

Nuclear Magnetic Resonance Studies of ^{19}F - ^{19}F Spin-Spin Coupling. 1-Substituted 4,5-Difluoro-8-methylphenanthrenes

Kenneth L. Servis and Kai-Nan Fang

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received June 13, 1968

Abstract: The fluorine chemical shifts and the fluorine-fluorine spin-spin coupling constants have been determined for a series of 1-substituted 4,5-difluoro-8-methylphenanthrenes. The through space interaction of the fluorine nuclei *via* the nonbonding electrons has been shown to provide the most suitable explanation for both the magnitude of the observed F-F coupling and its independence of the fluorine chemical shift.

Proton nuclear magnetic resonance spectroscopy has become a powerful structural and stereochemical tool for the organic chemist.¹ Studies of the effect of controlled structural variations among related compounds have led to empirical correlations of structural properties with chemical shifts and coupling constants.² Attempts to understand the molecular origin of these correlations have provided insight into the detailed electronic structure of chemical bonds. Similar use of fluorine nuclear magnetic resonance spectroscopy has been much more restricted.² Correlations of structural properties with chemical shifts and in particular coupling constants have not been extensively developed largely due to the inavailability of suitably related compounds with a controlled structural variation.³⁻⁶ The necessity of including the additional p-type electrons⁷ and the comparable magnitude of the contributions of both one-electron and two-electron spin and orbital interactions to nuclear spin coupling make calculations of F-F coupling constants⁷ considerably more difficult than calculations of H-H coupling constants.⁸ Although none of the attempts at theoretical calculations of F-F coupling constants have achieved any substantial degree of success,⁹ they do indicate an important contribution from the Fermi-contact type of interaction.

We have begun an investigation of electronic and stereochemical effects on the fluorine-fluorine coupling constants in structurally well-defined systems. In this paper, we report the ^{19}F chemical shifts and ^{19}F - ^{19}F coupling constants for a series of 1-substituted 4,5-difluoro-8-methylphenanthrenes.

Results

The key intermediates for the synthesis of 1-substituted 4,5-difluoro-8-methylphenanthrenes are 2,2'-dimethyl-5,5'-difluoro-*trans*-stilbene (**19a**) and 1,8-dimethyl-4,5-difluorophenanthrene (**1a**). Of the numerous methods available for synthesis of stilbenes, the condensation of benzaldehyde and a phosphorus benzylide *via* a Wittig reaction was chosen.¹⁰ The photochemical cyclooxidation of the stilbene by the Mallory procedure gave the phenanthrene.¹¹ Reactions of non-fluorinated materials were used as models for the reactions of the fluorinated compounds. Compounds previously unreported have been included in the Experimental Section.

Treatment of 4-fluoro-2-iodotoluene with magnesium followed by ethyl orthoformate gave a 75% yield of 2-methyl-5-fluorobenzaldehyde (**15a**) (Scheme I). Reduction of **15a** with lithium aluminum hydride yielded 2-methyl-5-fluorobenzyl alcohol (**16a**) which on treatment with gaseous hydrogen chloride gave 2-methyl-5-fluorobenzyl chloride (**17a**). Diethyl 2-methyl-5-fluorobenzylphosphonate (**18a**) was prepared from **17a** and triethyl phosphite and gave, upon treatment with sodium hydride in the presence of **15a**, a 70% yield of 2,2'-dimethyl-5,5'-difluoro-*trans*-stilbene (**19a**), mp 117°, $\nu_{\text{max}}^{\text{cyclohexane}}$ 285 $\text{m}\mu$ ($\log \epsilon$ 4.8).

Alumina chromatography of the product mixture resulting from the photolysis of **19a** by the Mallory procedure¹¹ gave a 48.6% yield of **1a**, and a 12.9% yield of 2-methyl-4,7-difluorophenanthrene (**21**).¹² The structure of **1a** was established on the basis of its elemental analysis and infrared, ultraviolet, and nmr spectral properties. It exhibits $\lambda_{\text{max}}^{\text{cyclohexane}}$ 248 $\text{m}\mu$ ($\log \epsilon$ 4.9);¹³ $\nu_{\text{max}}^{\text{CS}_2}$ 1250, 818, 735, 703 cm^{-1} ; δ (ppm) 2.58 (singlet, 6 H), 6.90-7.30 (multiplet, 4 H), and 7.69 (triplet, 2 H), and a single ^{19}F nmr absorption 59.22 ppm downfield from hexafluorobenzene. All of the data are as expected, *vide infra*, for the assigned structure.

The structure of **21** was assigned on the basis of elemental analysis in conjunction with its infrared, ultraviolet, and nmr spectral properties. It exhibits $\lambda_{\text{max}}^{\text{cyclohexane}}$

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(7) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

