*Journal of Fluorine Chemistry, 68* (1994) 165–167

# The prediction of the $^{19}$F NMR spectra of fluoro-substituted arenetricarbonylchromium complexes. Part III

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(Received June 17, 1993; accepted August 27, 1993)

**Abstract**

A $^{19}$F NMR data set for fluoroarenetricarbonylchromium complexes has been used to compute statistical SCS values for a number of groups. When these values are used to predict the $^{19}$F NMR signal positions of these compounds they give a correlation coefficient of predicted versus observed values of 0.992 with a standard deviation of 1.89.

## Introduction

In Part II [1] of this series we used mathematical modeling techniques to predict the $^{19}$F NMR spectra of arenetricarbonylchromium complexes. The most precise model used the field, $\mathcal{F}$, resonance, $\mathcal{R}$ and the Charton steric parameters together with molar refractivity to predict the signals from 42 mono- and disubstituted fluoroarene complexes with a correlation coefficient for the observed versus predicted signal positions of 0.99. This model is considerably less sophisticated than the one recently described for the free arenes themselves [2]. We have also recently reported a new method for the statistical determination of substituent chemical shift values (statistical SCS or SSCS values) which we have successfully used in the study of derivatives of fluorobenzene [3] and of fluoropyridine together with 1,2-, 1,3- and 1,4-diazines, and 1,3,5-diazines [4].

We now report the SSCS values for fluoro-substituted arenetricarbonylchromium complexes using the data base from ref. 1. Although this data base lists nearly all available $^{19}$F NMR spectra for these complexes, it is small in comparison with the amount of data available for the free arenes. This is mainly due to the synthetic difficulties in preparing these complexes with a large variety of different substituents [5]. We feel, however, that the limited number of SSCS values presented here is a useful addition to the literature. To our knowledge there is no report of the conventional SCS values having been computed for the $^{19}$F NMR spectra of arenetricarbonylchromium complexes.

## The 'statistical' SCS method

The method for the determination of SSCS values was described in detail in a previous publication [3].

## Results and discussion

Table 1 gives the data base used for the computations together with the predicted values and residuals. It should be noted that entries No. 1–35 are monofluoro derivatives whereas entries No. 36–46 represent the seven difluoro complexes studied. The symmetrical complexes have one signal while the unsymmetrical ones have two signals. These two signals were treated independently in the computations.

Table 2 lists the SSCS values which can be generated from the above data base. The values for electron-donating groups in both the *ortho* and *para* positions are negative while electron-withdrawing groups generally have positive values. Table 2 also compares the SSCS values for the complexes and the SSCS values for the same groups in the free arene [3]. The SSCS values in the *ortho* position in both the free arenes and the complexes are virtually identical ($r = 0.999$), the values in the *meta* position are difficult to compare as they are all fairly close to zero ($r = -0.71$), but in the values for the *para* position several distinct trends can be discerned ($r = 0.88$). For most electron-donating groups and fluorine the values become more positive (less negative) as we go from the free arene to the

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0022-1139/94/$07.00
*SSDI* 0022-1139(93)03037-M

TABLE 1. Observed and SSCS predicted $^{19}$F NMR signals together with residuals for 46 signals from 42 fluoroarenetricarbonylchromium complexes

