# CHEMISTRY OF FLUORINATED QUINONES. PART II. PROTON AND FLUORINE NMR SPECTRA

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#### SUMMARY

Proton and fluorine NMR spectra of nineteen fluorinated quinones are presented. Coupling constants were found for HH: <u>o</u> 10.5, <u>m</u> 2.2, <u>p</u> -0.3-0; for FF: <u>o</u> 4.5-5.6, <u>m</u> 0.3-1.7, <u>p</u> 1.5-3.0; and for HF: <u>o</u> 8.2-10.1, <u>m</u> 6.0-8.4, and <u>p</u> 0.6-0.9.

#### INTRODUCTION

In one of our papers [1] we described results of our measurements of proton and fluorine NMR spectra of quinonoid systems, fluorinated diazooxides and trifluoro-p-benzoquinone. We found that coupling constants in these systems differ considerably from the couplings in aromatic rings. Since the literature on the NMR measurements of quinones is very scanty [2] we prepared a series of fluorinated p-benzoquinones and characterized them as to their chemical shifts of protons and fluorines and as to HH, HF, and FF coupling constants. Since the spin-spin couplings were of the primary interest to us we concentrated mainly on quinones which show at least one coupling (H,H; F,F; or H,F).

## RESULTS AND DISCUSSION

### Chemical Shifts

Proton chemical shifts are controlled primarily by the <u>ortho</u> substituent. Comparison of the proton shifts in Table 1 with the value of 6.79 for <u>p</u>-benzoquinone shows that fluorine shifts an <u>ortho</u>-proton upfield to about 6.5 ppm, whereas <u>ortho</u>-chlorine, bromine, and iodine induce downfield shifts to about 7.0, 7.3, and 7.8 ppm, respectively.

Fluorine chemical shifts are also determined mainly by the nature of the <u>ortho</u> substituent. If the fluorine shifts in Table 1 are compared with that of fluoranil, V, it is seen that <u>ortho</u> hydrogen, chlorine, bromine, and iodine induce large downfield shifts (30-55 ppm), whereas a methoxy or ethoxy group gives a small upfield shift (~6 ppm). When in a <u>meta</u>-orientation, the alkoxy group exerts very little influence, while the other groups, H, Cl, Br, and presumably I, induce a small downfield shift (~6 ppm). Groups located in the <u>para</u> position have very little effect on the fluorine chemical shift.

## Coupling Constants

The proton-proton coupling constants found in compounds XII, XIII, and XVI are consistent with values found in the literature for various non-fluorinated quinones [3-5]. The non-first-order behavior of XVI permitted the determination of the negative sign for the para proton-proton coupling. This, too, is consistent with earlier reports [4,5]. Protonfluorine couplings fall into the following ranges: <u>ortho</u>, 8.2-10.1; <u>meta</u>, 6.2-8.4; <u>para</u>, 0.6-0.9 Hz. Because of the behavior of compound XVI it can be tentatively stated that these three couplings are all positive. Fluorine-fluorine coupling constants are: <u>ortho</u>, 4.5-5.6; <u>meta</u>, 0.3-1.4; <u>para</u>, 1.6-3.0 Hz. These values are fairly consistent with the coupling constants reported for 2-pentafluorophenyltrifluoro-p-benzoquinone [2]. However, it does appear that the assignments made for fluorines 1 and 2 in this compound should be reversed. Because of the first-order behavior of the fluorine spectra it was not possible to determine the signs of the fluorine-fluorine coupling constants.

The coupling constants found for these fluorinated quinones, particularly the fluorine-fluorine couplings, differ dramatically from values found for similarly constituted aromatic compounds. Not enough compounds are currently available for a study of the correlation of the magnitude of the various coupling constants with other substituents present in the molecule. However, it does appear that some such correlations might be possible, for the value of the <u>meta</u> H-F coupling seems to increase as the remaining two positions are changed from fluorine to iodine (compounds XI, IX, VII, and X).