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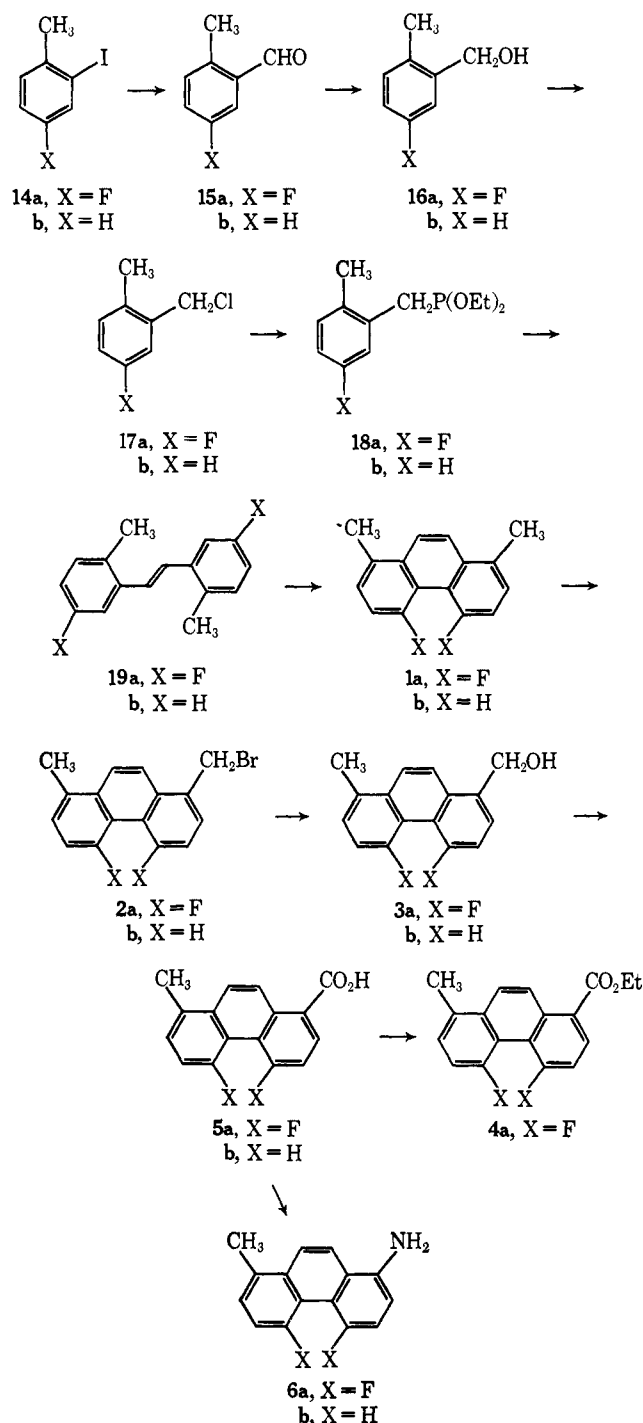
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(12) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **84**, 4361 (1962); *ibid.*, **85**, 828 (1963); *ibid.*, **86**, 3094 (1964); K. L. Servis and Kai-Nan Fang, *Tetrahedron Lett.*, 967 (1968).

(13) Typical values for phenanthrenes are λ_{max} 250 $\text{m}\mu$ ($\log \epsilon$ 5.0): "Constants of Organic Compounds," M. Kotake, Ed., Asakura Publishing Co., Tokyo, Japan, 1963, p 131.

Scheme I. Total Synthesis of 1-Substituted 8-Methyl-4,5-difluorophenanthrenes



249 $m\mu$ ($\log \epsilon$ 5.0); ν_{\max}^{CS} 1300, 1250, 1210, 1198, 1130, 1071, 950, 863, 826, 815, 775, 735, 700, 602, and 591 cm^{-1} all as expected for a phenanthrene molecule of low symmetry. In the nmr spectrum, resonances characteristic of a single methyl group at 2.42 ppm, six aromatic protons at 6.88–7.65 ppm, and a single 4-phenanthryl proton at 8.91 ppm, were observed. In addition two ^{19}F resonances of equal intensity were observed at 49.0 and 50.5 ppm downfield from C_6F_6 . No significant F–F coupling could be observed. Infrared studies of the initial photolysis solution verify that the formation of **21** occurs in an initial process and not by a subsequent reaction. Both **1a** and **21** were found to be stable under the photolysis conditions.

Adaptation of standard aromatic side-chain reactions was used to convert **1a** into the desired derivatives **2a**, **3a**, **4a**, **5a**, and **6a**.¹⁴ The synthetic sequence is summarized in Scheme I.

The ^{19}F nmr spectra of compounds **1a**, **2a**, **3a**, **4a**, and **6a** were obtained in acetone- d_6 at 94.1 Mc. The fluorine chemical shifts and coupling constants so obtained are presented in Table I. Attempts to determine

Table I. ^{19}F Chemical Shifts^a and Coupling Constants^b at 94.1 Mc

	1a	2a	3a	4a	6a
δ_{F_4}	59.22	64.72	60.94	70.28	47.68
δ_{F_8}	59.22	59.48	59.05	59.23	59.40
$J_{\text{F-F}}$		170 ± 2	170 ± 2	167 ± 2	167 ± 2
$\delta_{\text{F}_8} + \delta_{\text{F}_5}^c$	118.44	124.20	119.99	129.51	107.08

^a Chemical shifts were measured in acetone- d_6 and reported in parts per million downfield from hexafluorobenzene as internal standard. ^b In cycles per second. ^c The sum of the ^{19}F chemical shifts.

the F–F coupling constant for **1a** from the ^{13}C satellite spectrum were unsuccessful. Since the F–F coupling constant, *vide supra*, is of the same order of magnitude as the ^{13}C – ^{19}F coupling constant, the ^{13}C satellite spectrum is buried under the main absorption band and could not be observed. The ^{19}F chemical shift and the F–F coupling constants were also determined in other solvents. The results are presented in Table II. No solvent dependence of the F–F coupling constants was observed; the ^{19}F chemical shifts show only small irregular variation upon changing solvents.

