_2 solution of 2,4 difluorotoluene, at 300 MHz and 300 K . The linewidths at half-height are 0.08 Hz.

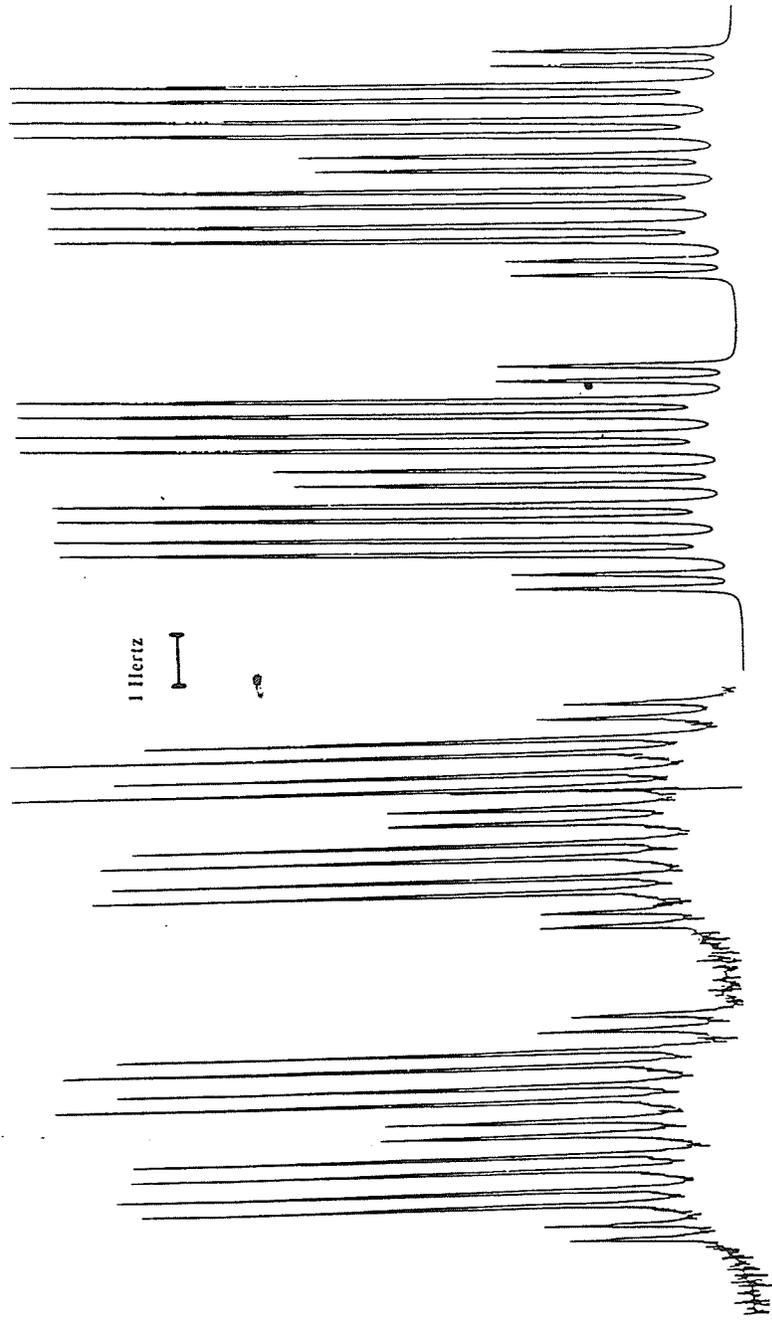


Figure 7

Figure 7.

The observed (left) and calculated (right) proton nmr spectrum for the ortho protons (H_2) in a 2.5 mol% solution of 3-bromo-4-fluorotoluene in CS_2 at 300 K. The linewidths at half-height are 0.05 Hz. The smallest coupling of 0.26 Hz namely, $^5J(H_2, H_5)$, is clearly visible throughout the spectral region, giving rise to the doublets within the various multiplets.

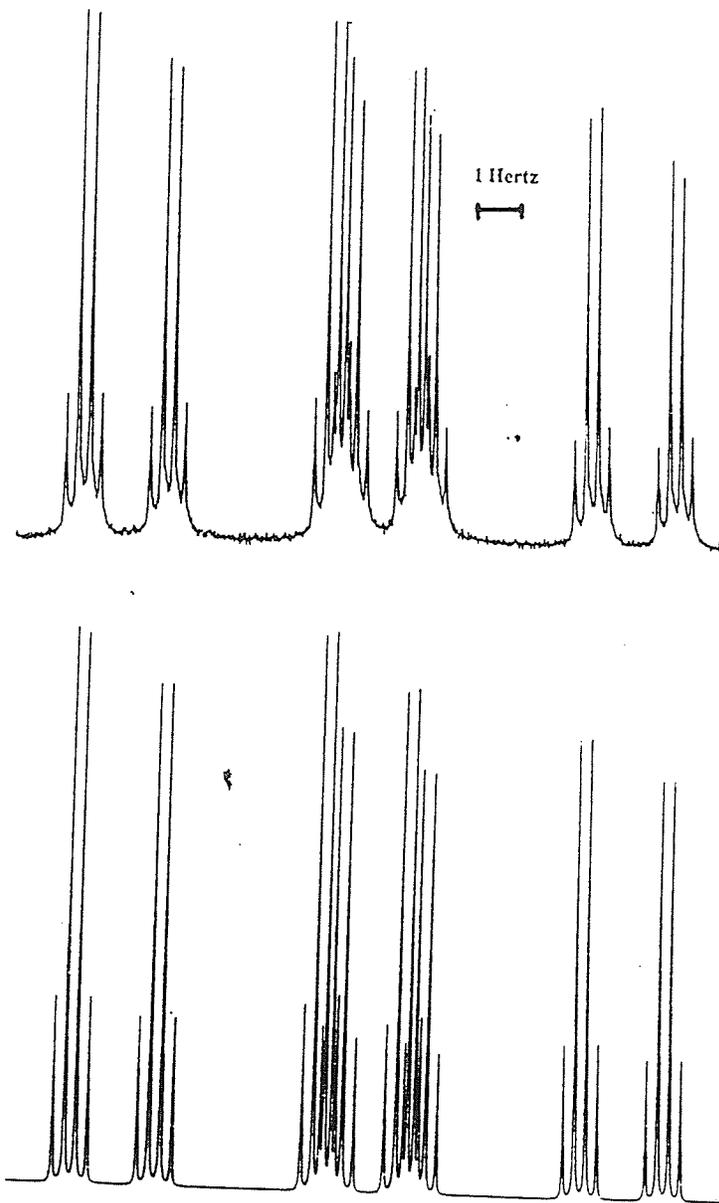


Figure 8

Figure 8.

The observed (top) and calculated spectrum (bottom) for the meta proton (H_3) of a 2.5 mol% solution of 2-chloro-4-fluorotoluene in CS_2 solution, at 300 MHz and 300 K . Linewidths at half-height are 0.08 Hz.

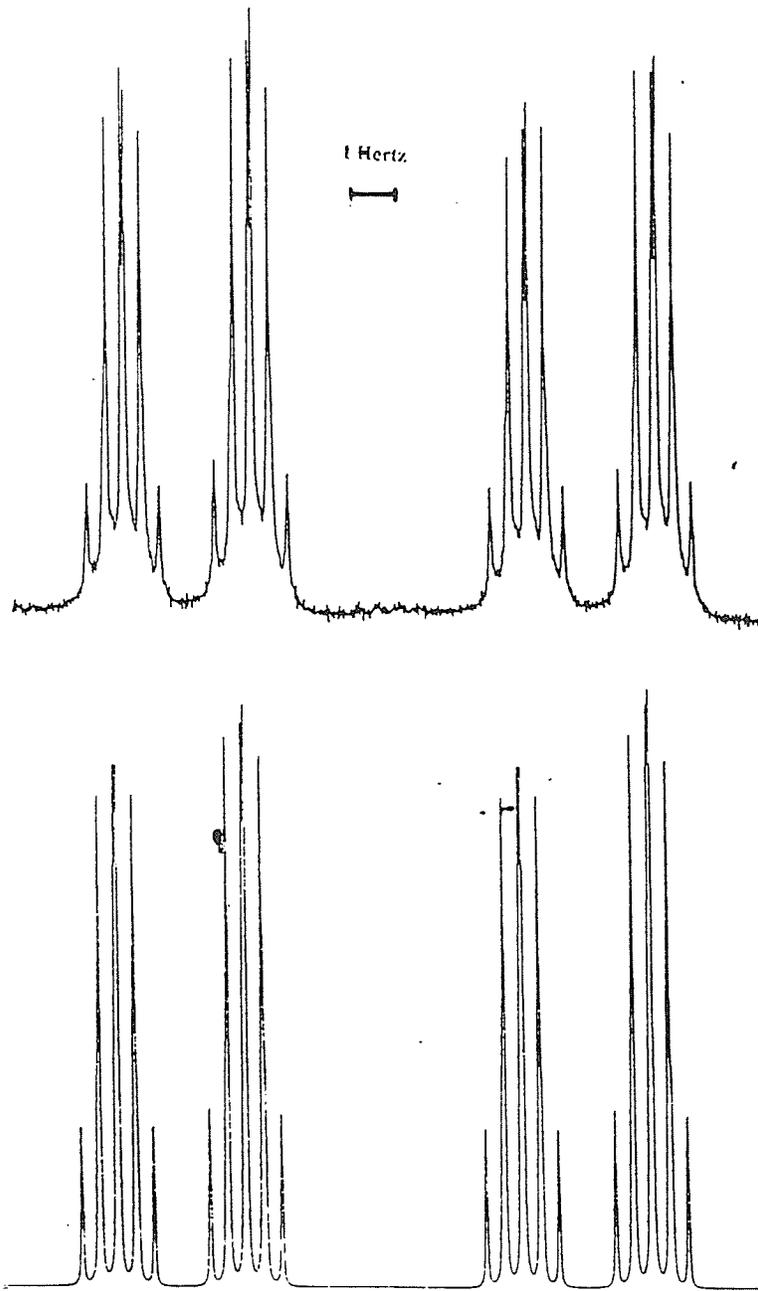


Figure 9

Figure 9.