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Number	Formula	H Chemical Shift, ppm	<sup>19</sup> F Chemical Shift, ppm (C <sub>6</sub> F <sub>6</sub> )	Coupling Constants J(Hz)
I	$ \begin{array}{c} 0 \\ F \\ Br \\ Br \\ 0 \end{array} $ Br		φ 65.0	
II	$ \begin{array}{c} 0 \\ F \\ F \\ F \\ F \\ 0 \end{array} $ $ \begin{array}{c} 0 \\ C1 \\ F \\ F \\ 0 \end{array} $		φ <sub>3</sub> 49.5 φ <sub>5</sub> 19.4 φ <sub>6</sub> 25.5	$J_{3,5}$ 1.1 $J_{3,6}$ 3.0 $J_{5,6}$ 4.5
III	$ \begin{array}{c} 0 \\ F \\ C1 \\ 0 \end{array} $ F C1 C1 C1 C1 C1 C1 C1 C1		φ 49.6	J <sub>FF</sub> 1.0
IV			φ 53.9	
v			φ 19.4	
VI	$H \xrightarrow{0}_{F \xrightarrow{H}} Br$	ə <b>6.</b> 64	φ 53.8	J <sub>HF</sub> 8.3

TABLE I  ${}^{1}_{\rm H}$  and  ${}^{19}_{\rm F}$  NMR Measurements of Fluorinated Quinones

Number	Formula	<sup>1</sup> H Chemical Shift, ppm	<sup>19</sup> F Chemical Shift, ppm (C <sub>6</sub> F <sub>6</sub> )	Coupling Constants J(Hz)
VII	0 H Br 0 Br 0 Br	ə 7 <b>.</b> 34	φ 63.5	J <sub>HF</sub> 7.6
VIII	$H = \begin{bmatrix} 0 \\ H \\$	ə 6.55	φ 52.6	J <sub>HF</sub> 8.3
IX		ə <b>7.0</b> 2	φ 54.5	J <sub>HF</sub> 7.1
X		ə <b>7.</b> 84	φ 80.6	J <sub>HF</sub> 7.9
XI	$ \begin{array}{c} 0 \\ H \\ \hline 16 \\ F \\ \hline 15 \\ 3 \\ F \\ 0 \end{array} $ F	ə 6.45	φ <sub>2</sub> 24.8 φ <sub>3</sub> 18.4 φ <sub>5</sub> 49.6	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
XII	$\begin{array}{c} 0 \\ H \\ 16 \\ 2 \\ F \\ 15 \\ 3 \\ H \\ 0 \end{array}$	a <sub>3</sub> 7.32 a <sub>6</sub> 6.62	φ 51.4	$J_{3,6}$ 0 $J_{3,5}$ 8.0 $J_{5,6}$ 9.2
XIII	$\begin{array}{c} \begin{array}{c} 0 \\ H \\ H \\ H \\ F \\ \end{array} \begin{array}{c} 0 \\ 15 \\ 3 \\ H \\ 0 \end{array} \begin{array}{c} 0 \\ 15 \\ 15 \\ 10 \end{array} \begin{array}{c} 0 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\$	ə <sub>3</sub> 7.03 ə <sub>6</sub> 6.58	φ 51.9	$J_{3,6}^{J}$ $J_{3,5}^{J}$ $J_{5,6}^{J}$ $J_{5,6}^{J}$

TABLE I (continued)