Table II. ^{19}F Chemical Shifts^a and F–F Coupling Constants^b in Various Solvents

Compd	δ or J	Acetone- d_6	Acetone	Benzene
1a	$\delta_{\text{F}_4}, \delta_{\text{F}_8}$	59.22 ^c	58.99 ^c	59.42 ^c
2a	δ_{F_8}	0.26	0.38	–0.44
	δ_{F_4}	5.50	5.08	6.26
	$J_{\text{F-F}}$	170 ± 2	170 ± 2	170 ± 2
3a	δ_{F_8}	–0.17	0.33	
	δ_{F_4}	1.72	2.16	
	$J_{\text{F-F}}$	170 ± 2	170 ± 2	
4a	δ_{F_8}	0.01		0.01 ^d
	δ_{F_4}	11.06		11.28 ^d
	$J_{\text{F-F}}$	167 ± 2		167 ± 2 ^d
6a	δ_{F_4}	0.18		
	δ_{F_8}	–11.54		
	$J_{\text{F-F}}$	167 ± 2		
21	δ_{F_4}	–8.95	–8.50	
	δ_{F_7}	–10.01	–10.01	

^a In parts per million downfield from **1a**. ^b In cycles per second. ^c In parts per million downfield from C_6F_6 . ^d In ether.

The ^1H nmr spectra of compounds **1a**, **2a**, **3a**, **4a**, and **6a** were obtained in acetone- d_6 at 100 Mc. The proton chemical shifts so obtained are presented in Table III. The 100-Mc ^1H nmr spectrum of 1-carboethoxy-4,5-difluoro-8-methylphenanthrene (**4a**) is the ABCDEF part (ring protons only) of an ABCDEFXY-type spectrum. The large chemical shift difference between proton H_2 (A), H_9 (E), and H_{10} (F) and the rest of the ring protons (BCD) permitted a determination of individual proton chemical shifts and coupling con-

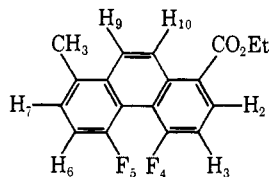
(14) P. J. C. Fierens, R. H. Marties, and J. Van Rysselberge, *Helv. Chim. Acta*, **38**, 2005 (1955).

Table III. ^1H Chemical Shifts^{a,b} of 1-Substituted 8-Methyl-4,5-difluorophenanthrenes at 100 Mc

Protons	1a	2a	3a	4a	6a
H ₂	7.36 m	7.69 q	7.64 q	8.31 q	6.87 q
H ₃	7.14 m	7.04-7.47 m	7.05-7.48 m	7.45 q	7.02-7.48 m
H ₆	7.14 m	7.04-7.47 m	7.05-7.48 m	7.31 q	7.02-7.48 m
H ₇	7.36 m	7.04-7.47 m	7.05-7.48 m	7.54 q	7.02-7.48 m
H ₉	7.72 t	7.93 t	7.90 q	8.01 q	7.80 q
H ₁₀				8.82 q	

^a Chemical shifts measured in acetone-*d*₆ with tetramethylsilane as internal standard. ^b In parts per million; m = multiplet, q = quartet, t = triplet.

stants by proton spin decoupling techniques in conjunction with computer calculations using the program of Swalen and Reilly.¹⁵ The computer analysis of the spectrum was accomplished by separating the total, spin system into three noninteracting parts—ABX, CDY, and EFX. The resultant H-H and H-F coupling constants are presented in Table IV.

Table IV. H-H and H-F Coupling Constants^a for 1-Carbethoxy-4,5-difluoro-8-methylphenanthrene

$J_{2,3} = 8.45 \pm 0.02$	$J_{5,6} = 12.72 \pm 0.1$
$J_{2,4} = 4.98 \pm 0.02$	$J_{5,7} = 4.76 \pm 0.1$
$J_{3,4} = 11.81 \pm 0.02$	$J_{5,9} = 2.22 \pm 0.08$
$J_{4,5} = 170 \pm 2$	$J_{6,7} = 8.44 \pm 0.1$
$J_{4,10} = 2.22 \pm 0.08$	$J_{9,10} = 9.90 \pm 0.08$

^a In cycles per second, determined from ^1H and ^{19}F nmr spectra at 100.0 and 94.1 Mc, respectively.

The resonances due to protons at the 9 and 10 positions for **1a** were readily assignable since they exhibit only H-F (2.2 cps) and not H-H coupling. For compounds **2a**, **3a**, **4a**, and **6a**, the resonances due to the 9 and 10 protons were assigned by analogy to **1a**. The magnitude of $J_{\text{H}_9\text{-H}_{10}}$ also serves to identify H-9 and H-10. For the remaining protons, the resonance exhibiting the largest chemical shift dependence on substituent was assigned to the H-2 proton. The proton at the 3 position could then be identified as the one coupled to H-2. The resonances of H-6 and H-7 were assigned to the protons with coupling constants similar to H-2 and H-3. The observed *meta* H-F coupling constants (4.76 and 4.98 cps) are smaller than those usually reported (6.2-8.3 cps)¹⁶ for fluorobenzene, while the observed *ortho* H-F coupling constants (11.81 and 12.72 cps) are larger than those usually reported (6.2-10.1 cps)¹⁶ for fluorobenzene.

