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The prediction of the ^{19}F NMR spectra of fluoroarenes using mathematical modeling techniques

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Abstract

The prediction of the ^{19}F NMR spectra for fluoroarenes has been investigated using mathematical modeling techniques. A large data set ($n = 839$) was investigated and a number of models developed. Simple linear models were developed for fluoroarenes containing a single *meta* or *para* substituent while more sophisticated quadratic or cubic models were used for *ortho* or polysubstituted compounds. Eleven models are described here, the most precise of which used 34 variables and had a correlation coefficient of observed versus predicted line positions of 0.992 and an average error of prediction of 1.9 ppm.

Introduction

Since the discovery of ^{19}F NMR spectroscopy some 30 years ago, the technique has been extensively used in the elucidation of the bonding, structure and reactivity of fluoro compounds [1–86]. Parallelling this discovery have been attempts to predict these spectra by various means. Pioneering work by Taft *et al.* correlated the signal positions in *meta* [1] and *para* [2] disubstituted fluorobenzenes with various substituent parameters. There was, however, no successful correlation with compounds containing *ortho* substituents. Other methods have included a CNDO/II approach utilizing charge densities and bond orders to develop multiple regression equations that account for the ^{19}F NMR chemical shift [3]. Some of these models have shown nonlinearity in, for example, plots of ^{13}C NMR substituent chemical shift (SCS) values for mono-substituted fluorobenzenes versus the corresponding *para*-substituted ^{19}F NMR SCS value for a wide variety of substituents.

A chemical shift additivity method using SCS values has also been studied and found useful in the prediction of these spectra [4]. The latter has the

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disadvantage that the SCS values can only be known for a group in a particular position if the spectrum for the compound containing this group in that particular position is known. The SCS values are also somewhat solvent-dependent, markedly so in the case of *ortho*-iodo substituents [4].

Another recent approach was to utilize a computer data base, but this, at least at present, applies only to perfluoro compounds [5]. In the past, there have also been several studies on the prediction of the ^{19}F NMR spectra of fluoroarenes bonded to metal moieties. These have included the tricarbonylchromium [6] and bisbenzenechromium systems [7].

It was during a recent study of the statistical prediction of the fluorine NMR position in fluoroarenetricarbonylchromium complexes that we found that the signal position for *ortho*- as well as *meta*- and *para*-substituted complexes could be predicted with a high degree of accuracy using mathematical modeling techniques [8].

We now report a similar study on fluoroarenes using a large data set ($n > 800$) in which relatively sophisticated mathematical modeling techniques have been used. We believe this is the first time a ^{19}F NMR study has been performed for fluoroaromatic compounds using such a large data set. This data set was extracted from the literature for the period 1951 until 1989 and is given together with references in Table 1.

Results and discussion

The data base

As noted in the Introduction, the literature was surveyed for the ^{19}F NMR spectra of fluoro-substituted arenes for the period 1951 to 1989 [1–86]. From this, a data base was extracted in which:

1. The fluoroarene contained only one aromatic ring. No fused ring or heterocyclic compounds or complexes containing metal fragments were considered.
2. The arene contained groups where the field, resonance and Charton steric parameters together with the molar refractivity were known in the literature [86–88].
3. The solvent had been reported for the ^{19}F NMR spectrum. Data where the solvent was not given, was unclear or where mixed solvent systems were used were not included in the data base.

This data base contains 839 resonances, some of which are for different fluorine atoms in the same molecule and some of which are the same signal observed in different solvents. This data set is given in Table 1.