The observed (top) and calculated (bottom) nmr spectrum for the meta proton (H_5) for a 2.5 mol% solution of 2-chloro-4-fluorotoluene in CS_2 , at 300 MHz. and 300 K. The smallest coupling observed is ${}^5J(CH_3, H_5)$.

1 Hertz

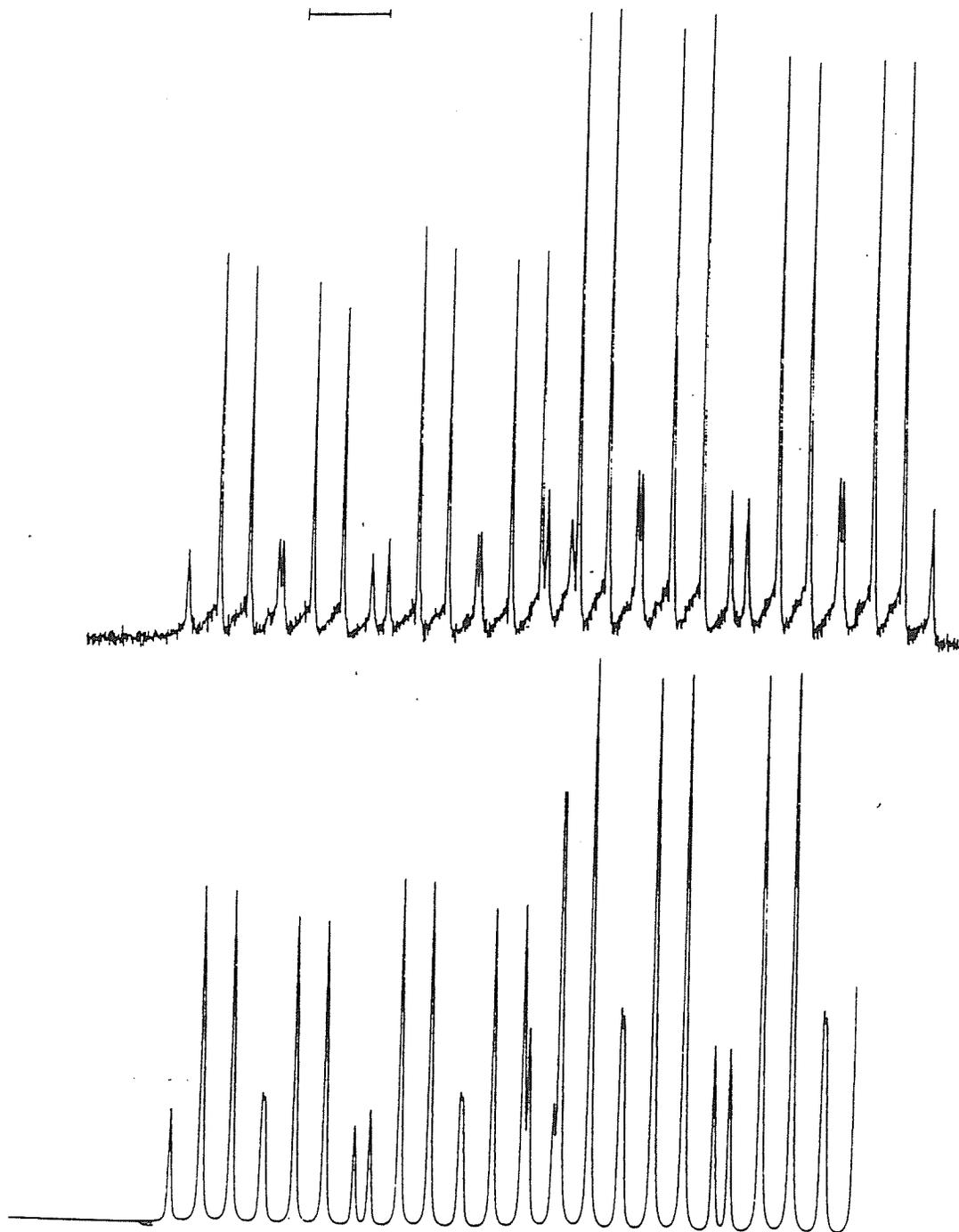


Figure 10

Figure 10.

The observed (top) and calculated (bottom) ortho proton(H_6) nmr spectrum for a 2.5 mol% solution of 3-bromo-4-fluorotoluene in CS_2 . The linewidths at half height are 0.05 Hz at 300 MHz and 300 K. The eight quartets from the four-bond (CH_3 - H_6) coupling constant of the methyl group may be distinctly identified throughout the spectral region.

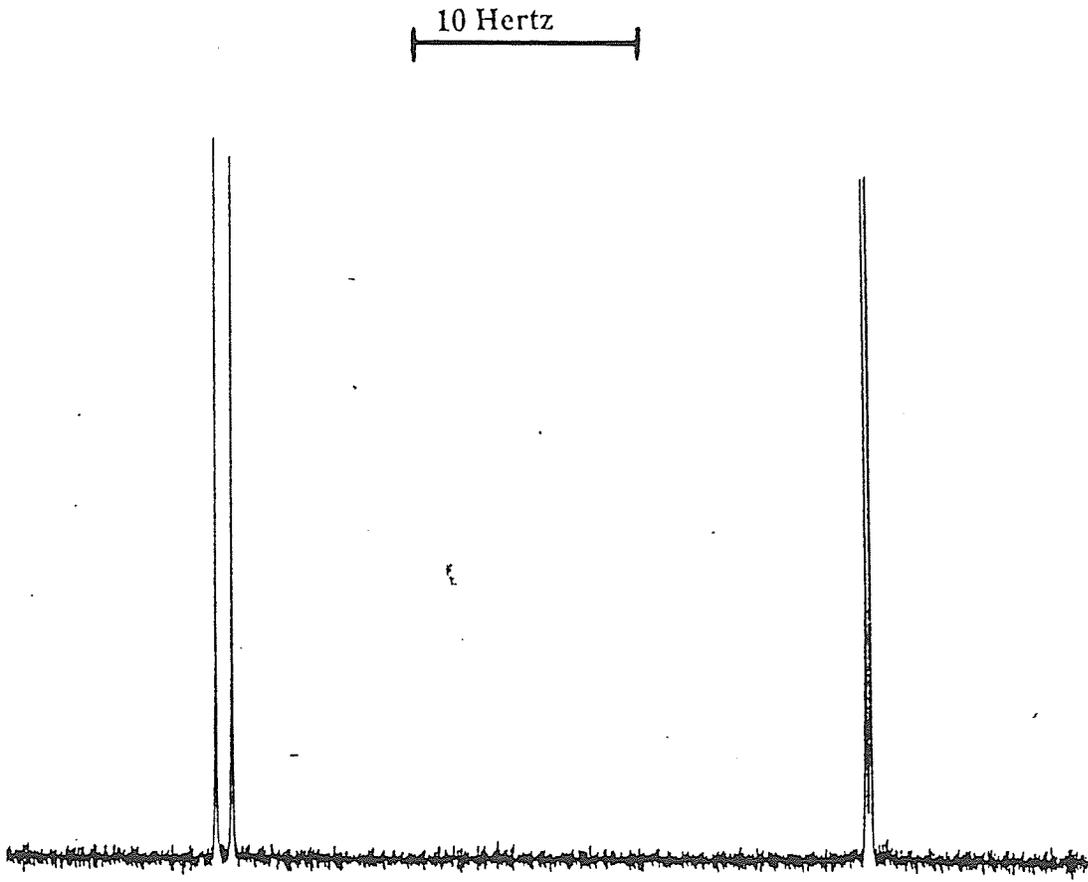


Figure 11

Figure 11.

The experimental ^{13}C methyl spectral region for a 10 mol% solution of 2-methyl-4-fluorotoluene in CS_2 solution at 300 K; the smaller coupling constant corresponds to the five-bond ^{13}C - ^{19}F and the larger to the four-bond ^{13}C - ^{19}F coupling constant. $^5\text{J}(^{13}\text{C}, ^{19}\text{F}) = -0.47(4)\text{Hz}$ and $^4\text{J}(^{13}\text{C}, ^{19}\text{F}) = 1.64(4)\text{ Hz}$; the digital resolution is 0.024 Hz/point.