Both the magnitude of the H₉-H₁₀ coupling constant (9.9 cps)¹⁷ and the low-field chemical shifts of the H₁₀ protons serve to identify them.

(15) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(16) See ref 2, Vol. II, p 903.

(17) E. Clar, B. A. McAndrew, and M. Zander, *Tetrahedron*, **23**, 985 (1967).

Discussion

Several empirical rationalizations of F-F coupling constant data have been offered. A linear correlation of F-F geminal coupling constants with fluorine chemical shifts in compounds of the type $\text{F}_2\text{C}=\text{CXY}$ has been shown to exist.⁶ This has been ascribed to a change in the density of the nuclear spin information carrying electrons at the intervening carbon atom due to valence bond resonance structures such as $\text{F}_2\text{C}^+-\text{CF}=\text{CF}-\text{O}^-$. If the substituent is electron withdrawing, then both the coupling constant and the nuclear shielding would be decreased. Similarly the geminal F-F coupling in compounds of the type QCF_2CFHCl have been correlated with the electronegativity of the substituted group.¹⁸ Again it was suggested that a decrease in the electron density at the intervening carbon atom decrease $J_{\text{F-F}}^{\text{gem}}$.

Long-range F-F coupling constants have been found to be both structurally and stereochemically dependent. Sederholm, *et al.*, upon consideration of the then available data suggested that long-range F-F coupling does not occur through the bonding electrons but by a "through-space" mechanism involving nonbonded F-F interactions.¹⁹ Later work has pointed out some of the inadequacies of this proposal²⁰ but indirect support for the basic premise has continued to accumulate. From studies of substituted benzotrifluorides and α -fluoro-substituted toluenes, an approximately dependence²¹ of the F-F spin-spin coupling constant upon the dihedral angle between the α -C-F and the 2C-F bonds was obtained. A single large five-bond F-F coupling constant was observed for the conformationally immobile *gauche* form of bis(ditrifluoromethyl)tetrachloroethane and was ascribed to the two fluorines in closest proximity to one another.²² The available results do support the existence of a major, "through-space" contribution to the F-F coupling but as yet calculations have not shown that nonbonded interactions should be important for F-F coupling nor that the coupling *via* the σ and π bonds is insufficient to account for the observed dependence of $J_{\text{F-F}}$ upon molecular geometry.

The F-F coupling constant between the fluorine at the 4 and 5 positions of **2a-6a** is extraordinarily large. It exceeds not only the largest previously reported five-bond F-F coupling constant but also all reported three- and four-bond coupling constants and is only slightly smaller than normal geminal F-F coupling constants.² Not only is the coupling constant large, it is also independent of the substituent at the 1 position. The sum of the chemical shifts ($\delta_{\text{F}_4} + \delta_{\text{F}_5}$) decreases by 22.5 ppm upon changing the 1-amino substituent to a 1-carbethoxy substituent but the coupling constant remains invariant at 168 cps. Both the magnitude and constancy of the F-F coupling constant must be

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(19) (a) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); (b) S. Ng and C. H. Sederholm, *ibid.*, **40**, 2090 (1964).

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(21) (a) H. S. Gutowsky and V. D. Mochel, *J. Chem. Phys.*, **39**, 1195 (1963); (b) J. Jonas and H. S. Gutowsky, *ibid.*, **42**, 140 (1965); (c) J. Jonas, L. Borowski, and H. S. Gutowsky, *ibid.*, **47**, 2441 (1967); (d) J. Jonas, *ibid.*, **47**, 4884 (1967).

(22) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 3577 (1968).

accounted for by any explanation offered for the present results.


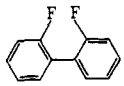
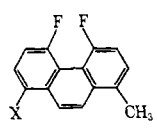

Calculations indicate that the largest non-Fermi-contact type interaction which contributes to F-F spin coupling arises from electron orbital interaction.⁹ Pople has shown that the electron-orbital contribution should be proportional to the bond anisotropy,^{9b} while Saika and Slichter have shown that fluorine chemical shifts are also proportional to bond anisotropies.²³ One might therefore expect any electron-orbital contribution to F-F coupling to be dependent on the fluorine chemical shifts. Although electron-orbital interaction contributions might be invoked to explain the variability of the geminal coupling constants for 1,1-difluoroalkenes, it quite obviously cannot account for the results for the 4,5-difluorophenanthrenes where no chemical shift dependence is observed.

Use of the approximate, theoretical expression developed by Pople^{9b} for the orbital contribution leads to a calculated value of $J_{orb}^{FF} = -8.6$ cps (based on normal bond angles and a planar aromatic system).

Fermi-contact interaction defines only the type of interaction between the electron spin and the nuclear spin but does not define the mechanisms by which the polarization of the electron spin is communicated from one nuclear position to another. *A priori*, one might consider σ -electron interaction, π -electron interaction, or direct interaction of the nonbonding electrons as being responsible for the coupling.

The F-F coupling constants determined for other molecules containing the F-C=C-C=C-F moiety are presented in Table V. If coupling were occurring *via* the σ electrons, a variation of nearly two orders of magnitude in the five-bond coupling would not be expected. Furthermore, since σ -electron spin polarization should attenuate rapidly with the number of intervening bonds, a five-bond coupling constant of 170 cps would appear to be too large to account for by this mechanism.