The sort code

In order that the compounds could be sorted logically and so that a particular structure could be found quickly and easily, a sort code was

TABLE 1

Entire data set employed giving the sort codes, solvents, observed ^{19}F NMR position, the predicted position using model K, model residuals for models F, G, J and K and the original reference

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
1	FAAAAA	L	–112.7	–114.6	0.6	–2.7	–2.0	–1.9	53
2	FAAAAA	F	–112.9	–114.6	0.8	–2.5	–1.8	–1.7	53
3	FAAAAA	S	–113.3	–114.6	1.2	–2.1	–1.4	–1.3	53
4	FAAAAA	E	–113.4	–114.6	1.3	–2.0	–1.3	–1.2	53
5	FAAAAA	H	–113.8	–114.6	1.7	–1.6	–0.9	–0.8	4
6	FAAAAA	J	–112.6	–114.6	0.5	–2.8	–2.1	–2.0	4
7	FAAAAA	K	–113.1	–114.6	1.0	–2.3	–1.6	–1.5	6
8	FAAAAB	F	–107.0	–108.7	–18.5	–10.2	–2.9	–1.7	13
9	FAAAAB	H	–108.1	–108.7	–17.4	–9.1	–1.8	–0.6	4
10	FAAAAB	J	–107.7	–108.7	–17.8	–9.5	–2.2	–1.0	4
11	FAAAAB	T	–107.6	–108.7	–17.9	–9.6	–2.3	–1.1	60
12	FAAAAC	F	–115.3	–114.6	–8.9	–4.7	0.6	0.7	13
13	FAAAAC	S	–115.5	–114.6	–8.7	–4.5	0.8	0.9	53
14	FAAAAC	D	–115.8	–114.6	–8.4	–4.2	1.1	1.2	53
15	FAAAAC	H	–116.3	–114.6	–7.9	–3.7	1.6	1.7	4
16	FAAAAC	J	–115.9	–114.6	–8.3	–4.1	1.2	1.3	4
17	FAAAAC	A	–115.8	–114.6	–8.4	–4.2	1.1	1.2	65
18	FAAAAC	T	–115.8	–114.6	–8.4	–4.2	1.1	1.2	60
19	FAAAAC	A	–116.0	–114.6	–8.2	–4.0	1.3	1.4	66
20	FAAAAC	K	–119.0	–114.6	–5.2	–1.0	4.3	4.4	86
21	FAAAAD	H	–136.3	–134.6	–4.4	0.2	–1.4	1.7	4
22	FAAAAD	J	–134.9	–134.6	–5.8	–1.2	–2.8	0.3	4
23	FAAAAD	T	–136.2	–134.6	–4.5	0.1	–1.5	1.6	60
24	FAAAAF	F	–138.0	–138.6	5.6	0.8	–0.2	–0.6	13
25	FAAAAF	F	–138.6	–138.6	6.2	1.4	0.4	0.0	45
26	FAAAAF	F	–138.1	–138.6	5.7	0.9	–0.1	–0.5	53
27	FAAAAF	S	–138.4	–138.6	6.0	1.2	0.2	–0.2	53
28	FAAAAF	D	–138.8	–138.6	6.4	1.6	0.6	0.2	53
29	FAAAAF	H	–139.7	–138.6	7.3	2.5	1.5	1.1	4
30	FAAAAF	J	–138.8	–138.6	6.4	1.6	0.6	0.2	4
31	FAAAAF	T	–139.0	–138.6	6.6	1.8	0.8	0.4	60
32	FAAAAF	K	–139.0	–138.6	6.6	1.8	0.8	0.4	86
33	FAAAAH	F	–140.9	–137.1	–2.0	–3.3	4.3	3.8	13
34	FAAAAH	H	–138.0	–137.1	–4.9	–6.2	1.4	0.9	4
35	FAAAAH	J	–136.3	–137.1	–6.6	–7.9	–0.3	–0.8	4
36	FAAAAH	T	–138.1	–137.1	–4.8	–6.1	1.5	1.0	60
37	FAAAAI	F	–93.2	–94.5	–32.5	–16.6	–2.6	–1.3	13
38	FAAAAI	H	–94.4	–94.5	–31.3	–15.4	–1.4	–0.1	4
39	FAAAAI	J	–106.2	–94.5	–19.5	–3.6	10.4	11.7	4
40	FAAAAI	T	–93.8	–94.5	–31.9	–16.0	–2.0	–0.7	60
41	FAAAAL	F	–135.2	–133.4	–1.8	4.0	–0.2	1.8	13
42	FAAAAL	H	–136.1	–133.4	–0.9	4.9	0.7	2.7	4