| No | Substituents and positions on the aromatic ring | | | | | | $^{19}$F NMR signal position | | Residual |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | Obs. | Pred. | |
| 1 | F | H | H | H | H | H | −135.9 | −135.3 | 0.6 |
| 2 | F | H | Cl | H | H | H | −136.6 | −136.6 | 0.0 |
| 3 | F | H | H | Cl | H | H | −137.2 | −137.2 | 0.0 |
| 4 | F | $CH_3$ | H | H | H | H | −138.6 | −139.6 | −1.0 |
| 5 | F | H | $CH_3$ | H | H | H | −135.3 | −135.1 | 0.2 |
| 6 | F | H | H | $CH_3$ | H | H | −137.8 | −138.0 | −0.2 |
| 7 | F | $CH_3$ | $CH_3$ | H | H | H | −137.3 | −139.4 | −2.1 |
| 8 | F | $CH_3$ | H | $CH_3$ | H | H | −142.9 | −142.3 | 0.6 |
| 9 | F | $CH_3$ | H | H | H | $CH_3$ | −143.8 | −143.9 | −0.1 |
| 10 | F | H | $CH_3$ | $CH_3$ | H | H | −137.1 | −137.8 | −0.7 |
| 11 | F | H | $CH_3$ | H | $CH_3$ | H | −136.1 | −134.8 | 1.3 |
| 12 | F | $CH_3$ | H | $CH_3$ | H | $CH_3$ | −148.2 | −146.6 | 1.6 |
| 13 | F | H | H | $CHMe_2$ | H | H | −136.4 | −136.4 | 0.0 |
| 14 | F | H | $CF_3$ | H | H | H | −135.8 | −135.8 | 0.0 |
| 15 | F | H | H | $CF_3$ | H | H | −133.5 | −133.5 | 0.0 |
| 16 | F | H | H | $CH{=}CH_2$ | H | H | −136.0 | −136.0 | 0.0 |
| 17 | F | $OCH_3$ | H | H | H | H | −154.8 | −153.5 | 1.3 |
| 18 | F | H | $OCH_3$ | H | H | H | −136.7 | −136.5 | 0.2 |
| 19 | F | H | H | $OCH_3$ | H | H | −142.4 | −141.6 | 0.8 |
| 20 | F | H | $OCH_3$ | $OCH_3$ | H | H | −140.2 | −142.8 | −2.6 |
| 21 | F | H | $OCH_3$ | H | $OCH_3$ | H | −138.9 | −137.7 | 1.2 |
| 22 | F | $CH_3$ | H | $OCH_3$ | H | H | −147.7 | −145.9 | 1.8 |
| 23 | F | $NH_2$ | H | H | H | H | −156.3 | −156.8 | −0.5 |
| 24 | F | H | $NH_2$ | H | H | H | −136.3 | −135.3 | 1.0 |
| 25 | F | H | H | $NH_2$ | H | H | −146.2 | −144.9 | 1.3 |
| 26 | F | H | H | $NHCH_3$ | H | H | −146.1 | −146.1 | 0.0 |
| 27 | F | H | H | $NMe_2$ | H | H | −146.8 | −146.8 | 0.0 |
| 28 | F | $NH_2$ | H | $CH_3$ | H | H | −160.1 | −159.5 | 0.6 |
| 29 | F | $CH_3$ | $NH_2$ | H | H | H | −138.0 | −139.6 | −1.6 |
| 30 | F | H | $NH_2$ | H | H | $CH_3$ | −138.9 | −139.6 | −0.7 |
| 31 | F | H | $NH_2$ | $CH_3$ | H | H | −136.2 | −138.0 | −1.8 |
| 32 | F | $OCH_3$ | $NH_2$ | H | H | H | −152.3 | −153.6 | −1.3 |
| 33 | F | H | $CH_3$ | $COCH_3$ | H | H | −134.1 | −134.1 | 0.0 |
| 34 | F | COOEt | H | H | H | H | −133.4 | −133.4 | 0.0 |
| 35 | F | H | H | COOEt | H | H | −133.7 | −133.7 | 0.0 |
| 36 | F | H | F | H | H | H | −136.4 | −136.0 | 0.4 |
| 37 | F | H | H | F | H | H | −134.0 | −137.3 | −3.3 |
| 38 | F | F | H | H | H | $NH_2$ | −178.8 | −179.9 | −1.1 |
| 39 | F | F | $NH_2$ | H | H | H | −158.7 | −158.4 | 0.3 |
| 40 | F | H | F | H | H | $NH_2$ | −155.8 | −157.5 | −1.7 |
| 41 | F | H | F | $NH_2$ | H | H | −143.4 | −145.6 | −2.2 |
| 42 | F | $NH_2$ | H | F | H | H | −161.7 | −158.9 | 2.8 |
| 43 | F | H | $NH_2$ | F | H | H | −137.8 | −137.3 | 0.5 |
| 44 | F | H | $NH_2$ | H | H | F | −158.3 | −158.4 | −0.1 |
| 45 | F | F | H | $NH_2$ | H | H | −169.0 | −168.0 | 1.0 |
| 46 | F | H | F | H | $NH_2$ | H | −139.6 | −136.0 | 3.6 |

complex, and for electron-withdrawing groups they become less positive as we go from the free arene to the complex. These data presumably mean that the $^{19}$F NMR signal position is influenced most by ring steric effects in the *ortho* position, is not influenced greatly by steric or electronic effects in the *meta* position, and is influenced more by electronic rather than steric effects in *para* position as we add the $Cr(CO)_3$ group to the aromatic ring.