Table V. Five-Bond Fluorine-Fluorine Coupling Constants

	$J_{1-5} = 35.7^a$ $J_{1-5} = 8.0^a$ $J_{1-5} = 4.8^a$
	$J_{1-5} = 16.5^b$
	$J_{1-5} = 170^b$
	$J_{1-5} = 23.2^a$ $J_{1-5} = 6.7^a$ $J_{1-5} = 7.6^a$

^a Reference 5. ^b This work.

It has been shown that fluorine chemical shifts for *meta*- and *para*-substituted fluorobenzenes are related to the carbon-fluorine π -bond order (or equivalently, the fluorine π -electron charge density).²⁴ The magnitude of the spin polarization of the π electrons should

also be dependent on the C-F π -bond order. Changing the substituent at the 1 position should change the C-F π -bond order and thereby the magnitude of the spin polarization of the π electrons. The observed insensitivity of the F-F coupling constant to substituent changes at the 1 position makes it unlikely that π -electron spin polarization is a major contribution to the F-F coupling constant.

Direct interaction of the nonbonding electrons should occur over the same range of internuclear distances as the distances over which intermolecular electron correlations can occur. If direct internuclear bonding is not possible, this interaction should be relatively small at large internuclear distances and becomes significant only at short distances characteristic of the steep portions of the van der Waal's curve. Previous studies have indicated that this spin-coupling mechanism is not a major contributor to the observed F-F coupling if the internuclear separation is in the range of the sum of the van der Waal's radii.⁵ The equilibrium F-F separation for the 4,5-difluorophenanthrenes results from a balance of the nonbonded F-F repulsion against the large out-of-plane distortion energy for the phenanthrene skeleton and must be appreciably smaller than the sum of the van der Waal's radii for two fluorines. This type of interaction should also be sensibly independent of the C-F π -bond order as measured by the fluorine chemical shift.

The through space interaction of the fluorine nuclei *via* the nonbonding electrons provides the most suitable explanation for both the magnitude of the observed five-bond F-F coupling and its independence of the fluorine chemical shift. If the foregoing conclusions are correct, it may be possible to distinguish through-space F-F coupling by its insensitivity to substitution which affects only the fluorine chemical shifts.

Experimental Section

Melting points were determined with a capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Eleck Microanalytical Laboratory, Los Angeles, Calif. The infrared data were obtained with a Perkin-Elmer Infracord 337 or 137 and measured in carbon disulfide, unless otherwise specified. Ultraviolet spectra were measured with a Cary 14 spectrophotometer. ¹H nmr spectra were obtained on Varian A-60 and HA-100 spectrometers at 60 and 100 Mc, using tetramethylsilane as internal standard. ¹⁹F nmr spectra were determined on a Varian HA-100 at 94.1 Mc using hexafluorobenzene as internal standard; chemical shifts are in parts per million downfield from hexafluorobenzene. Spectra analyses were carried-out on the Honeywell-800 computer and followed the method of Swalen and Reilly.¹⁶

2-Methyl-5-fluorobenzaldehyde (15a).²⁵ To a 200-ml, three-necked flask (flame-dried), Mg turnings (5 g, 0.21 g-atom) and ether (100 ml) were added. After using a small crystal of iodine for initiation, 4-fluoro-2-iodotoluene (40 g, 0.17 mol) was added slowly. After the addition was completed, the mixture was refluxed for 1.5 hr and then cooled in an ice bath. Triethyl orthoformate (30 g, 0.203 mol) was added and the mixture refluxed for 6 hr. The ether was removed on the steam bath and hydrogen chloride (1:1) solution added under nitrogen until the organic layer separated clearly. The aqueous layer was extracted with ether and the combined ether extracts were washed with saturated sodium thiosulfate solution to remove the excess iodine and extracted with ether again. The combined ether extracts were dried over magnesium sulfate and distilled to give 2-methyl-5-fluorobenzaldehyde (20.51 g, 87.5% yield), bp 99° (30 mm).

Spectral data showed ν_{max}^{neat} 1690, 1605, 1570, 1240, 1150, 715 cm^{-1} ; ¹H nmr at 60 Mc in CCl₄, 2.60 (s), 7.05-7.69 (m), 10.3 ppm (d).

(25) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

(23) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(24) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1962).

2-Methyl-5-fluorobenzyl Alcohol (16a). A solution of lithium aluminum hydride (4.5 g, 0.119 mol) in ether (100 ml) was placed in a 200-ml, three-necked flask and 2-methyl-5-fluorobenzaldehyde (16.5 g, 0.12 mol) added. After the mixture was refluxed for 3 hr, saturated sodium chloride solution was added to decompose the excess of lithium aluminum hydride. The solution was filtered and ether removed to give crude product which was distilled to give 2-methyl-5-fluorobenzyl alcohol (15 g, 92% yield), bp 72° (0.4 mm), mp 33–33.5°.

Spectral data showed ν_{\max}^{neat} 3400–3300, 1605, 1590, 1245, 1145, 1100, 1350, 865, 805, 708 cm^{-1} ; ^1H nmr at 60 Mc in CCl_4 , 2.20 (s), 2.31 (s), 4.47 (s), 6.78–7.58 ppm (m).