(continued)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
43	FAAAAL	J	–135.3	–133.4	–1.7	4.1	–0.1	1.9	4
44	FAAAAL	T	–135.5	–133.4	–1.5	4.3	0.1	2.1	60
45	FAAAAM	F	–117.7	–119.7	0.7	8.5	3.6	–2.0	13
46	FAAAAM	H	–118.4	–119.7	1.4	9.2	4.3	–1.3	4
47	FAAAAM	J	–117.3	–119.7	0.3	8.1	3.2	–2.4	4
48	FAAAAM	T	–118.1	–119.7	1.1	8.9	4.0	–1.6	60
49	FAAAAM	K	–118.1	–119.7	1.1	8.9	4.0	–1.6	86
50	FAAAAk	T	–134.8	–133.1	1.2	14.3	3.6	1.7	60
51	FAAABA	H	–111.2	–110.4	2.2	–0.6	0.8	0.8	14
52	FAAABA	H	–110.8	–110.4	1.8	–1.0	0.4	0.4	4
53	FAAABA	J	–110.0	–110.4	1.0	–1.8	–0.4	–0.4	4
54	FAAABA	T	–110.7	–110.4	1.7	–1.1	0.3	0.3	60
55	FAAABA	B	–110.8	–110.4	1.8	–1.0	0.4	0.4	76
56	FAAABA	F	–110.8	–110.4	1.8	–1.0	0.4	0.4	63
57	FAAABA	F	–110.9	–110.4	1.9	–0.9	0.5	0.5	62
58	FAAABA	K	–111.3	–110.4	2.3	–0.5	0.9	0.9	79
59	FAAACA	H	–111.5	–110.9	2.3	–0.7	0.6	0.6	14
60	FAAACA	H	–111.2	–110.9	2.0	–1.0	0.3	0.3	4
61	FAAACA	J	–110.3	–110.9	1.1	–1.9	–0.6	–0.6	4
62	FAAACA	A	–111.0	–110.9	1.8	–1.2	0.1	0.1	65
63	FAAACA	T	–111.0	–110.9	1.8	–1.2	0.1	0.1	60
64	FAAACA	B	–111.1	–110.9	1.9	–1.1	0.2	0.2	76
65	FAAACA	F	–111.1	–110.9	1.9	–1.1	0.2	0.2	62
66	FAAACA	K	–113.0	–110.9	3.8	0.8	2.1	2.1	86
67	FAAACF	S	–133.6	–134.9	4.2	–0.4	–0.8	–1.3	53
68	FAAADA	H	–114.5	–115.1	–0.6	–3.2	–0.8	–0.6	14
69	FAAADA	H	–115.6	–115.1	0.5	–2.1	0.3	0.5	4
70	FAAADA	J	–113.5	–115.1	–1.6	–4.2	–1.8	–1.6	4
71	FAAADA	F	–112.9	–115.1	–2.2	–4.8	–2.4	–2.2	62
72	FAAADA	T	–113.3	–115.1	–1.8	–4.4	–2.0	–1.8	60
73	FAAADA	F	–113.5	–115.1	–1.6	–4.2	–1.8	–1.6	63
74	FAAADA	B	–113.6	–115.1	–1.5	–4.1	–1.7	–1.5	76
75	FAAADA	O	–115.6	–115.1	0.5	–2.1	0.3	0.5	79
76	FAAAEA	K	–114.1	–114.3	1.0	–0.4	–0.2	–0.2	74
77	FAAAFA	H	–110.7	–111.5	0.8	–3.2	–0.9	–0.8	14
78	FAAAFA	H	–110.6	–111.5	0.7	–3.3	–1.0	–0.9	4
79	FAAAFA	J	–109.5	–111.5	–0.4	–4.4	–2.1	–2.0	4
80	FAAAFA	T	–110.0	–111.5	0.1	–3.9	–1.6	–1.5	60
81	FAAAFA	F	–110.1	–111.5	0.2	–3.8	–1.5	–1.4	62
82	FAAAFA	K	–110.1	–111.5	0.2	–3.8	–1.5	–1.4	86
83	FAAAFB	J	–105.8	–105.6	–17.4	–10.0	–1.0	0.2	4
84	FAAAFD	H	–133.2	–131.4	–5.2	–1.4	–1.4	1.8	4
85	FAAAHA	H	–113.2	–113.0	0.7	–2.9	0.0	0.2	4
86	FAAAHA	J	–112.1	–113.0	–0.4	–4.0	–1.1	–0.9	4
87	FAAAHA	B	–111.6	–113.0	–0.9	–4.5	–1.6	–1.4	76