Number	Formula	1 H Chemical Shift, ppm	<sup>19</sup> F Chemical Shift, ppm (C <sub>6</sub> F <sub>6</sub> )	Coupling Constants J(Hz)
XIV	$ \begin{array}{c} H \\ H \\ F \\ F \\ 0 \end{array} $ $ \begin{array}{c} 0 \\ F \\ 0 \\ H \end{array} $ $ \begin{array}{c} 0 \\ F \\ H \\ H \end{array} $	ə 6.46	¢ 52 <b>.</b> 9	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
XV	$\begin{array}{c} F \\ H \\ H \\ 0 \end{array} \begin{array}{c} 0 \\ 1 \\ 5 \\ 0 \end{array} \begin{array}{c} 0 \\ 1 \\ 1 \\ 0 \end{array} \begin{array}{c} F \\ F \\ H \\ 0 \end{array} \begin{array}{c} 0 \\ 1 \\ 1 \\ 0 \end{array} \begin{array}{c} 0 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\$	ə <b>6.4</b> 6	φ <b>47.0</b>	J <sub>2,3+2,5</sub> 8.7
XVI	$H \xrightarrow{0} F$ $H \xrightarrow{0} F$ $H \xrightarrow{0} F$ $H \xrightarrow{0} H$ $H \xrightarrow{0} H$	a 3 6.40 a 5 6.76 a 6 6.79	φ 51.4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
XVII	$ \begin{array}{c} & 0 \\ & F \\ & F \\ & F \\ & F \\ & 0 \\ & 0 \end{array} \begin{array}{c} 0 \\ & 0 \\ & 0 \\ & F \end{array} \begin{array}{c} 0 \\ & 0 \\ & 0 \\ & F \end{array} \begin{array}{c} 0 \\ & 0 \\ & 0 \\ & F \end{array} $	ə <b>4.16</b>	$\phi_3$ 11.7 $\phi_5$ 17.6 (18.1) $\phi_6$ 18.1 (17.6)	$\begin{array}{c} & J_{3,5} & 1.7 \\ J_{CH_3,F_3} & 3.6 & J_{3,6} & 1.6 \\ & & J_{5,6} & 5.6 \end{array}$
XVIII	$F \underbrace{\downarrow_{5_3}^{0}}_{F} F \underbrace{\downarrow_{5_3}^{0}}_{0} F F$	<sup>5</sup> <sup>9</sup> <sub>CH3</sub> <sup>1.48</sup> <sup>9</sup> <sub>CH2</sub> <sup>4.50</sup>	φ <sub>3</sub> 13.4 φ <sub>5</sub> 18.0 (18.6) φ <sub>6</sub> 18.6 (18.0)	$ \begin{array}{c} J_{CH_3,CH_2} & 6.8 & J_{3,5} & 1.6 \\ J_{CH_3,F_3} & 0.4 & J_{3,6} & 1.7 \\ J_{CH_2,F_3} & 2.4 & J_{5,6} & 5.6 \end{array} $
XIX СН	$ \begin{array}{c} & 0 \\ & & $	<sup>ә</sup> сн <sub>3</sub> 4.15	φ 13.1	J <sub>CH3,F</sub> 3.5 (ortho)

Starting Material	Reagent	Product	M.p.°C (CC1 <sub>4</sub> ) Found	M.p.°C Reported	Refe	cence
$ \begin{array}{c} \begin{array}{c} 0\\ H\\ F\\ H\\ Br\\ Br\\ 0 \end{array} $	HBr H <sub>2</sub> 0 <sub>2</sub>	I	243-244.5		This	paper
C <sub>6</sub> ClF <sub>5</sub>	hno <sub>3</sub>	II	185-185.5	185-185.5		6
1,3,5-C <sub>6</sub> C1 <sub>3</sub> F <sub>3</sub>	HN03	III	212	208-209	. <u> </u>	6
	нс1 <sup>Н</sup> 2 <sup>0</sup> 2	IV	a) 230-240		This	paper
C <sub>6</sub> F <sub>6</sub>	hno <sub>3</sub>			179		6
commercial chemical (PCR)		V	182-185	179		7
$\mathbf{F} = \begin{bmatrix} 0 & \mathbf{Br} \\ \mathbf{F} & \mathbf{I} \\ \mathbf{F} & \mathbf{H} \\ \mathbf{F} & \mathbf{H} \end{bmatrix}$	HBr H <sub>2</sub> 0 <sub>2</sub>	VI	ь) 143-155		This	paper
$ \begin{array}{c}     0H \\     Br \\     H \\     Br \\     Br \end{array} $	hno3	VII	c) 172-173	150		8
	нс1 <sup>Н</sup> 2 <sup>0</sup> 2	VIII	d) 178-182		This	paper