2-Methyl-5-fluorobenzyl Chloride (17a). Anhydrous hydrogen chloride gas was passed directly from a gas container (Matheson Co.) into a solution of 2-methyl-5-fluorobenzyl alcohol (14.8 g, 0.105 mol). After 10 hr, the solution was dried over calcium chloride and distilled to give 2-methyl-5-fluorobenzyl chloride (12.3 g, 75%), bp 46° (0.4 mm).

Spectral data showed ν_{\max}^{neat} 1602, 1600, 1248, 1138, 1150, 958, 870, 810, 745, 718, 672, 600 cm^{-1} ; ^1H nmr at 60 Mc in CCl_4 , 2.18 (s), 4.45 (s), 6.70–7.20 ppm (m).

Diethyl 2-Methyl-5-fluorobenzylphosphonate (18a). 2-Methyl-5-fluorobenzyl chloride (12.3 g, 0.077 mol) was mixed with triethyl phosphite (14 g, 0.084 mol) and the mixture refluxed for 24 hr. The mixture was distilled to give diethyl 2-methyl-5-fluorobenzylphosphonate (18.23 g, 90.5% yield), bp 125° (0.4 mm).

Spectral data showed ν_{\max}^{neat} 1602, 1600, 1240, 1010–1050, 940–970 (broad), 870, 850, 780–800, 713, 690 cm^{-1} ; ^1H nmr at 60 Mc (neat), 1.10 (t), 2.15 (s), 2.93 (d), 3.70 (quintet), 6.47 ppm (m).

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3\text{FP}$: C, 55.38; H, 6.97. Found: C, 55.34; H, 7.08.

2,2'-Dimethyl-5,5'-difluoro-*trans*-stilbene (19a).²³ Sodium hydride (4 g, 59.4% in mineral oil) (washed with ether before use) was added to a mixture of dimethylformamide (40 ml) and benzene (30 ml) in a 200-ml, three-necked flask. Diethyl 2-methyl-5-fluorobenzylphosphonate (15.8 g, 0.0608 mol) was added slowly followed by 2-methyl-5-fluorobenzaldehyde (8.5 g, 0.0615 mol). The mixture was refluxed for 3 hr and poured into cold water then extracted with ether. The combined ether extracts were dried over magnesium sulfate and evaporated to dryness to give crude 2,2'-dimethyl-5,5'-difluoro-*trans*-stilbene which was purified by column chromatography and recrystallized from absolute ethanol to give white crystals (10.18 g, 68.8% yield), mp 117°.

Spectral data showed ν_{\max} 1260, 1155, 1090, 1000, 956, 861, 802, 725 cm^{-1} ; ^1H nmr at 100 Mc in CS_2 , 2.38 (s), 6.70–7.28 ppm (m); ^{19}F nmr at 94.1 Mc in acetone- d_6 4293.2 cps (q).

Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2$: C, 78.69; H, 5.74. Found: C, 78.53; H, 5.80.

1,8-Dimethyl-4,5-difluorophenanthrene (1a).¹¹ **A. Photochemical Reactor.** A 100-W General Electric H100A4/T mercury lamp was modified by cutting away the outer glass envelope and also by detaching the inner quartz bulb from the screw base on which it was mounted. The two electrical leads from the lamp were then connected by means of insulated wire to a General Electric 9T64Y-1019 transformer. The modified mercury lamp was then inserted into a 17-mm i.d. quartz tube which was sealed on one end.

B. Procedure. A mixture of 2,2'-dimethyl-5,5'-difluoro-*trans*-stilbene (2.44 g, 0.01 mol) and iodine (0.127 g, 0.005 mol) was dissolved in cyclohexane (1.61 l) in a 2-l. modified erlenmeyer flask. The flask was placed in a cold-water bath and the solution was stirred magnetically. The quartz tube containing the mercury lamp was immersed in the solution and the lamp was started. The irradiation was continued for 6 hr. The procedure was repeated two times. The combined reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in 50 ml of warm cyclohexane and the solution was poured onto a column of acid-washed alumina (Kimax 500-ml column). The column was eluted with four portions of 100 ml of cyclohexane. The second and third fractions (2.12 g), mp 102°, were recrystallized from absolute ethanol to give 1,8-dimethyl-4,5-difluorophenanthrene, mp 103.5°.

Spectral data showed ν_{\max} 1250, 818, 735, 703 cm^{-1} ; $\lambda_{\max}^{\text{cyclohexane}}$ 248 $\text{m}\mu$ (log ϵ 4.89); ^1H nmr at 100 Mc in acetone- d_6 , 2.58 (s), 7.14 (m), 7.36 (m), 7.72 ppm (t); ^{19}F nmr at 94.1 Mc in acetone- d_6 5572.8 cps (s) (broad); in benzene, 5591.0 cps (s); in acetone, 5581.2 cps (s).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_2$: C, 79.33; H, 4.95. Found: C, 79.17; H, 5.04.

The first fraction (2.06 g) was irradiated again by the procedure

described above. The irradiation was continued for 11.5 hr and the mixture was purified by column chromatography.

The crude crystalline first fraction (0.586 g) was purified by sublimation to give a 12.9% yield sample of colorless crystal (0.2736 g), mp 56–57°.