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
88	FAAAHA	F	–111.8	–113.0	–0.7	–4.3	–1.4	–1.2	63
89	FAAAHA	T	–112.2	–113.0	–0.3	–3.9	–1.0	–0.8	60
90	FAAAHA	K	–112.7	–113.0	0.2	–3.4	–0.5	–0.3	79
91	FAAAIA	H	–111.2	–110.3	1.7	–0.6	0.9	0.9	14
92	FAAAIA	H	–110.4	–110.3	0.9	–1.4	0.1	0.1	4
93	FAAAIA	J	–110.3	–110.3	0.8	–1.5	0.0	0.0	4
94	FAAAIA	T	–110.5	–110.3	1.0	–1.3	0.2	0.2	60
95	FAAAIA	F	–110.7	–110.3	1.2	–1.1	0.4	0.4	63
96	FAAALA	H	–112.6	–112.6	0.4	–2.9	–0.1	0.0	14
97	FAAALA	H	–112.6	–112.6	0.4	–2.9	–0.1	0.0	4
98	FAAALA	J	–111.4	–112.6	–0.8	–4.1	–1.3	–1.2	4
99	FAAALA	F	–112.0	–112.6	–0.2	–3.5	–0.7	–0.6	62
100	FAAALA	F	–112.1	–112.6	–0.1	–3.4	–0.6	–0.5	1
101	FAAAMA	H	–115.0	–114.7	1.9	0.3	0.3	0.3	14
102	FAAAMA	H	–114.4	–114.7	1.3	–0.3	–0.3	–0.3	4
103	FAAAMA	J	–113.7	–114.7	0.6	–1.0	–1.0	–1.0	4
104	FAAAMA	T	–114.0	–114.7	0.9	–0.7	–0.7	–0.7	60
105	FAAAMA	B	–114.2	–114.7	1.1	–0.5	–0.5	–0.5	76
106	FAAAMA	F	–114.3	–114.7	1.2	–0.4	–0.4	–0.4	62
107	FAAAMA	K	–114.4	–114.7	1.3	–0.3	–0.3	–0.3	74
108	FAAAMA	K	–115.0	–114.7	1.9	0.3	0.3	0.3	79
109	FAAAMA	K	–114.0	–114.7	0.9	–0.7	–0.7	–0.7	86
110	FAAAMM	K	–118.6	–119.8	0.7	10.1	4.5	–1.2	39
111	FAAAMM	H	–121.9	–119.8	4.0	13.4	7.8	2.1	4
112	FAAAOA	F	–112.8	–112.0	1.6	–0.4	0.8	0.8	1
113	FAAARA	K	–113.8	–113.9	0.7	0.0	0.0	–0.1	74
114	FAAASA	K	–113.7	–113.7	0.3	1.1	0.1	0.0	74
115	FAAAVA	F	–113.0	–114.0	–2.5	–5.2	–1.1	–1.0	63
116	FAAAeA	F	–113.8	–113.2	1.9	2.4	0.6	0.6	1
117	FAAAkA	T	–111.8	–112.4	–0.4	–3.2	–0.6	–0.6	60
118	FAABAA	H	–115.6	–113.8	3.6	1.4	1.8	1.8	4
119	FAABAA	J	–114.7	–113.8	2.7	0.5	0.9	0.9	4
120	FAABAA	T	–115.4	–113.8	3.4	1.2	1.6	1.6	60
121	FAABAA	B	–115.6	–113.8	3.6	1.4	1.8	1.8	76
122	FAABAA	F	–115.6	–113.8	3.6	1.4	1.8	1.8	2
123	FAABAA	A	–116.1	–113.8	4.1	1.9	2.3	2.3	65
124	FAACAA	D	–116.3	–114.4	4.5	1.2	1.9	1.9	53
125	FAACAA	S	–116.5	–114.4	4.7	1.4	2.1	2.1	53
126	FAACAA	H	–116.7	–114.4	4.9	1.6	2.3	2.3	4
127	FAACAA	J	–115.2	–114.4	3.4	0.1	0.8	0.8	4
128	FAACAA	K	–116.1	–114.4	4.3	1.0	1.7	1.7	6
129	FAACAA	T	–115.5	–114.4	3.7	0.4	1.1	1.1	60
130	FAACAA	I	–115.7	–114.4	3.9	0.6	1.3	1.3	72
131	FAACAA	B	–116.2	–114.4	4.4	1.1	1.8	1.8	76
132	FAACAA	F	–116.2	–114.4	4.4	1.1	1.8	1.8	2

