

Sixteen ^{13}C — ^{19}F Spin-Spin Coupling Constants in the ^{13}C NMR Spectrum of 1-Fluoropyrene ($\text{C}_{16}\text{H}_9\text{F}$)

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In a recent ^{13}C NMR study on ^{13}C — ^{19}F spin coupling constants in fluorine substituted aromatic compounds Weigert and Roberts¹ reported on the observation and assignment of ten ^{13}C — ^{19}F couplings in 1-fluoronaphthalene (I) and six, all being assigned to the carbons in the fluorine substituted ring, in 2-fluoronaphthalene (II). It was suggested that the distance between the carbon and the fluorine is the relevant factor in the inter-ring couplings and that no inter-ring couplings would be expected in 2-fluoronaphthalene. We now report on the observation and almost complete assignment of sixteen ^{13}C — ^{19}F coupling constants in the proton noise-decoupled ^{13}C NMR spectrum of 1-fluoropyrene² (III).

The ^{13}C — ^{19}F coupling constants, ^{13}C chemical shifts, and the fluorine substituent

effects on the chemical shifts in (III) are collected in Table 1. Fig. 1 shows a 4 ppm range of the natural abundance ^{13}C -spectrum of (III); twenty well-resolved lines, corresponding to ten ^{13}C resonances, are observed. The three doublets at higher field to this region were easily assigned to C(10), C(11), and C(2) on comparison with the fluorine substituent effects on ^{13}C chemical shifts and with the ^{13}C — ^{19}F couplings in (I) and (II); this was independently confirmed by selective proton decoupling experiments. Similarly the three doublets at lower field to the region shown in Fig. 1 were assigned to C(1), C(13), and C(14); however, nothing could be said for a particular assignment (out of the six possible) of the four almost equally spaced lines for C(13) and C(14).

Assignments of the ten ^{13}C — ^{19}F couplings appearing in Fig. 1 followed from five single-frequency decoupling experiments in the proton spectrum (for which the approximate order of the proton chemical shifts had been determined) taking into account the fluorine substituent effects on the chemical shifts as expected from the results for (I) and (II). Still, there is no way of distinguishing between the two doublets for C(6) and C(8) as these sharpen at almost the same proton decoupling frequency (within ± 0.5 Hz). The same could be said for the two doublets for C(4) and C(5).

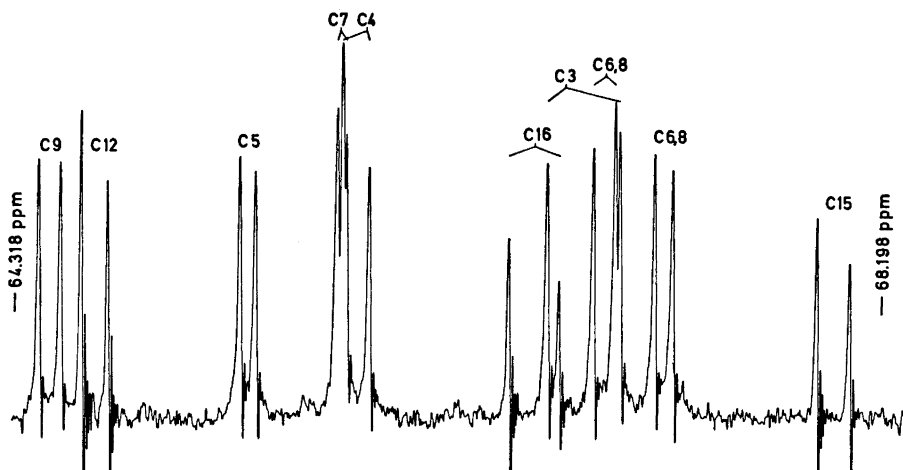


Fig. 1. A 4 ppm range of the natural abundance ^{13}C NMR spectrum of 1-fluoropyrene (130 scans). The ten carbon resonances in this region are all split into doublets. The ppm scale is upfield from internal CS_2 .

Table 1. ^{13}C NMR chemical shifts, substituent effects, and $^{13}\text{C}-^{19}\text{F}$ coupling constants in 1-fluoropyrene.^{a,b}

Carbon	Chemical shift ^c	Substituent effect ^d	$J(^{13}\text{C}^{19}\text{F})^e$
C(1)	35.80	-31.47	(-)251.1
C(2)	79.82	+13.45	+22.17
C(3)	66.86	-0.41	+8.21
C(4), (5)	65.35	+0.48	1.75
C(5), (4)	65.84	+0.97	2.99
C(6), (8)	66.95	-0.32	2.44
C(7)	65.78	-0.59	1.08
C(8), (6)	67.21	-0.06	2.06
C(9)	64.47	-0.40	2.45
C(10)	73.23	+8.36	4.59
C(11)	73.63	+12.41	(+)15.36
C(12)	64.67	+3.45	(+)2.97
C(13), (14)	61.23	+0.01	1.98
	61.20	-0.02	1.47
C(13), (14)	61.25	+0.03	1.11
	61.18	-0.04	0.60
C(13), (14)	61.22	+0.00	2.58
	61.21	-0.01	0.87
C(15)	67.98	+0.32	3.70
C(16)	66.64	-1.02	(+)5.65

^a As a solution (17 % w/w) in CS_2 (70 % w/w) and $(\text{CD}_3)_2\text{CO}$ (13 % w/w). Temperature 32°.