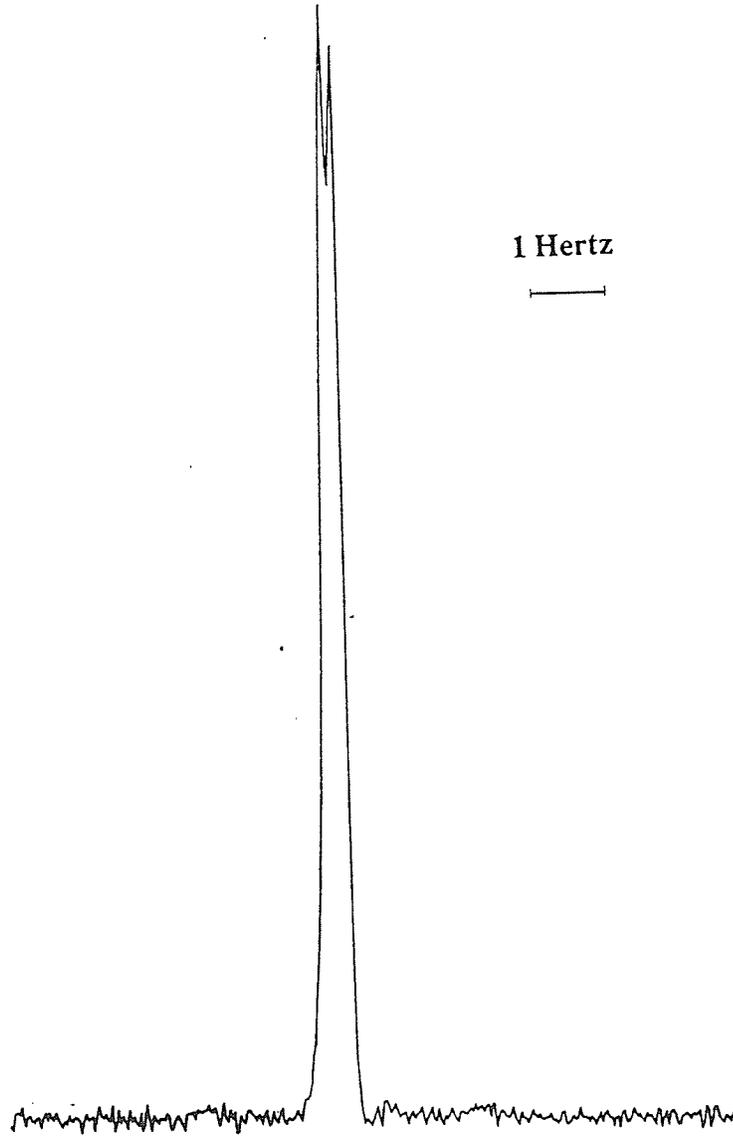


Figure 12

Figure 12.

The observed ^{13}C methyl spectrum for a 10 mol% solution of 2-bromo-4-fluorotoluene in carbon disulfide at 300 K. The measured coupling is 0.14(5)Hz; digital resolution is 0.029Hz/point.

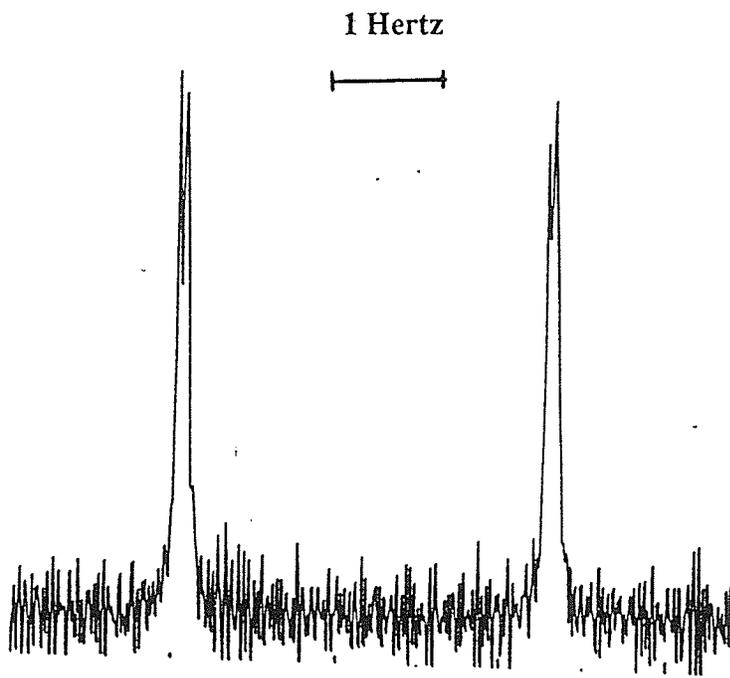


Figure 13

Figure 13

The observed ^{13}C methyl spectrum for a 10 mol% solution of 2,4-difluorotoluene in acetone- d_6 solution. The larger splitting, 3.4 Hz, corresponds to the three-bond ^{13}C - ^{19}F coupling constant and the smaller to the five-bond. The procedure of Jackman and Sternhell²³ for imperfect resolution gives the corrected coupling as 0.06(2)Hz; digital resolution is 0.012Hz/point.

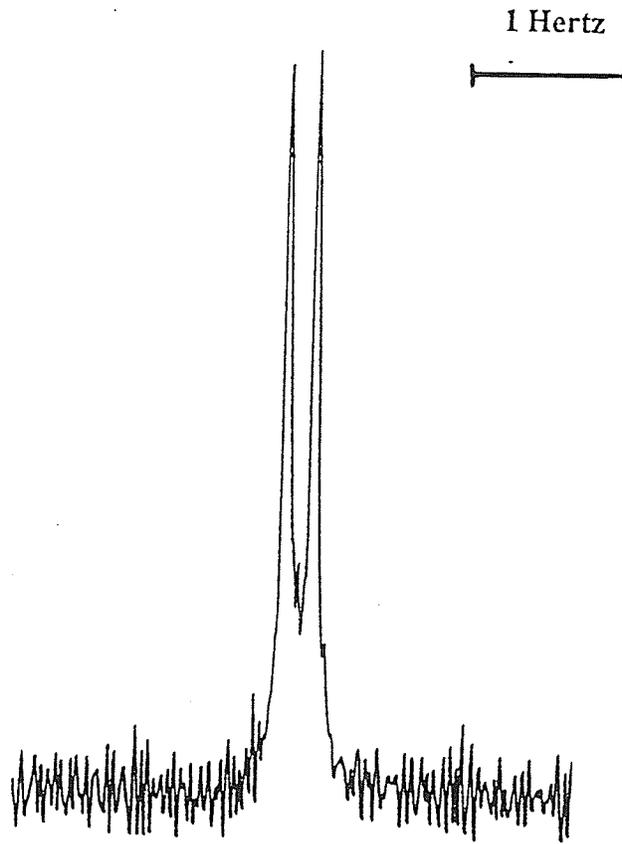


Figure 14

Figure 14.

The observed ^{13}C methyl spectrum for a 10 mol% solution of 3-bromo-4-fluorotoluene in acetone- d_6 at 300 K. $^5J(^{13}\text{C},\text{F})$ is $-0.18(2)$ Hz.

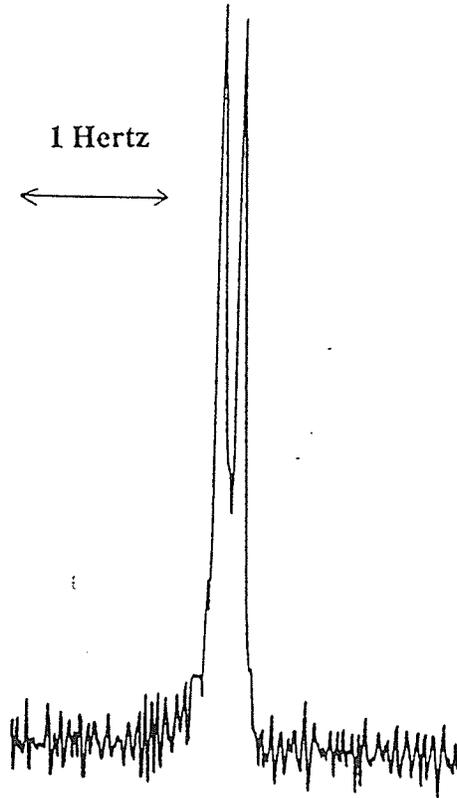


Figure 15

Figure 15.

The experimental methyl ^{13}C nmr spectrum for a 10 mol% solution of 2-chloro-4-fluorotoluene in carbon disulphide at 300 K. $^5\text{J}(^{13}\text{C},\text{F}) = -0.14(2)\text{Hz}$.

DISCUSSION

${}^6J_{H,F}$ in 4-fluorotoluene and some derivatives.