Spectral data showed $\lambda_{\max}^{\text{cyclohexane}}$ 249 $\text{m}\mu$ (log ϵ 5.0); ν_{\max} 1300, 1250, 1210, 1158, 1071, 950, 863, 826, 815, 775, 735, 700, 602, 591 cm^{-1} ; ^1H nmr at 100 Mc in CDCl_3 , 2.42 (s) (3 H), 6.88–7.65 (m) (6 H), 8.80–9.02 ppm (quintet) (1 H); ^{19}F nmr at 94.1 Mc in CDCl_3 , 4646.6 (d), 4479.6 cps (q); in acetone, 4751.4 (d), 4609.4 cps (q); in acetone- d_6 , 4730.4 (d), 4583 cps (q).

Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{F}_2$: C, 78.94; H, 4.39; F, 16.67. Found: C, 78.87; H, 4.56; F, 16.17.

The second fraction (0.58 g) was identical with 1a.

Bromination of 1,8-Dimethyl-4,5-difluorophenanthrene. 1,8-Dimethyl-4,5-difluorophenanthrene (2.2 g, 0.009 mol) was dissolved in carbon tetrachloride (75 ml) and N-bromosuccinimide (1.62 g, 0.009 mol) and α,α -azodiisobutyronitrile (trace) added.¹⁰ The mixture was refluxed for 24 hr under ultraviolet irradiation and then filtered. The filtrate was evaporated to dryness to give crude 1-bromomethyl-8-methyl-4,5-difluorophenanthrene (2a, 2.28 g).

Spectral data showed ν_{\max} 1380, 1250, 1200, 817, 736, 705, 658, 620, 595, 576, 550 cm^{-1} ; ^1H nmr at 100 Mc in acetone- d_6 , 2.58 (s), 4.82 (s), 7.04–7.47 (m), 7.69 (q), 7.72 (t), 7.93 ppm (t); ^{19}F nmr at 94.1 Mc in acetone, 6129.7 (d), 6032.7 (s), 5959.7 (d), 5656.4 (d), 5581.2 (s), 5486.4 cps (d); $J_{\text{F-F}} = 170 \pm 2$ cps.

The absorptions at 5581.2 and 6032.7 cps were assigned as starting material (1a) and 1,8-(bisbromomethyl)-4,5-difluorophenanthrene (2a), respectively.

Hydrolysis of 1-Bromomethyl-8-methyl-4,5-difluorophenanthrene. The crude 1-bromomethyl-8-methyl-4,5-difluorophenanthrene (2.28 g, 0.0065 mol) was dissolved in dioxane (120 ml) and sodium hydroxide (4 g) in water (30 ml) added. The mixture was refluxed for 27 hr and poured into cold water and then extracted with ether. The ether extracts were dried and the solvent was removed to give crude 1-methylol-8-methyl-4,5-difluorophenanthrene (3a, 2.25 g).

A portion of the crude alcohol (0.364 g) was purified by column chromatography (base-washed alumina) and then sublimed to give colorless crystals, mp 126–127°.

Spectral data showed ν_{\max} 3600 (sharp), 2800–3200, 1310, 1295, 1250, 1210, 1160, 1061, 1055, 1008, 818, 735, 702 cm^{-1} ; ^1H nmr at 100 Mc in acetone- d_6 , 2.65 (s), 4.38 (t), 5.07 (d), 7.05–7.48 (m), 7.64 (q), 7.90 ppm (q); ^{19}F nmr at 94.1 Mc in acetone- d_6 , 5557.0 (q), 5734.8 cps (q), $J_{\text{F-F}} = 170 \pm 2$ cps; in acetone, 5582.1 (q), 5754.1 cps (q), $J_{\text{F-F}} = 167.8 \pm 2$ cps.

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{OF}_2$: C, 74.42; H, 4.65; F, 14.73. Found: C, 74.15; H, 5.15; F, 13.38.

1-Carboxy-8-methyl-4,5-difluorophenanthrene. 1-Hydroxy-8-methyl-4,5-difluorophenanthrene (0.1185 g) was dissolved in acetone (20 ml) and cooled in a Dry Ice-acetone bath. Jones reagent (2 ml, 0.004 equiv/ml) was added slowly to the solution with vigorous stirring. After 10 min, the mixture was allowed to warm up to room temperature for 30 min. Isopropyl alcohol was added to destroy the excess of Jones reagent. The mixture was poured into cold water and extracted with ether. The ether extracts were dried over magnesium sulfate and solvent was removed to give crude 1-carboxy-8-methyl-4,5-difluorophenanthrene (5a). Acid-catalyzed esterification gave, after purification, colorless needles of 4a, mp 55°.

Spectral data showed ν_{\max} 2820, 2970, 1720, 1310, 1296, 1250, 1210, 1194, 1178, 1132, 1095, 1061, 1031, 820, 758, 738, 706 cm^{-1} ; ^1H nmr at 100 Mc in acetone- d_6 , 2.41 (t), 2.64 (s), 4.41 (q), 7.31 (q), 7.45 (q), 7.54 (q), 8.00 (q), 8.82 ppm (q); ^{19}F nmr at 94.1 Mc in acetone- d_6 , 5573.1 (q), 6613.1 cps (q), $J_{\text{F-F}} = 167 \pm 2$ cps; in ether, 5592.5 cps (q), 6652.5 cps (q), $J_{\text{F-F}} = 167 \pm 2$ cps.