# TABLE II

Syntheses and Melting Points of Fluorinated Quinones

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Starting Material	Reagent	Product	M.p.°C (CC1 <sub>4</sub> ) Found	M.p.°C Reported	Reference
$\begin{array}{c} C1 \\ H \\ C1 \\ H \\ C1 \\ F \end{array}$	hno <sub>3</sub>	IX	144.5-146	145	8
	hno <sub>3</sub>	X	197-200	195	8
F H F F F	HNO 3 BF 3	XI	148-149	148-149	1
	HBr <sup>H</sup> 2 <sup>0</sup> 2	XII	115.5-118		This paper
	нс1 <sup>н</sup> 2 <sup>0</sup> 2	XIII	123-125	126-127	9
1,2,4,5-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	HNO H <sub>2</sub> Sd <sub>4</sub> ,sc	XIV 3	172-173	171.5-172	10
F F H	hno <sub>3</sub>	XV	(83-85)		This paper

Starting Material	Reagent	Product	M.p.°C (CC1 <sub>4</sub> ) Found	M.p.°C Reported	Reference
H H NH <sub>2</sub> H	<sup>Na</sup> 2 <sup>Cr</sup> 2 <sup>0</sup> 7, <sup>H</sup> 2 <sup>S0</sup> 4	XVI	79-80.5	80.5-81.5	11
<sup>C</sup> 6 <sup>F</sup> 4 <sup>0</sup> 2	сн <sub>з</sub> он	XVII	159-161.5	159	12
<sup>C</sup> 6 <sup>F</sup> 4 <sup>0</sup> 2	с <sub>2</sub> н <sub>5</sub> он	XVIII	122.5-123.5		This paper
<sup>C</sup> 6 <sup>F</sup> 4 <sup>0</sup> 2	снзон	XIX	154-156	159.5	12

### TABLE II (continued)

a) The highest observed m.p. of the coumpound always contaminated with some  $\rm C_{6}HCl_{2}FO_{2}.$ 

b) The highest observed m.p. of the compound still contaminated.

c) Analysis: Found: C, 25, 33%; H, 0.41%. Calculated for C<sub>6</sub>HBr<sub>2</sub>FO<sub>2</sub> (283.9): C, 25.39%; H, 0.36%.

d) The highest observed m.p. of the compound still contaminated with some  $\rm C_6Cl_3F0_2$ 

### EXPERIMENTAL

Most of the fluorinated quinones whose NMR spectra we took are known compounds and have been prepared according to the literature. The methods of synthesis, melting points (not corrected; sealed capillary), and references are surveyed in Table 2. Experimental details are given below for the seven new compounds reported in this paper.

# Fluorotribromo-p-benzoquinone (I)

2,3-Dibromo-5-fluoro-p-benzoquinone (VI) (0.2 g, 0.0007 mole) was stirred with 5 ml (0.044 mole) of 48% hydrobromic acid, the mixture was

heated up to 95° over a period of 45 minutes, and kept at this temperature for an additional 30 minutes. The yellow mixture gradually turned light beige without passing completely into solution. After the mixture had been cooled to 15°, 1 ml (0.01 mole) of 30% hydrogen peroxide was added followed by 3 ml of water. The temperature rose to  $45^{\circ}-50^{\circ}$ , bright orange crystals started depositing, and bromine was liberated. The crystals were filtered off with suction giving 0.21 g (83%) of I, m.p. 243-244.5° (decomp.) (CC1<sub>4</sub>). Analysis: Found: C, 19.96%; H, 0.07%. Calculated for C<sub>6</sub>Br<sub>3</sub>FO<sub>2</sub> (362.79): C, 19.87%; H, 0%.