The measured values of ${}^6J_{H,F}$ are shown in table 16a for both carbon disulfide and acetone- d_6 solutions. A maximum value is observed for 3,4-difluorotoluene at 1.262(1) Hz and a minimum value is recorded at 1.111(1) Hz for the 2-amino-4-fluorotoluene. In general the nitro derivatives have larger coupling constants than the measured value for 4-fluorotoluene at 1.153(1) Hz. The amino derivatives have lower values than for the parent compound. For the halogen substituents at the three positions the electronegativity of the halogen atom seems to be the primary factor influencing the size of the six-bond coupling constant. However, for the 2-halogen substituents the electronegativity of the substituent does not seem to be the only factor. We also note that the trend concerning the electronegativity of the substituent cannot be extended to include group electronegativity for all substituents. For example, the amino group is more electronegative than the methyl group, yet there is a reversal of trend for these two cases with respect to group electronegativity among the 2-substituents. In general, the ${}^6J_{H,F}$ values for the halogen substituents are intermediate between the ${}^6J_{H,F}$ values for the nitro substituents and the amino substituents for a given series of substituted 4-fluorotoluenes. Values for the 3-substituted are consistently higher in magnitude than for the corresponding 2-substituted parafluorotoluene derivatives.

TABLE 16a. Experimental ${}^6\text{J}_{\text{H},\text{F}}$ and ${}^1\text{J}_{\text{C},\text{F}}$ values in Hz.

X	${}^6\text{J}_{\text{H},\text{F}}$		${}^1\text{J}_{\text{C},\text{F}}$	
	CS_2	Acetone- d_6	CS_2	Acetone- d_6
2F	1.218(1)	1.211(1) ^a	-247.4(1)	-245.6(1)
2Cl	1.223(1)		-248.1(1)	-245.3(1)
2Br	1.214(1)		-249.5(1)	
2I	1.194(1)	1.187(1)	-250.6(1)	
2Me	1.192(1)		-243.9(1)	-240.8(1)
2NH ₂	1.111(1)	1.091(2)	-241.4(1)	-238.0(1)
2NO ₂	1.254(2)	1.217(2)	-249.4(1)	
3F	1.262(1)		-248.2(1)	
3Cl	1.245(1)		-247.2(1)	
3Br	1.243(1)		-248.3(1)	
3I	1.230(1)		-244.3(1)	
3NH ₂	1.118(2)	1.092(2)	-236.0(1)	
3Me	1.13(2) ^b			
3NO ₂	1.254(5)	1.219(5)	-262.5(1)	
H	1.153(1) ^c	1.15(2) ^d		-241.1(1)

Footnotes

^aValues in parentheses are the standard deviations in the last significant figure as calculated by NUMARIT¹⁵ for ${}^1\text{H}$ nmr analysis, and are twice the digital resolution for ${}^{13}\text{C}$ nmr analysis.

^bEstimated coupling constant from the fluorine spectrum.

^cFrom unpublished work in the laboratory.

^dFrom reference (1).

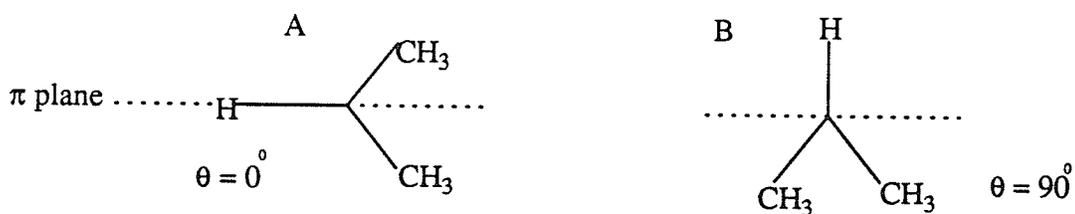
Solvent effects

A comparison of the measured values of ${}^6J^{H,F}$ in both carbon disulfide and acetone- d_6 solutions in table 16a reveals that this coupling constant is not very solvent dependent. In fact, on comparing the values for 2-nitrotoluene in the two solvents, a variation of at most 4% can be attributed to solvent effects. In other words, solvent effects are small for this spin-spin coupling constant.

Estimate of the error for the twofold potential barrier due to intrinsic substituent perturbations of ${}^6J^{H,F}$

From data in table 16a and the fact that $\langle \sin^2\theta \rangle$ is always 0.5 for 4-fluorotoluene and its ring derivatives, ${}^6J_{90}^{H,F}$ is calculated to be 2.30 Hz from [6] for 4-fluorotoluene, and increases to 2.51 Hz for 3-nitro-4-fluorotoluene due to the intrinsic substituent perturbation of ${}^6J^{H,F}$. Suppose that the measured ${}^6J^{H,F}$ is 0.60 Hz for 3-nitro-4-fluoroisopropylbenzene. If one neglects the intrinsic substituent perturbation of ${}^6J^{H,F}$, $\langle \sin^2\theta \rangle$ is computed as 0.26 and a barrier of 5.5 kJ/mol is obtained from table 16b. However, if the substituent perturbation is taken into account, then one uses a ${}^6J_{90}$ of 2.51 Hz to compute $\langle \sin^2\theta \rangle$ as 0.24; this leads to a twofold barrier height of 6.0 kJ/mol. Thus an error of about 8% in V_2 is obtained as a result of neglecting the substituent perturbation of ${}^6J^{H,F}$. A similar calculation results with an error of about 27% in V_2 for a benzyl derivative of 4-fluorotoluene. It turns out that if one also considers the errors in the measurement of the coupling itself, then a total error in V_2 of 10% and 30% for benzylidene and benzyl derivatives, respectively, is computed. From the results of the preceding data a variation of about 10%

TABLE 16b. Classical expectation values for 4-fluoroisopropylbenzene derivatives, for V_2 in the range 0-10 kJ mol⁻¹. The side chain is assumed to adopt conformations A or B as the low and high energy conformations respectively.



$V_2(\theta)$	$\langle \sin^2\theta \rangle_A$	$\langle \sin^2\theta \rangle_B$
0.00	0.5000	0.5000
0.50	0.4750	0.5250
1.00	0.4501	0.5499
1.50	0.4257	0.5743
2.00	0.4017	0.5983
2.50	0.3785	0.6215
3.00	0.3561	0.6439
3.50	0.3346	0.6654
4.00	0.3141	0.6859
4.50	0.2947	0.7053
5.00	0.2764	0.7236
5.50	0.2592	0.7408
6.00	0.2432	0.7568
6.50	0.2282	0.7718

7.00	0.2144	0.7856
7.50	0.2015	0.7985
8.00	0.1896	0.8104
8.50	0.1787	0.8213
9.00	0.1686	0.8314
9.50	0.1593	0.8407
10.0	0.1507	0.8493

Footnotes

^aThe numbers refer to a reduced moment of inertia of 1.0×10^{-38} g cm², and 300 K.

^bThe range of $\langle \sin^2\theta \rangle$ is 0.5 - 0.0 , 0.5 - 1.0 for A and B.

^cThe potential is of the form $V(\theta) = V_2 \sin^2\theta$.

in ${}^6J_{H,F}$ can be attributed directly to intrinsic substituent perturbations of the coupling mechanism. ${}^6J_{H,F}$ has been used to determine both the preferred conformations and the internal rotational barriers for benzyl and benzyldiene derivatives of 4-fluorotoluenes. It is desirable to know the magnitude of the concomitant errors in the twofold rotational barriers as a result of the intrinsic ring substituent perturbations of ${}^6J_{H,F}$. Such information becomes crucial for an accurate assessment of the rotational barrier heights in conformational work. It seems reasonable to attribute an error of 10% and 30% in V_2 to intrinsic substituent perturbations of ${}^6J_{H,F}$ corresponding to benzyldiene and benzyl derivatives of 4-fluorotoluenes, respectively.

Table 17, which compares the values of the twofold barriers obtained *via* ${}^6J_{H,F}$ and those obtained *via* ${}^6J_{H,H}$, reveals that the V_2 values determined through the two long-range coupling constants are different and in some cases the discrepancy is quite substantial. It appears that apparent V_2 values are generally higher for the 4-fluorophenyl than for the phenyl derivatives. It is conceivable that a 4-fluorine substituent causes a change in the internal barrier by altering the energy of either the low or the high energy conformations. It is also possible that the sidechain itself alters the hyperfine interaction of the C-F bond and therefore changes ${}^6J_{90}$. It would seem that ${}^6J_{H,F}$ can still be used to determine ground state conformations and to reach a rough assessment of the energetics of the internal rearrangements in benzyldiene and benzyl compounds even in the presence of ring substituent perturbations.

TABLE 17. Comparison of twofold barriers^a obtained from ${}^6J_{H,F}$ and ${}^6J_{H,H}$.

Fragment	$\langle \sin^2\theta \rangle$		V_2 kJ/mol.	
	${}^6J_{H,F}$	${}^6J_{H,H}$	${}^6J_{H,F}$	${}^6J_{H,H}$
CH ₂ CN	0.46	0.49	1.7 ± 0.8^b	0.4 ± 0.4^b
CH ₂ Cl	0.32	0.34	11 ± 1^c	8.8 ± 0.4^c
CH ₂ Br	0.26	0.28	$>12^d$	$>12^d$
CH(CH ₃) ₂	0.26	0.23	5.7 ± 0.8^e	6.5 ± 0.6^e
CHCl ₂	0.12	0.19	12.1 ± 1.2^d	8.1 ± 0.9^d
CH ₂ CH ₃	0.36	0.39	6.5 ± 0.3^g	5.3 ± 0.3^g

Footnotes

^aIn CS₂ solution unless otherwise stated.^bFrom reference (27).^cFrom reference (28).^dFrom reference (7).^eFrom reference (29).^fFrom reference (29).^gIn acetone-d₆ and from reference (30).