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
133	FAACAA	K	–119.0	–114.4	7.2	3.9	4.6	4.6	86
134	FAACAF	S	–135.1	–138.5	3.0	–1.8	–2.8	–3.4	53
135	FAACAF	F	–133.7	–138.5	1.6	–3.2	–4.2	–4.8	68
136	FAACCA	F	–110.5	–110.7	1.6	–1.4	–0.1	–0.2	15
137	FAACCC	B	–107.2	–110.7	–13.7	–9.3	–3.4	–3.5	43
138	FAADAA	J	–130.0	–130.5	0.9	–2.8	–0.7	–0.5	55
139	FAADAA	H	–129.7	–130.5	0.6	–3.1	–1.0	–0.8	4
140	FAADAA	J	–129.4	–130.5	0.3	–3.4	–1.3	–1.1	4
141	FAADAA	K	–127.1	–130.5	–2.0	–5.7	–3.6	–3.4	6
142	FAADAA	B	–127.1	–130.5	–2.0	–5.7	–3.6	–3.4	76
143	FAADAA	F	–127.3	–130.5	–1.8	–5.5	–3.4	–3.2	2
144	FAADAA	T	–127.7	–130.5	–1.4	–5.1	–3.0	–2.8	60
145	FAADAA	I	–130.0	–130.5	0.9	–2.8	–0.7	–0.5	72
146	FAAEAA	F	–118.1	–115.4	2.9	2.9	2.5	2.7	2
147	FAAEAA	K	–118.3	–115.4	3.1	3.1	2.7	2.9	74
148	FAAFAA	F	–119.7	–120.0	3.3	–2.3	–0.3	–0.3	53
149	FAAFAA	D	–120.0	–120.0	3.6	–2.0	0.0	0.0	53
150	FAAFAA	S	–120.1	–120.0	3.7	–1.9	0.1	0.1	53
151	FAAFAA	H	–120.0	–120.0	3.6	–2.0	0.0	0.0	4
152	FAAFAA	J	–118.8	–120.0	2.4	–3.2	–1.2	–1.2	4
153	FAAFAA	K	–120.0	–120.0	3.6	–2.0	0.0	0.0	6
154	FAAFAA	T	–119.5	–120.0	3.1	–2.5	–0.5	–0.5	60
155	FAAFAA	F	–119.9	–120.0	3.5	–2.1	–0.1	–0.1	2
156	FAAFAA	K	–119.5	–120.0	3.1	–2.5	–0.5	–0.5	86
157	FAAFAB	F	–114.0	–114.1	–15.7	–9.8	–1.3	–0.1	86
158	FAAFAC	D	–121.8	–120.0	–6.7	–4.8	1.8	1.8	53
159	FAAFAD	H	–142.3	–140.0	–2.7	–0.4	–0.7	2.3	4
160	FAAFAF	S	–143.8	–144.1	7.1	0.0	0.3	–0.3	53
161	FAAFBA	F	–119.7	–115.9	6.4	1.3	4.0	3.8	32
162	FAAFBA	H	–117.3	–115.9	4.0	–1.1	1.6	1.4	4
163	FAAFCA	D	–117.3	–116.3	3.8	–1.5	1.1	1.0	53
164	FAAFDA	H	–119.6	–120.6	0.2	–4.7	–1.0	–1.0	4
165	FAAFFA	S	–116.1	–116.9	1.9	–4.4	–0.8	–0.8	53
166	FAAFFF	D	–139.8	–141.0	5.4	–2.5	–0.7	–1.2	21
167	FAAGAA	D	–103.0	–104.1	0.8	–0.9	–1.1	–1.1	53
168	FAAGAA	H	–104.0	–104.1	1.8	0.1	–0.1	–0.1	4
169	FAAGAA	J	–102.8	–104.1	0.6	–1.1	–1.3	–1.3	4
170	FAAGAA	I	–103.4	–104.1	1.2	–0.5	–0.7	–0.7	72
171	FAAGAA	T	–103.5	–104.1	1.3	–0.4	–0.6	–0.6	60
172	FAAGAA	F	–103.7	–104.1	1.5	–0.2	–0.4	–0.4	62
173	FAAGAA	F	–103.9	–104.1	1.7	0.0	–0.2	–0.2	63
174	FAAHAA	J	–126.3	–128.1	0.9	–4.4	–1.9	–1.8	55
175	FAAHAA	H	–126.8	–128.1	1.4	–3.9	–1.4	–1.3	4
176	FAAHAA	J	–125.0	–128.1	–0.4	–5.7	–3.2	–3.1	4
177	FAAHAA	B	–123.5	–128.1	–1.9	–7.2	–4.7	–4.6	76