### 2,3-Dibromo-5-fluoro-p-benzoquinone (VI)

2-Bromo-5-fluoro-p-benzoquinone (XII) (0.6 g, 0.003 mole) was stirred with 6 ml (0.053 mole) of 48% hydrobromic acid, and the mixture was heated at  $45^{\circ}$ - $55^{\circ}$  until the crystals dissolved to give a brown solution (45 minutes). After cooling, 5 g of ice was added, followed by 1.5 ml (0.015 mole) of 30% hydrogen peroxide. Orange crystals precipitated after 10 minutes. Filtration with suction gave 0.6 g (72%) of bright yellow crystals of VI. The compound gave good spectra but could not be completely freed of contaminants either by crystallization or by sublimation. The highest m.p. found was 143-155° (after sintering at 138°).

# 2,3-Dichloro-5-fluoro-p-benzoquinone (VIII) and Fluorotrichloro-pbenzoquinone (IV)

The reaction product resulting from the action of hydrochloric acid and hydrogen peroxide on fluoro-p-benzoquinone and consisting of a mixture of 2-chloro-5-fluoro-p-benzoquinone and 2,3-dichloro-5-fluoro-p-benzoquinone (0.35 g) was treated with 8 ml of concentrated hydrochloric acid. The crystals did not dissolve at room temperature. The mixture was heated to 80° and all dissolved after 10 minutes. The solution was kept at 70-80° for 2.5 hours. After cooling, 1.5 ml of 30% hydrogen peroxide was added, the yellow crystals were filtered off, dissolved in 20 ml of benzene, the benzene solution was washed free of acid, dried, and evaporated <u>in vacuo</u> to give 0.39 g of yellow crystals of VIII and IV. Crystallization from carbon tetrachloride gave 0.14 g of bright yellow crystals consisting, according to NMR spectra, of 27% of dichloro- and 73% of trichlorofluorg-p-benzoquinone.

### 2-Bromo-5-fluoro-p-benzoquinone (XII)

Following a procedure for the preparation of 2,5-dichlorodifluorop-benzoquinone [9], 0.5 g (0.004 mole) of fluoro-p-benzoquinone (XVI) was dissolved in 5 ml (0.044 mole) of 48% hydrobromic acid. The dark brown solution turned light-orange within 1 minute of stirring. The stirring was continued for 10 minutes at room temperature. After 5 g of ice and 1.5 ml (0.015 mole) of 30% hydrogen peroxide had been added and the mixture stirred for 10 minutes at room temperature, an orange precipitate was filtered off with suction to give 0.7 g (78%) of XII, bright yellow crystals, m.p. 115.5-118° (after crystallization from carbon tetrachloride followed by sublimation at 100° at 15 mm). Analysis: Found: C, 35.09%, H, 0.73%. Calculated for  $C_6H_2BrFO_2$  (205.0): C, 35.16%; H,0.98%.

## 2-Chloro-5-fluoro-p-benzoquinone (XIII)

The title compound was prepared similarly to XII [9] by treatment of 1.3 g (0.01 mole) of fluoro-p-benzoquinone XVI with 30 ml (0.36 mole) of 37% hydrochloric acid followed by 3 ml (0.03 mole) of 30% hydrogen peroxide. A mixture of 2-chloro-5-fluoro-p-benzoquinone with 2,3dichloro-5-fluoro-p-benzoquinone and fluorotrichloro-p-benzoquinone (1.45 g) could not be separated into the components either by crystallization or by chromatography on silica gel. Most of the mixture passed through the column in hexane elution. Only a small amount (0.1 g, 6%) was eluted with benzene and gave the correct melting point of XIII (123-125°) after sublimation at 100° at 13 mm. Analysis: Found: C, 43.87%; H, 1.13%. Calculated for  $C_6H_2$ CIFO<sub>2</sub> (160.5): C, 44.89%; H, 1.26%.