The nature of the intrinsic electronic substituent perturbation of ${}^6J_{H,F}$

Figure 16 is a plot of ${}^6J_{H,F} - {}^6J_{PFT}{}^{H,F} \equiv \Delta^6J$ against σ_{ST}^{10} , corresponding to the values in table 18. There appears to be a direct correlation between Δ^6J and σ_{ST} (meta) for 2-substituted derivatives of 4-fluorotoluene. The correlation coefficient is 0.97, significant at the 99% confidence level. The correlation is taken as support for the view that the main reason for the variation of ${}^6J_{H,F}$ in the presence of ring substituents is that the C-F bond can alter its double bond character in response to the intrinsic substituent perturbations. In terms of the σ - π spin-spin interaction mechanism¹⁹, an increase in the double bond character at the C-F bond is expected to increase Q_{CF} and thus lead to an increase in ${}^6J_{H,F}$.

For the plot of figure 16 and subsequent similar plots indicating linear relationships between two parameters, the straight lines are the regression lines for the two variables.

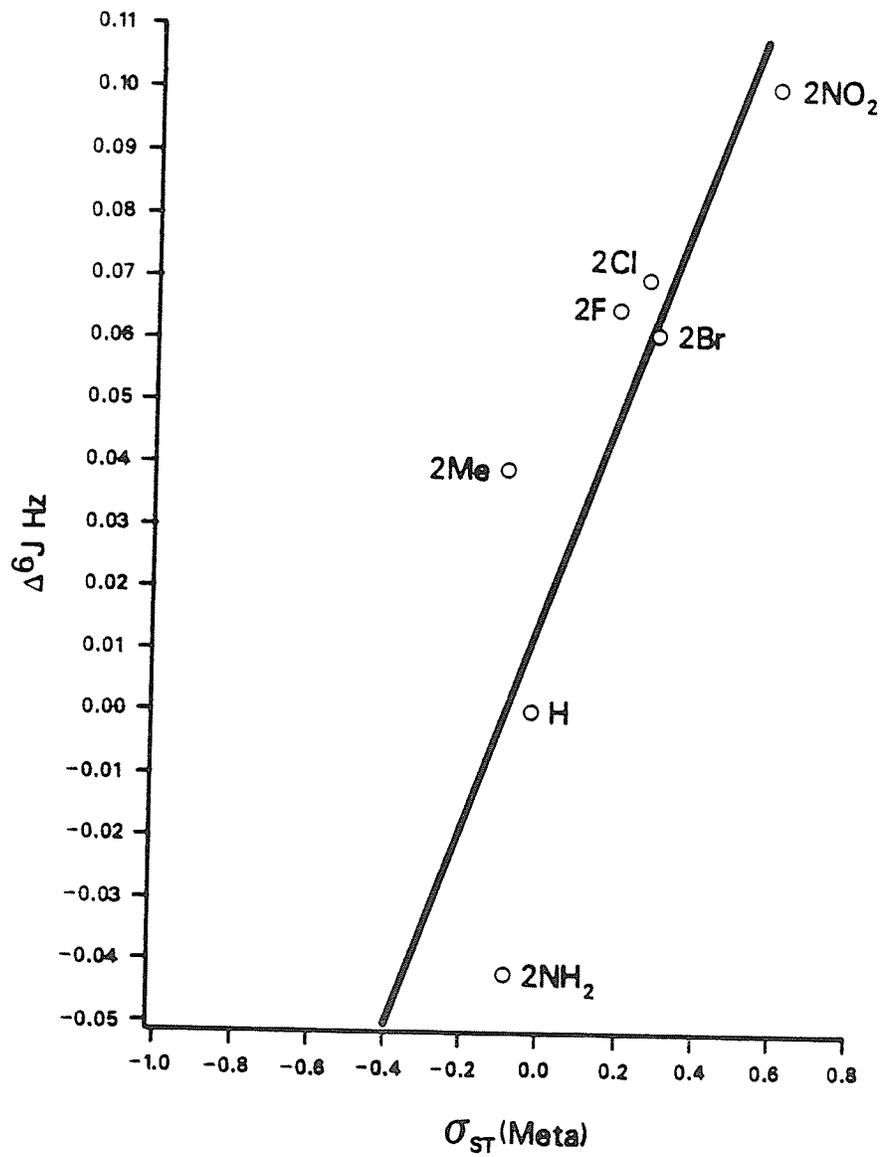


Figure 16

Figure 16 shows a plot of Δ^6J^a against $\sigma_{ST}^b(\text{meta})$ for some 2-substituted derivatives of 4-fluorotoluene. The plotted values appear in table 18 and the correlation coefficient is 0.97, significant at the 99% confidence level.

Notes

^a $\Delta^6J = [{}^6J_{H,F} - {}^6J_{P,FT}]$.

^b $\sigma_{ST}(\text{meta})$ is the substituent parameter based on β ^{13}C substituent chemical shifts¹⁰ for styrenes.

TABLE 18. ${}^6J_P^{H,F}$ and $\sigma_{ST}(\text{meta})$.

Substituent	$\Delta {}^6J_P^{H,F}$	$\sigma_{ST}(\text{meta})$
H	0.00	0.00
2F	0.065	0.24
2Cl	0.070	0.32
2Br	0.061	0.34
2Me	0.039	-0.05
2NH ₂	-0.042	-0.08
2NO ₂	0.101	0.67

Footnotes

$\sigma_{ST}(\text{meta})$ is the σ standard substituent parameter based on the ${}^{13}\text{C}$ substituent chemical shifts at the β site for meta ring substituted styrenes¹⁰.

$$\Delta {}^6J^{H,F} = \{ {}^6J^{H,F}, {}^6J_{PFT}^{H,F} \}$$

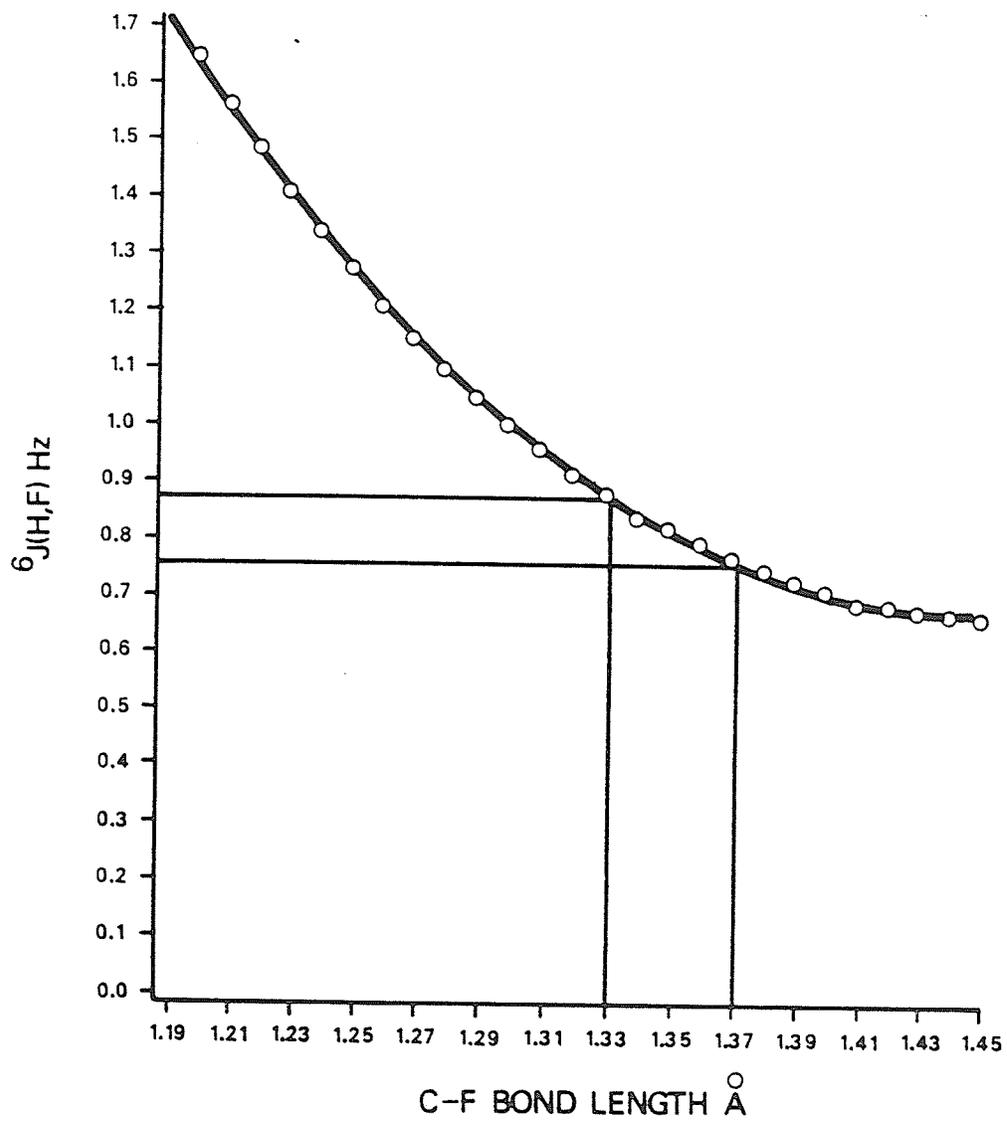


Figure 17

Figure 17 shows a theoretical plot of INDO computed ${}^6J^{H,F}$ against the C-F bond length in Ångstrom units. The curve is best described by a general quadratic equation. The vertical and horizontal lines indicate the region on the plot corresponding to physically realizable bond length changes due to substituent perturbations.