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
178	FAAHAA	T	–123.7	–128.1	–1.7	–7.0	–4.5	–4.4	60
179	FAAHAA	F	–123.9	–128.1	–1.5	–6.8	–4.3	–4.2	62
180	FAAHAA	F	–124.0	–128.1	–1.4	–6.7	–4.2	–4.1	2
181	FAAHCA	J	–123.7	–124.4	1.2	–3.8	–0.7	–0.7	4
182	FAAHFA	H	–124.4	–125.0	1.2	–4.8	–0.7	–0.6	4
183	FAAHFA	J	–122.7	–125.0	–0.5	–6.5	–2.4	–2.3	4
184	FAAIAA	H	–114.8	–112.8	1.9	2.0	1.8	2.0	4
185	FAAIAA	J	–114.2	–112.8	1.3	1.4	1.2	1.4	4
186	FAAIAA	T	–114.6	–112.8	1.7	1.8	1.6	1.8	60
187	FAAIAA	F	–114.7	–112.8	1.8	1.9	1.7	1.9	2
188	FAAJAA	H	–108.0	–108.6	4.5	–0.1	–0.3	–0.6	4
189	FAAJAA	J	–106.8	–108.6	3.3	–1.3	–1.5	–1.8	4
190	FAAJAA	K	–108.3	–108.6	4.8	0.2	0.0	–0.3	6
191	FAAJAA	I	–107.4	–108.6	3.9	–0.7	–0.9	–1.2	72
192	FAAJAA	F	–108.0	–108.6	4.5	–0.1	–0.3	–0.6	2
193	FAAJAA	B	–108.1	–108.6	4.6	0.0	–0.2	–0.5	76
194	FAAJAA	A	–108.7	–108.6	5.2	0.6	0.4	0.1	65
195	FAAJAC	H	–110.5	–108.6	–5.1	–2.2	2.2	1.9	4
196	FAAJAC	J	–109.4	–108.6	–6.2	–3.3	1.1	0.8	4
197	FAAJAD	H	–135.5	–128.6	3.4	6.7	4.2	6.9	4
198	FAAJCA	J	–102.5	–104.9	1.9	–2.4	–2.0	–2.4	4
199	FAALAA	J	–124.4	–122.9	2.0	–0.2	1.3	1.5	55
200	FAALAA	H	–125.2	–122.9	2.8	0.6	2.1	2.3	4
201	FAALAA	J	–124.0	–122.9	1.6	–0.6	0.9	1.1	4
202	FAALAA	K	–124.4	–122.9	2.0	–0.2	1.3	1.5	6
203	FAALAA	T	–124.5	–122.9	2.1	–0.1	1.4	1.6	60
204	FAALAA	F	–124.6	–122.9	2.2	0.0	1.5	1.7	2
205	FAALAA	A	–125.2	–122.9	2.8	0.6	2.1	2.3	65
206	FAAMAA	J	–118.5	–118.2	2.7	0.0	0.3	0.3	56
207	FAAMAA	H	–119.2	–118.2	3.4	0.7	1.0	1.0	4
208	FAAMAA	J	–118.0	–118.2	2.2	–0.5	–0.2	–0.2	4
209	FAAMAA	K	–118.8	–118.2	3.0	0.3	0.6	0.6	6
210	FAAMAA	F	–118.5	–118.2	2.7	0.0	0.3	0.3	2
211	FAAMAA	I	–118.5	–118.2	2.7	0.0	0.3	0.3	72
212	FAAMAA	B	–118.6	–118.2	2.8	0.1	0.4	0.4	76
213	FAAMAA	K	–118.6	–118.2	2.8	0.1	0.4	0.4	74
214	FAAMAA	T	–118.6	–118.2	2.8	0.1	0.4	0.4	60
215	FAAMAA	O	–118.7	–118.2	2.9	0.2	0.5	0.5	67
216	FAAMAA	A	–119.3	–118.2	3.5	0.8	1.1	1.1	65
217	FAAMMA	H	–119.2	–118.2	2.4	1.4	1.0	1.0	4
218	FAANAA	D	–102.7	–103.8	1.3	–0.9	–1.1	–1.1	53
219	FAANAA	H	–103.6	–103.8	2.2	0.0	–0.2	–0.2	4
220	FAANAA	J	–102.4	–103.8	1.0	–1.2	–1.4	–1.4	4
221	FAANAA	T	–102.3	–103.8	0.9	–1.3	–1.5	–1.5	60
222	FAANAA	A	–103.0	–103.8	1.6	–0.6	–0.8	–0.8	65