1-Amino-8-methyl-4,5-difluorophenanthrene. A portion of crude acid (0.105 g) 5a was dissolved in a mixture of trifluoroacetic acid (15 ml) and trifluoroacetic anhydride (15 ml) and a few drops of concentrated sulfuric acid. Sodium azide was added slowly while the mixture was cooled in an ice-salt bath. The mixture was then warmed up to room temperature, poured into ice water, and extracted with ether. The solvent was removed and the residue dissolved in 70% ethanol (40 ml) and sodium hydroxide (1 g) added. The mixture was refluxed for 5 hr and poured into cold water, then extracted with ether. The ether extracts were washed with water and the combined ether extracts were dried over magnesium sulfate. The solvent was removed to give crude 1-amino-8-methyl-4,5-difluorophenanthrene (6a) which was sublimed to give yellow crystals (0.041 g), mp 116–117°.

Spectral data showed ν_{\max} 3400, 3370, 1360, 1310, 1257, 1250, 1135, 1090, 1055, 1020, 817, 801, 735, 701 cm^{-1} ; ^1H nmr at 100 Mc in acetone- d_6 , 2.68 (s), 3.59 (m), 6.87, 7.02–7.50 (m), 7.80 ppm (q); ^{19}F nmr at 94.1 Mc in acetone- d_6 , 4486.6 (q), 5589.2 cps (q), $J_{\text{F-F}} = 166.6 \pm 2$ cps.

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Dihedral Angle and Bond Angle Dependence of Vicinal Proton–Fluorine Spin–Spin Coupling¹

Kenneth L. Williamson, Yuan-Fang Li Hsu,^{2a} Frances H. Hall,^{2b} Susan Swager, and Margaret S. Coulter^{2b}

Contribution from the Department of Chemistry, Mount Holyoke College, South Hadley, Massachusetts 01075. Received July 1, 1968

Abstract: From an analysis of the nmr spectra of compounds of fixed and known stereochemistry the vicinal proton–fluorine coupling constant has been found to be a function of dihedral angle; the dependence is like vicinal J_{HH} —a maximum at 0° (ca. 31 Hz), a minimum at 90° (ca. 0 Hz), and a maximum at 180° (ca. 44 Hz)—and *not* a linear dependence as has been reported. $J_{\text{HF-vic}}$ is extremely dependent on bond angle, being ca. 31 Hz for a bond angle near 109° and dropping to 0.9 Hz for a bond angle near 118° (dihedral angle fixed at 0°). Evidence is presented for a bond length dependence of $J_{\text{HF-vic}}$.

The dihedral angle dependence of vicinal proton–proton coupling constants has proved of immense value in structural studies of organic molecules. The purpose of the present work was to determine if a similar relationship exists for proton–fluorine coupling constants. It has been widely assumed that $J_{\text{HF-vic}}$ depends on the dihedral angle between the coupling nuclei in the same way that $J_{\text{HH'-vic}}$ does,³ *i.e.*, that $J_{\text{HF-vic}}$ should have a maximum value when the dihedral angle, ϕ , between H and F is 0 and 180° and a minimum value when the dihedral angle is 90° . However, White⁴ has reported that J_{HF} is a *linear* function of dihedral angle, being 5.8, 11.4, 14.6, and 17.8 Hz for 0 , 60 , 90 , and 120° , respectively.

Karplus,⁵ utilizing a nonionic six-electron, six-orbital fragment in a valence bond σ -electron calculation, predicted that the vicinal coupling constant in the fragment H–C–C'–H' should be a function of (1) the electronegativity of substituents on the system, (2) bond length, (3) bond angle, and (4) the dihedral angle between the coupling protons. In order to see if a similar relationship holds for H–F coupling, it is necessary to try to hold three of these variables constant while examining the fourth.

(1) Presented at the 2nd International Symposium on Nuclear Magnetic Resonance, Sao Paulo, Brazil, July 1968. See K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *J. Am. Chem. Soc.*, **88**, 5678 (1966), for a preliminary report on a portion of this work.

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In the present work, in order to focus our attention on the *dihedral angle* dependence of J_{HF} , we have attempted to minimize substituent effects in the compounds we have synthesized. Similarly, to determine the effect of *bond angle* on the vicinal proton–fluorine coupling constant we have examined compounds with dihedral angles constrained to 0° in which the H–C–C and C–C–F bond angles change by virtue of changes in the sizes of the rings in which the H–C–C–F system appears, again attempting in so far as possible to minimize the effect of substituents.

Naturally a large number of vicinal H–F coupling constants have been reported in the past few years but it has proved difficult to ascertain the dihedral angle dependence from these data because the molecules are conformationally flexible. Many of the studies have been made on highly halogenated alkanes in which rotation about the carbon–carbon bond can occur or on fluorinated cyclohexanes and cyclobutanes in which inversion of the ring system can occur. At sufficiently low temperature, ring inversion and rotation can be stopped, but exact values of J_{HF} are often not obtained because of the tendency of fluorine to couple with all protons within four or five chemical bonds, giving poorly resolved spectra. Even when this problem is overcome, one obtains values for J_{HF} at only two dihedral angles, 60 and 180° .

To obviate these difficulties, we have examined vicinal proton–fluorine coupling in bicyclic compounds where the dihedral angle is fixed and known. Since we can anticipate a large substituent effect on J_{HF} , as has been observed for J_{HH} ,⁶ we have, where possible, kept the substituents the same by preparing derivatives of fluoromaleic acid. In the compounds chosen for synthesis we have also attempted to keep the number of

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