Over small range of physically realizable bondlength changes dependence of ${}^6J^{H,F}$ and C-F bondlength approximates a linear relationship. It is possible that substituents perturb the C-F bondlength and this causes variation in ${}^6J^{H,F}$ through changes in Q_{CF} . Table 19 shows the values of ${}^6J^{H,F}$ the square of the mobile bond order P_{CF}^2 and the excess π charge density at the fluorine atom q_F , the latter two quantities are computed using approximate molecular orbital theories. Significant correlations between ${}^6J^{H,F}$ and P_{CF}^2 and ${}^6J^{H,F}$ with q_F are observed if two data points corresponding to $2NH_2$ and $3F$ are arbitrarily omitted from the calculation of the correlation coefficients.

It is pertinent to mention here that ${}^6J^{H,F}$ is also correlated with ${}^1J^{C,F}$, perhaps not surprisingly in view of the foregoing findings concerning the correlation of ${}^6J^{H,F}$ with σ_{ST} for meta substituents. More will be said about this correlation under the discussion of ${}^1J^{C,F}$.

TABLE 19 ${}^6J_{H,F}$, C-F π bond orders squared^a and excess π charge density^b at the fluorine carbon atom.

Substituent	${}^6J_{H,F}$	P_{CF}^2	q_F
H	1.153(1)	0.0115	0.0459
2F	1.218(1)	0.0122	0.0477
2Cl	1.223(1)	0.0115	0.0460
2Me	1.192(1)	0.0119	0.0468
2NH ₂	1.111(1)	0.0121	0.0473
2NO ₂	1.254(2)	0.0119	0.0473
3NH ₂	1.118(1)	0.0104	0.0433
3Me	1.13(2) ^c	0.0110	0.0447
3NO ₂	1.254(5)	0.0119	0.0475
3F	1.262(1)	0.0104	0.0434
3Cl	1.245(1)	0.0104	0.0485

Notes:

^a P_{CF}^2 is the π bond order at the carbon-fluorine linkage.

^b q_F is the excess π charge density at the fluorine atom.

^cThe coupling is estimated from the fluorine spectrum.

Substituents perturbations of ${}^4J_{H,H}$ and ${}^5J_{H,H}$ (methyl to ring proton coupling constants).

The different components of the long-range methyl to ring proton coupling constants in benzene derivatives are generally formulated as in equations [8] to [10].

$${}^4J_{H,H} = {}^4J_{\sigma-\pi} + {}^4J_{\sigma} \quad [8]$$

${}^4J_{H,H}$ is negative. $J_{\sigma-\pi}$ and J_{σ} are the σ - π interaction component and the σ contribution to the spin-spin coupling constants, respectively.

$${}^5J_{H,H} = {}^5J_{\sigma-\pi} + {}^5J_{\sigma} \quad [9]$$

For ${}^5J_{H,H}$ the components are roughly equal in magnitude¹² and positive.

$${}^6J_{H,H} = {}^6J_{\sigma-\pi} \quad [10]$$

For 4-fluorotoluene derivatives (tables 20-21), a substituent in the 2-position increases both ${}^5J_{H,H5}$ and ${}^5J_{H,H3}$ compared to the parent compound. The latter coupling experiences a larger increase, in agreement with previous work on the effects of substituents on these coupling constants¹². In contrast, 2-substituents cause a reduction in ${}^4J_{H,H6}$ (or an increase in the magnitude of ${}^4J_{H,H6}$). A substituent meta to the methyl group reduces the single ${}^5J_{H,H5}$. In general, for the ortho couplings π electron withdrawing substituents tend to increase ${}^4J_{H,H6}$, and π electron donating substituents increase ${}^4J_{H,H2}$. Interestingly enough, the average value of ${}^4J_{H,H2}$ and ${}^4J_{H,H6}$ for a given meta substituted derivative of 4-fluorotoluene is -0.72 ± 0.01 Hz, the value observed for the parent compound within experimental

error. This may be a reasonably accurate way of deducing the value of the other ortho coupling in cases where it is only possible to determine one and not the other.

On the basis of the foregoing empirical formulations, plots of ${}^4J_{H,H}$ against ${}^5J_{H,H}$ are predicted to be significantly correlated because both couplings are dependent on very similar variables, namely ${}^4J_{\sigma}$, ${}^5J_{\sigma}$, ${}^4J_{\sigma-\pi}$ and ${}^5J_{\sigma-\pi}$. The two σ and or $\sigma-\pi$ components are expected to be similarly perturbed by ring substituents although not necessarily by equal amounts. Thus a correlation between ${}^4J_{H,H}$ and ${}^5J_{H,H}$ should be observed.

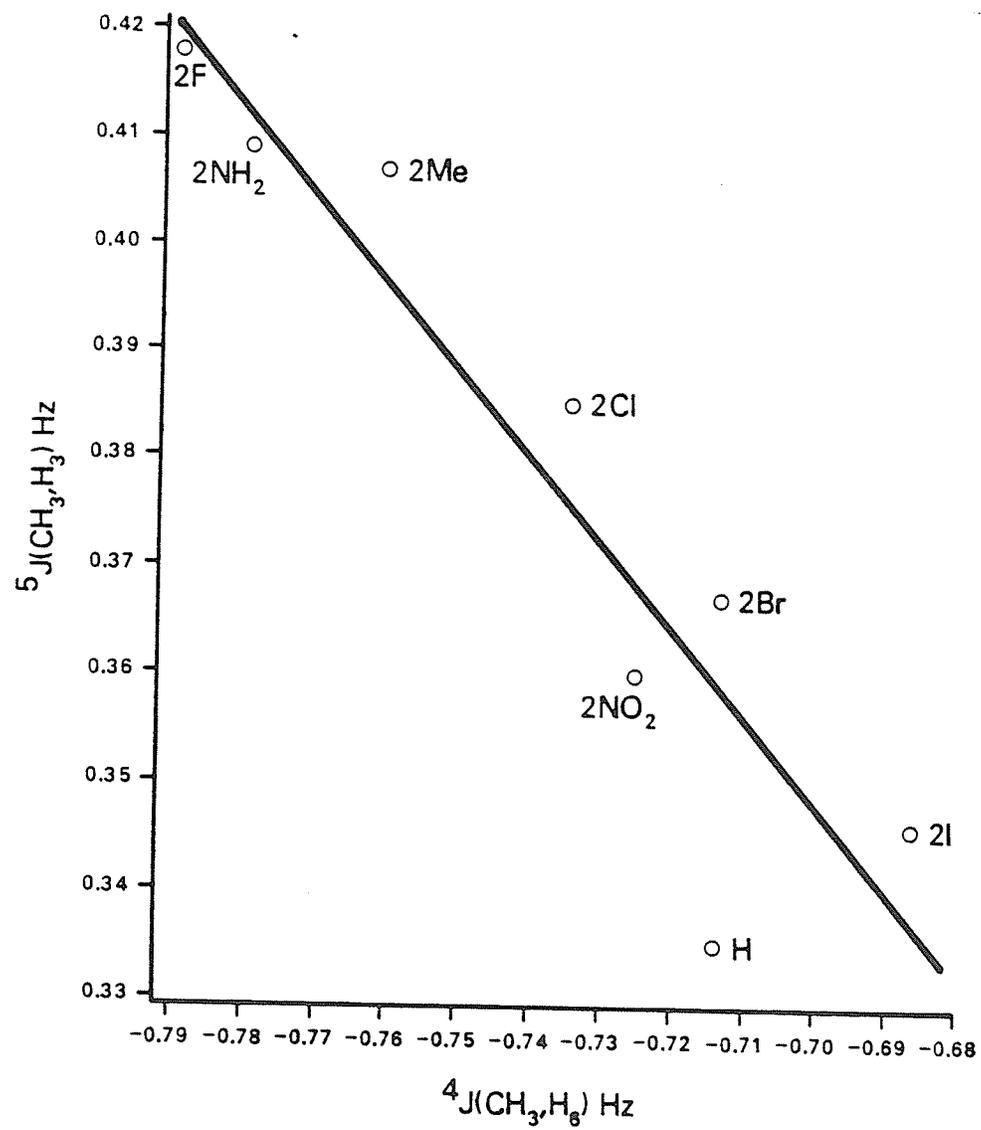


Figure 18

Figure 18 is a plot of ${}^5J(\text{CH}_3, \text{H}_3)$ against ${}^4J(\text{CH}_3, \text{H}_6)$ for the 2-substituted derivatives of 4-fluorotoluene in carbon disulfide solution. The plotted values are from tables 20 and 21. The linear correlation coefficient is -0.92, significant at the 99.9% confidence level.