^b C.w. ^{13}C spectra were recorded at 25.2 MHz (Varian XL-100-15 spectrometer; Varian C-1024 CAT).

^c In ppm upfield from internal CS_2 with errors ± 0.01 ppm.

^d In ppm from the corresponding position in pyrene (determined to be C(1): 67.27 ppm, C(2): 66.37 ppm, C(4): 64.87 ppm, C(11): 61.22 ppm, and C(15): 67.66 ppm upfield from internal CS_2); see also Ref. 4.

^e In Hz with errors ± 0.05 Hz except for C(1) (± 0.5 Hz); signs determined as described in the text, otherwise taken from monofluorobenzene¹ (parantheses) or undetermined.

Furthermore, as recently described,³ the residual $^1J_{\text{C-H}}$ splittings observed under conditions of off-resonance decoupling of H(2) and H(3) could be used to relate the signs of $^2J_{\text{C(2)-F}}$ and $^3J_{\text{C(3)-F}}$ to that of $^3J_{\text{H(2)-F}}$ and $^4J_{\text{H(3)-F}}$ (both positive), respectively. The sign thus obtained for $^2J_{\text{C(2)-F}}$ and $^3J_{\text{C(3)-F}}$ is positive as in monofluorobenzene.¹

Several of the observed $^{13}\text{C}-^{19}\text{F}$ couplings in (III) are of particular interest. The couplings to C(6), C(8), and C(7) represent the first reported six- and seven-bond $^{13}\text{C}-^{19}\text{F}$ couplings. The magnitudes of these couplings indicate that $^{13}\text{C}-^{19}\text{F}$ coupling constants in condensed aromatic compounds do not attenuate with the distance between the coupled nuclei in the manner suggested by Weigert and

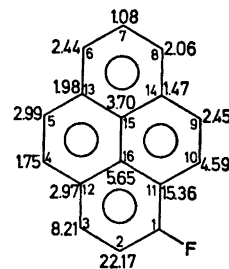


Fig. 2. Numbering of the carbon atoms in 1-fluoropyrene (III) and tentative assignment of the $^{13}\text{C}-^{19}\text{F}$ coupling constants (see text).

Roberts.¹ Accordingly, a reinvestigation of the ^{13}C NMR spectrum of (II) was undertaken and in contrast with the earlier reported results all ten possible $^{13}\text{C}-^{19}\text{F}$ couplings were resolved in its proton noise-decoupled ^{13}C -spectrum.⁵ Furthermore, it appears that the magnitudes of the $^{13}\text{C}-^{19}\text{F}$ couplings over more than four bonds in (II) and (III) decrease in an alternating way with increasing number of bonds, leading to the tentative assignment shown in Fig. 2.

Further studies on $^{13}\text{C}-^{19}\text{F}$ couplings which evidently may be of both experimental and theoretical interest, are in progress for other condensed aromatic systems.

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Mean Amplitudes of Vibration of Nickelocene

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We have recently reported the results of total vibrational analyses of several sandwich compounds (dibenzenechromium,¹ ferrocene,² and ruthenocene³). These calculations were initiated mainly

to calculate the mean amplitudes of vibration of these molecules in order to compare the results to the electron diffraction values as far as available.

We now want to continue the series by a study of nickelocene, $\text{Ni}(\text{C}_5\text{H}_5)_2$. An electron diffraction study of this molecule was recently published.⁴ On the basis of a new investigation of its vibrational spectra,⁵ it is now also possible to give an assignment of its vibrational frequencies which is more complete than the one previously published.^{6,7}

The vibrational frequencies for $\text{Ni}(\text{C}_5\text{H}_5)_2$ used in the present calculation are given in Table 1. The IR- and Raman-values of Refs. 5, 6, and 7 were taken for the assignment which was made in analogy to the previously reported investigation of $\text{Fe}(\text{C}_5\text{H}_5)_2$.² This means that in the case of closely neighbored $\text{Ni}(\text{C}_5\text{H}_5)_2$ frequencies the same sequence was followed through the symmetry blocks as in ferrocene. In this fashion a tentative assignment could be given for all frequencies except for the lowest A_2'' mode. For this mode we have used in a very approximate and arbitrary way the unchanged 355 cm^{-1} E_1' $\text{Ni}(\text{C}_5\text{H}_5)_2$ band. Only one band was observed in this spectral range for nickelocene so far.⁶ In ferrocene both the E_1' and the A_2'' modes are closely neighbored (at 490 and 477 cm^{-1} , resp.). Some of the other low frequency modes (the 125 cm^{-1} E_1' and the 186 cm^{-1} A_1'' bands, for example) must also be taken with some reservation.

The force constants used to calculate the mean amplitudes of $\text{Ni}(\text{C}_5\text{H}_5)_2$ were adjusted (starting with the ferrocene force field²) to reproduce exactly the frequencies of Table 1. The result of the amplitude calculations is given in Table 2 (mean amplitudes of vibration) and in Table 3 (perpendicular amplitude correction coefficients). It is usually possible to define many different force fields to reproduce a given set of experimental frequencies. This introduces some uncertainty into the calculated mean amplitudes. It must also be emphasized that the result of the calculations depends very much on the assignment of the experimental frequencies.

For the sake of comparison the available electron diffraction mean amplitudes of vibration⁴ are also given in Table 2. The agreement between observed and calculated values is only fair. It must be left open at this point whether the observed discrepancies are due to imperfec-