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
223	FAANAA	P	–103.0	–103.8	1.6	–0.6	–0.8	–0.8	67
224	FAANAA	F	–103.6	–103.8	2.2	0.0	–0.2	–0.2	2
225	FAANAA	B	–103.7	–103.8	2.3	0.1	–0.1	–0.1	76
226	FAANAA	F	–103.8	–103.8	2.4	0.2	0.0	0.0	63
227	FAANAF	B	–128.7	–127.8	7.1	3.3	1.4	0.9	44
228	FAANFA	B	–98.2	–100.7	–1.0	–3.9	–2.5	–2.5	44
229	FAANFF	B	–122.8	–124.7	3.4	–1.2	–1.4	–1.9	44
230	FAANLA	B	–101.0	–101.8	–0.5	–2.7	–0.8	–0.8	44
231	FAANLF	B	–126.8	–125.8	5.1	1.3	1.5	1.0	44
232	FAANMA	J	–104.9	–103.9	2.5	2.0	1.1	1.0	4
233	FAAOAA	F	–117.4	–113.8	2.7	3.8	3.4	3.6	2
234	FAAQAA	D	–106.3	–103.7	2.4	3.5	2.4	2.6	53
235	FAAQAA	H	–107.1	–103.7	3.2	4.3	3.2	3.4	4
236	FAAQAA	J	–105.9	–103.7	2.0	3.1	2.0	2.2	4
237	FAAQAA	F	–106.5	–103.7	2.6	3.7	2.6	2.8	2
238	FAAQAA	I	–106.5	–103.7	2.6	3.7	2.6	2.8	72
239	FAAQAA	A	–107.2	–103.7	3.3	4.4	3.3	3.5	65
240	FAARAA	K	–118.0	–114.2	2.8	4.6	3.6	3.8	74
241	FAASAA	K	–118.7	–115.3	2.6	4.8	3.3	3.4	74
242	FAAVAA	F	–128.8	–131.2	–5.6	–4.5	–2.9	–2.4	2
243	FAAVAA	T	–129.9	–131.2	–4.5	–3.4	–1.8	–1.3	60
244	FAAWAA	J	–130.2	–131.0	–1.8	–2.7	–1.1	–0.8	56
245	FAAXAA	J	–113.3	–109.2	3.4	5.0	3.9	4.1	56
246	FAAdAA	J	–116.4	–113.8	4.3	2.8	2.5	2.6	56
247	FAAdAA	F	–115.2	–113.8	3.1	1.6	1.3	1.4	2
248	FAAeAA	F	–114.5	–117.4	1.0	–2.1	–2.6	–2.9	2
249	FAAkAA	T	–124.6	–119.9	3.5	3.8	4.4	4.7	60
250	FABAAB	J	–104.5	–106.4	–17.8	–9.2	–3.3	–1.9	4
251	FABABA	H	–109.4	–108.2	3.5	1.1	1.1	1.2	14
252	FACAAC	S	–112.6	–112.6	–8.7	–4.2	–0.2	0.0	53
253	FACAAD	J	–131.7	–132.6	–6.0	–1.2	–4.1	–0.9	4
254	FACAAF	S	–140.4	–136.7	11.0	6.4	4.0	3.7	53
255	FACACC	B	–106.1	–108.9	–12.2	–7.5	–2.9	–2.8	43
256	FACAFC	B	–109.7	–109.5	–9.3	–5.6	0.0	0.2	43
257	FACCCA	B	–110.6	–108.8	4.7	1.9	1.8	1.8	43
258	FACCCC	B	–109.5	–108.8	–8.5	–3.8	0.8	0.7	42
259	FACCCF	B	–133.9	–132.8	7.7	3.3	1.6	1.1	42
260	FACCFA	B	–104.6	–109.4	–2.0	–5.9	–4.9	–4.8	43
261	FACCFC	B	–113.0	–109.4	–5.7	–2.0	3.6	3.6	42
262	FADADA	H	–115.2	–117.0	–2.9	–4.8	–2.8	–1.8	14
263	FADFOF	E	–145.5	–143.4	6.8	1.6	2.0	2.1	48
264	FAFAAD	T	–131.4	–134.2	–7.0	–3.2	–6.1	–2.8	60
265	FAFAAF	S	–133.7	–138.3	3.6	–2.1	–4.3	–4.6	53
266	FAFAAH	H	–133.4	–136.7	–7.2	–9.3	–3.0	–3.3	4
267	FAFAAH	J	–131.7	–136.7	–8.9	–11.0	–4.7	–5.0	4