# 2,6-Difluoro-p-benzoquinone (XV,

2,4,6-Trifluoroaniline (0.5 g, 0.0034 mole) was dissolved in 2.5 ml of 30% oleum and treated with 1 ml (0.02 mole) of 90% nitric acid at a temperature of  $-5-0^{\circ}$  over a period of 10 minutes. After 2.5 hours at room temperature the mixture was poured onto ice, extracted with 50 ml of benzene, the benzene solution was evaporated to dryness <u>in vacuo</u>, and the dark oily residue was sublimed at 60-70° at 15 mm to give 25 mg (5%) of XV, m.p. 83-85°. Since the small amount did not allow a recrystallization the melting point should be considered with reservation.

### Methoxytrifluoro-p-benzoquinone (XVII)

Fluoranil (0.3 g, 0.0017 mole) was dissolved in 4 ml of hot methanol and the solution was heated for 30 minutes at 100° in a sealed tube. Evaporation of the solution to dryness <u>in vacuo</u> gave 0.21 g (65%) of XVII contaminated with only a small amount of fluoranil. Crystallization from carbon tetrachloride gave compound, m.p. 159-161.5° (97.5% pure according to the NMR analysis). Analysis: Found: C, 42.96%; H, 1.46%. Calculated for  $C_7H_2F_3O_3$  (192.1): C, 43.77%; H, 1.58%.

### Ethoxytrifluoro-p-benzoquinone (XVIII)

Fluoranil (0.3 g, 0.0017 mole) was dissolved in 5 ml of absolute ethanol and the solution was heated for 2 hours at 100° in a sealed tube. Evaporation of the dark yellow solution <u>in vacuo</u> gave 0.15 g (44%) of XVIII, m.p. 123-124.5° (after crystallization from carbon tetrachloride and sublimation <u>in vacuo</u>). Analysis: Found: C, 46.50%; H, 2.67%. Calculated for  $C_8H_5F_3O_3$  (206.1): C, 46.62%; H, 2.45%.

# 2,5-Difluorodimethoxy-p-benzoquinone (XIX)

Fluoranil (0.2 g, 0.0011 mole) was dissolved in 5 ml of methanol and the solution was allowed to react in a column of acidic aluminum oxide (18 ml) for 3.5 hours. Elution with 30 ml of hexane and 30 ml of benzene gave 0.15 g (66%) of XIX, m.p. 154-156° (CCl<sub>4</sub>). Analysis: Found: C, 46.17%; H, 2.66%. Calculated for  $C_8H_6F_2O_4$  (204.1): C, 47.07%; H, 2.96%.

# MEASUREMENTS

Proton spectra were obtained at 100 MHz and fluorine spectra were obtained at 94 MHz on a JEOL PS-100 spectrometer, operated in the field sweep external lock mode. Proton spectra are referenced against tetramethylsilane, and fluorine spectra are referenced against hexafluorobenzene; in both cases downfield shifts are denoted by positive numbers. All spectra were determined in carbon tetrachloride at a concentration of approximately 0.025 g per 0.5 ml. Owing to the limited solubility of the fluorinated quinones, the sample temperature for most of the determinations was 70°C. The spectra of all compounds except XIV, XV, and XVI showed first-order splitting; therefore, coupling constants were obtained simply by measuring line spacings. The AA'XX' pattern shown by compound XV did not provide much useful information in the way of coupling constants for the spectrum consisted of rather sharp doublets, one for <sup>1</sup>H and one for <sup>19</sup>F. The analysis of XIV and XVI was carried out by a computer-assisted iterative least-squares line-matching procedure. Examination of the <sup>13</sup>C satellites afforded the coupling constant for III. Coupling constants for all spectra should be accurate to ±0:25 Hz.

## ACKNOWLEDGEMENT S

Our thanks are due to Ms. G. V. Harrison for preparing some of the quinones, to Ms. L. K. Cassity for carrying CHN analysis and to Mr. T. Glass for the analyses and NMR spectra measurements.

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