TABLE 20. ${}^4J(\text{CH}_3, \text{H}_{2/6})$ and the squares of the ring C-C π^a bond orders.

Substituent	${}^4J(\text{CH}_3, \text{H}_2)^b$	${}^4J(\text{CH}_3, \text{H}_6)$	$P^2_{\mu\nu}(\text{INDO})$	$P^2_{\mu\nu}(\text{CNDO})$
pft	-0.714(1)	-0.714(1)	0.106	0.106
2F	-----	-0.789(1)	0.108	0.100
2Cl	-----	-0.734(1)	0.107	0.097
2Br	-----	-0.713(1)	-----	-----
2I	-----	-0.686(1)	-----	-----
2Me	-----	-0.760(1)	0.108	0.100
2NH ₂	-----	-0.779(2)	0.108	0.100
2NO ₂	-----	-0.725(2)	0.106	0.104
3F	-0.694(1)	-0.726(1)	0.106	0.105
3Cl	-0.717(1)	-0.715(1)	0.109	0.104
3Br	-0.718(1)	-0.719(1)		
3I	-0.723(1)	-0.709(1)		
3NH ₂	-0.696(2)	-0.718(2)	0.106	0.106
3NO ₂	-0.760(2)	-0.701(2)	0.107	0.109

Footnotes

^a $P_{\mu\nu}$ is one half the total ring C-C π bond order for the intervening bond.

^bIn Hz and in CS₂ solution.

TABLE 21 . ${}^5J(\text{CH}_3, \text{H}_{3/5})^a$ and the sum of the squares of
(CNDO) π bond orders and the sum of the bond orders
squared for the intervening ring C-C bonds.

Substituent	${}^5J(\text{CH}_3, \text{H}_3)$	${}^5J(\text{CH}_3, \text{H}_5)$	$P_{\mu\nu} = p_{ij}^2 + p_{mn}^2$	$P_{\mu\nu} = (p_{ij} + p_{mn})^2$
H	0.335(1)	0.335(1)	0.213 ^b	0.436 ^c
2F	-----	0.350(1)	0.208	0.416
2F	0.418(1)	-----	0.220	0.433
2Cl	-----	0.367(1)	0.201	0.420
2CL	0.385(1)	-----	0.219	0.438
2Me	-----	0.370(2)	0.208	0.370
2Me	0.407(1)	-----	0.220	0.438
2NH ₂	-----	0.336(2)	0.207	0.413
2NH ₂	0.409(2)	-----	0.207	0.438
2NO ₂	-----	0.361(3)	0.208	0.415
2NO ₂	0.360(2)	-----	0.220	0.438
3F	0.302(1)	-----	0.213	0.436
3Cl	0.316(1)	-----	0.217	0.434
3NH ₂	-----	0.312(2)	0.214	0.429
3NO ₂	-----	0.329(3)	0.219	0.438

Footnotes

^aIn Hz and in CS₂.

^bIt turns out that the sum of the squares of the π mobile
bond orders gives better correlation.

$^5J_{H,H}$ and $^4J_{H,H}$ correlations with the square of the intervening ring C-C π bond orders

$^4J_{H,H}$ is reasonably well correlated with the square of the intervening ring C-C bond order, in agreement with similar work²¹⁻²³ reported. By extending the results for $^4J_{H,H}$ to $^5J_{H,H}$, it turns out that the latter is linearly correlated with the sum of the squares of the intervening ring C-C π bond orders, apparently for the 3-substituted 4-fluorotoluenes only, as evident in the plot of figure 19 for the data in table 21.

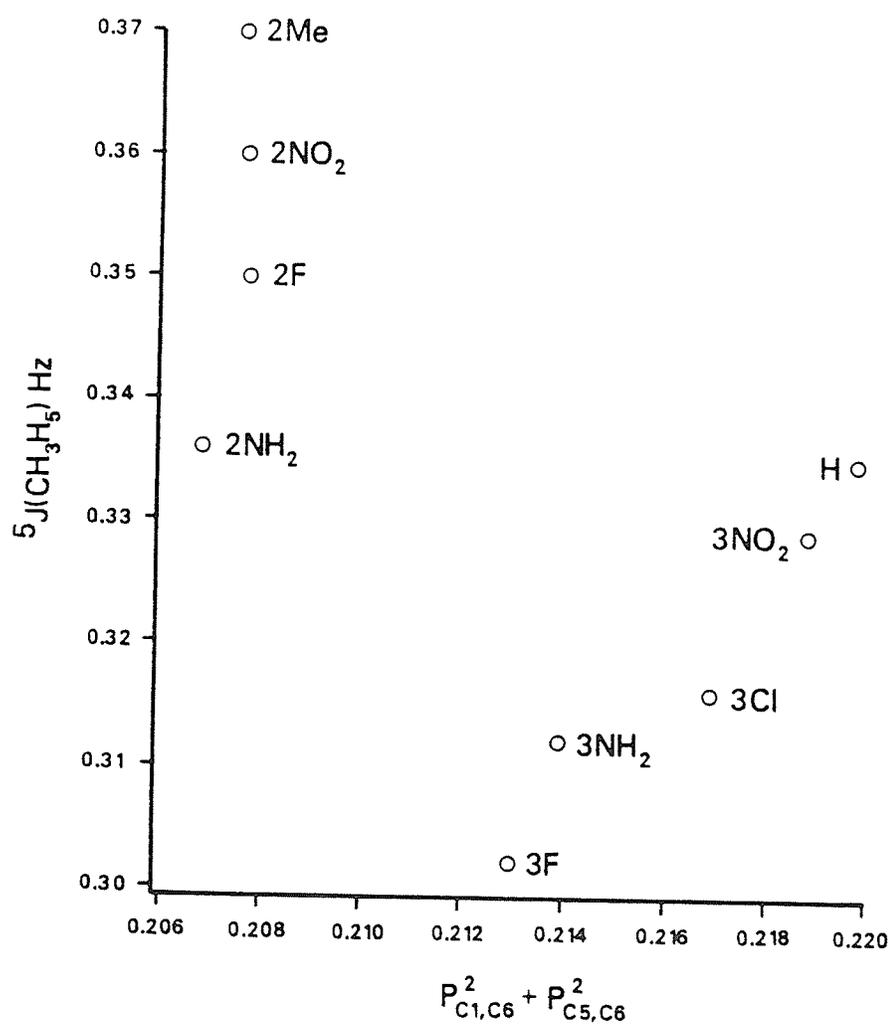


Figure 19

Figure 19 is a plot of ${}^5J(\text{CH}_3, \text{H}_5)$ against the sum of the squares of the π bond orders for the intervening ring C-C bonds, for ring substituted derivatives of 4-fluorotoluene in carbon disulfide solution. The plotted values are from table 21 (2Cl left out in order to get a convenient plot scale). The correlation coefficient is 0.97 (n=5, for 3-substituted derivatives only) and significant at the 99% confidence level.

$^1\text{J}_{\text{C},\text{F}}$ correlations

The behaviour of $^1\text{J}_{\text{C},\text{F}}$ towards substituent perturbations parallels that of $^6\text{J}_{\text{H},\text{F}}$. $^1\text{J}_{\text{C},\text{F}}$ and $^6\text{J}_{\text{H},\text{F}}$ are reasonably well correlated as depicted in figure 23. A systematic study of $^1\text{J}_{\text{C},\text{F}}$ was undertaken by Muller and Carr for some 52 organofluorine compounds in an attempt to determine how this coupling depended on the CF bond. The double bond character^{25a} emerged as perhaps the most important single parameter influencing $^1\text{J}_{\text{C},\text{F}}$. The present results are in accord with this work, perhaps on an even more quantitative basis as the correlations of $^1\text{J}_{\text{C},\text{F}}$ with the various CF bond electronic parameters show in table 23. Experimentally $^1\text{J}_{\text{C},\text{F}}$ is very easy to measure from a ^1H broad-band decoupled C-13 spectrum, although contrary to some reports in the literature, it is found to be little affected by solvent perturbations^{25b}. A maximum variation of about 4% is observed for $^6\text{J}_{\text{H},\text{F}}$ due to solvent effects, and for $^1\text{J}_{\text{C},\text{F}}$ the corresponding variation is only 1.5%. It seems pertinent to stress that $^1\text{J}_{\text{C},\text{F}}$ can only give a rough assessment of the actual values of $^6\text{J}_{\text{H},\text{F}}$ in the presence of ring substituents.