Figure 1 gives a plot of observed versus predicted values for the complexes.

## Experimental

The preparation of the complexes and the determination of the $^{19}$F NMR spectra has been described previously [1, 6].

TABLE 2. $^{19}F$ NMR SSCS values for arenes and arenetricarbonylchromium complexes

| Group | SSCS value | | | | | |
|---|---|---|---|---|---|---|
| | Arenetricarbonylchromium | | | Arene[a] | | |
| | *Ortho* | *Meta* | *Para* | *Ortho* | *Meta* | *Para* |
| H | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $CH_3$ | −4.3 | 0.2 | −2.7 | −3.9 | −0.4 | −3.6 |
| $OCH_3$ | −18.3 | −1.2 | −6.3 | −18.9 | 0.8 | −9.0 |
| $COCH_3$ | | | 1.0 | | | 7.6 |
| $CHMe_2$ | | | −1.1 | | | −4.1 |
| F | −23.1 | −0.7 | −2.1 | −23.2 | 2.0 | −6.5 |
| Cl | | −1.3 | −1.9 | | 3.4 | −0.7 |
| $CF_3$ | | −0.5 | 1.8 | | 3.1 | 5.8 |
| $NH_2$ | −21.5 | 0.0 | −9.6 | −22.9 | −1.3 | −17.4 |
| NHMe | | | −10.8 | | | −17.9 |
| $NMe_2$ | | | −11.5 | | | −7.5 |
| $CH{=}CH_2$ | | | −0.7 | | | −0.5 |
| COOEt | 1.9 | | 1.6 | 1.2 | | 6.4 |

[a] Data from ref. 3.

Statistical computations were undertaken using programs written in FORTRAN and SAS (Statistical Analysis System) running on a Digital Equipment Corporation Microvax model 3800.

## Acknowledgments

We thank the Auburn University at Montgomery Grant-in-Aid program, and the Chemistry and Mathematics Department for support.

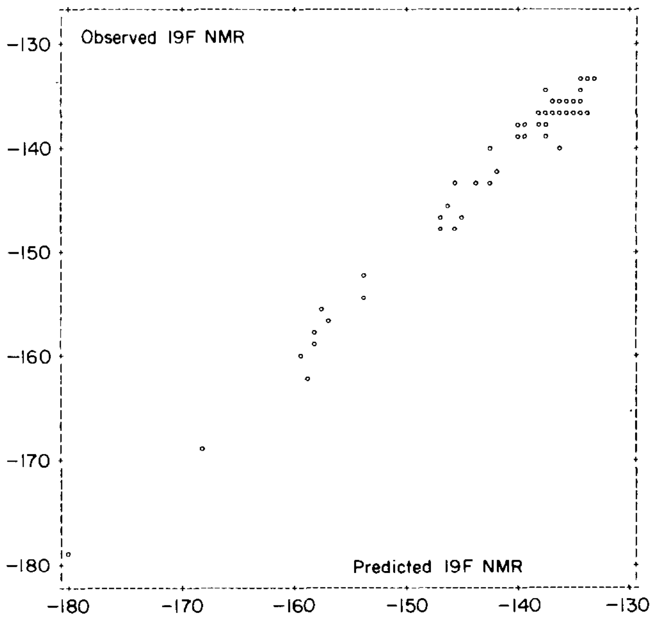

Fig. 1. Observed versus SSCS predicted $^{19}F$ NMR signal positions.

## References

1 J.R. Nanney and C.A.L. Mahaffy, *Inorg. Chim. Acta, 201* (1992) 55.
2 J.R. Nanney, A.K. Traylor and C.A.L. Mahaffy, *J. Fluorine Chem., 64* (1993) 217.
3 C.A.L. Mahaffy and J.R. Nanney, *J. Fluorine Chem., 67* (1994) 67.
4 J.R. Nanney and C.A.L. Mahaffy, *J. Fluorine Chem.,* in press.
5 For example, see G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry,* Pergamon, Oxford, 1982, Vol. 3.
6 B. Armstrong, A. Grier, J.B. Hamilton, H. Khuu, C.A.L. Mahaffy, J. Rawlings and J.R. Nanney, *Inorg. Chim. Acta, 191* (1992) 189.