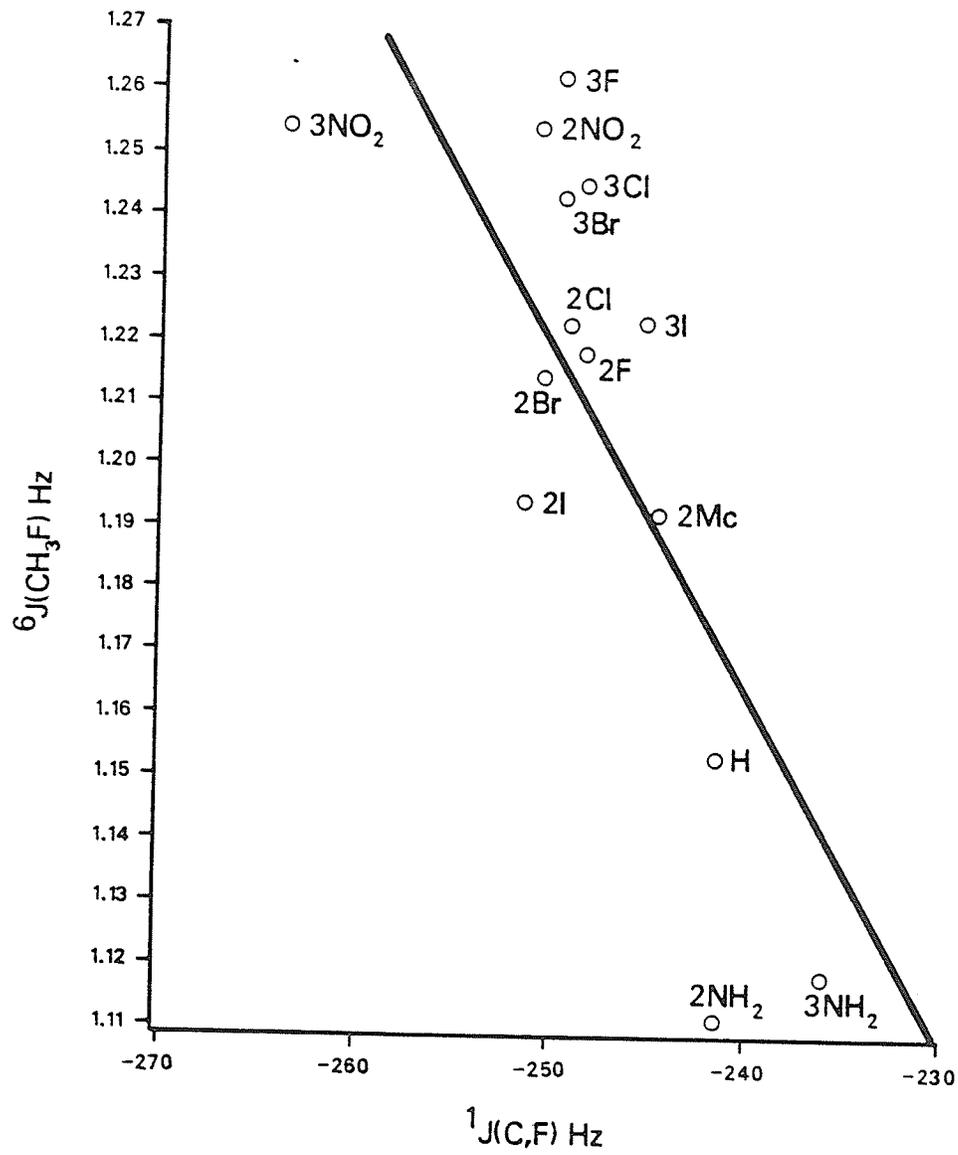


Figure 20

Figure 20 is a plot of ${}^6J_{H,F}$ against ${}^1J_{C,F}$ for ring substituted derivatives of 4-fluorotoluene in carbon disulfide solution. The plotted values are shown in table 19.

$^5\text{J}^{\text{C},\text{F}}$ correlations:

Table 22 reveals that $^5\text{J}^{\text{C},\text{F}}$ is very sensitive to intrinsic ring substituent perturbations and increases roughly as the electronegativity of the substituent increases. It approaches zero for the most electronegative substituent, fluorine, in the 2-position. The minimum value is observed for 4-fluorotoluene itself at $-0.73(1)$ Hz. Clearly this spin-spin coupling constant is not suitable for establishing the conformation and deducing internal rotational barriers for the side chain of benzyl and benzyldene derivatives of 4-fluorotoluenes. $^5\text{J}^{\text{C},\text{F}}$ correlates with the Hammett σ_1 constant and the substituent electronegativity based on the Sanderson³¹ scale; the correlation coefficients are 0.93 at the 99.9% confidence level and 0.89 at the 99% confidence level respectively.

TABLE 22. $^5J_{C,F}$ and the electronegativity^a of substituent and the Hammett σ_I constant^b.

Substituent	$^5J_{C,F}$	E_S	σ_I
2F	-0.06(2)	3.66	0.50
2Cl	-0.14(3)	3.35	0.46
2Br	-0.15(3)	3.22	0.44
2I		2.89	0.39
2Me	-0.53(2)	2.44	-0.04
2NH ₂	-0.37(2)	2.95	0.12
2NO ₂		3.70	0.65
3Br	-0.18(2)	3.22	0.44
3NH ₂	-0.63(6)	2.95	0.12
3NO ₂		3.70	0.65
pft	-0.73(2)	2.00	0.00

Footnotes

^aSanderson electronegativity³¹ scale.^bHammett parameter for field effect in the absence of resonance effects or π overlap effects (one of the dual substituent parameters).

TABLE 23. Correlations among the various observed and computed parameters.

Correlation	n	r	slope	intercept
$4J(\text{CH}_3, \text{H}_6):5J(\text{CH}_3, \text{H}_3)$	7	0.97	-1.30	0.24
$4J(\text{CH}_3, \text{H}_6):5J(\text{CH}_3, \text{H}_5)$	5	-0.94	-4.5	0.92
$5J(\text{CH}_3, \text{H}_5):4J(\text{CH}_3, \text{H}_2)$	6	0.93	-2.5	-0.93
$5J(\text{CH}_3, \text{H}_5):4J(\text{CH}_3, \text{H}_6)$	8	-0.92	-0.80	-0.21
$6J_{\text{H,F}}:(\sigma_{\text{ST}})^c$ meta	a5	0.97	8.4	0.00
$6J_{\text{H,F}}:q_{\text{F}}^g$	9	0.88	29	0.0
$6J_{\text{H,F}}:P^2$	8 ^h	0.86	75	0.3
$6J_{\text{H,F}}:1J_{\text{C,F}}$	13	-0.69	-167	-66
$6J_{\text{H,F}}:5J(\text{CH}_3, \text{H}_5)$	7	0.68	2.7	0.3
$1J_{\text{C,F}}:q_{\text{F}}$	8	-0.75	-2.6×10^{-4}	-1.7×10^{-2}
$1J_{\text{C,F}}:P^2$	8	-0.71	-9.5×10^{-4}	-1.1×10^{-2}
$1J_{\text{C,F}}:P$	8	-0.74	-4.9×10^{-4}	-1.1×10^{-2}
$5J(\text{CH}_3, \text{H}_5):P^2$ (CC)RING	b5	0.97	4.2	-0.59
$4J(\text{CH}_3, \text{H}):P^2$ (CC)RING	9	0.93	9.1	-1.7
$5J_{\text{C,F}}:eE_{\text{S}}$	8	0.89	0.4	-1.6
$5J_{\text{C,F}}:d\sigma_{\text{I}}$	8	0.93	1.0	-0.6

Footnotes

^aOnly meta substituent parameters available.

^{b5} $J(\text{CH}_3, \text{H}_5):P^2$ (CC)RING for 2-substituent derivatives is insensitive to changes of the squares of bond orders summed along the coupling path.

^c σ_{ST} meta are the sigma substituent parameters¹⁰ based on $\beta^{13}\text{C}$ substituent chemical shifts for styrene.

^d σ_{I} is the Hammett field effect without π -overlap substituent parameter.

^e E_{S} is the substituent electronegativity based on the Sanderson scale.

^f P^2 (CC)RING denotes the square of the ring C-C bond orders along the respective coupling path.

^gNo correlation observed if data points for 2NH_2 and 3F are included.

^hNo correlation observed if data points for 2NH_2 and 3F are included.

Summary and conclusions

${}^6J_{H,F}$ varies by about 10% due to intrinsic ring substituent perturbations and the estimated error in V_2 as a result of the variation in ${}^6J_{H,F}$ is of the order of 10 and 30% for benzylidene and benzyl derivatives of 4-fluorotoluenes, respectively. The substituent perturbations of the mechanism of ${}^6J_{H,F}$ appear to be correlated with the substituent induced electronic changes at the CF bond, and this observation tends to support the view that the CF bond in 4-fluorotoluene derivatives can alter its double bond character in response to intrinsic substituent perturbations.

For the long-range proton-proton coupling constants similar maximum variations as for ${}^6J_{H,F}$ are observed due to substituent perturbations, and these are correlated with the sum of the squares of the intervening ring CC bond orders in agreement with other similar work in the literature. ${}^1J_{C,F}$ appears to be correlated with ${}^6J_{H,F}$, ${}^5J_{C,F}$ appears to be correlated with σ_I and the electronegativity of the substituent based on the Sanderson scale³¹.

The conclusions that can be made from this work are that ${}^6J_{H,F}$ can be used for conformational work even in the presence of ring substituents provided that the intrinsic substituent perturbations of ${}^6J_{H,F}$ are built into the analysis, the CF bond plays a significant role in the substituent induced variations of ${}^6J_{H,F}$ and ${}^5J_{C,F}$ cannot be used for conformational work in derivatives of 4-fluorotoluenes.

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