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
268	FAFACC	B	–108.5	–110.5	–10.5	–6.8	–2.2	–2.0	43
269	FAFAFF	D	–132.2	–135.2	4.3	–2.1	–2.7	–3.0	21
270	FAFAFF	D	–132.3	–135.2	4.4	–2.0	–2.6	–2.9	21
271	FAFANF	B	–129.8	–131.7	6.4	0.4	–1.5	–1.9	44
272	FAFBFF	B	–133.2	–134.3	5.4	0.1	–0.8	–1.1	41
273	FAFBLF	B	–135.2	–135.4	5.1	0.6	0.1	–0.2	41
274	FAFCCC	B	–107.8	–110.3	–10.9	–7.2	–2.6	–2.5	42
275	FAFCFC	A	–112.8	–110.9	–6.6	–4.0	1.7	1.9	35
276	FAFCFC	B	–111.8	–110.9	–7.6	–5.0	0.7	0.9	42
277	FAFCFC	F	–111.9	–110.9	–7.5	–4.9	0.8	1.0	68
278	FAFCFF	A	–134.6	–135.0	7.0	0.6	0.0	–0.4	35
279	FAFFAF	D	–139.8	–143.7	5.4	–2.5	–3.5	–3.9	21
280	FAFFBF	B	–137.9	–139.5	6.6	–0.9	–1.2	–1.6	41
281	FAFFBL	B	–130.9	–134.3	–5.0	–1.8	–5.3	–3.4	41
282	FAFFFA	D	–114.2	–116.6	2.3	–4.8	–2.5	–2.4	21
283	FAFFFA	A	–112.8	–116.6	0.9	–6.2	–3.9	–3.8	84
284	FAFFFB	B	–109.7	–110.6	–15.6	–11.2	–2.3	–0.9	41
285	FAFFFC	A	–117.5	–116.6	–6.5	–6.1	0.8	0.9	35
286	FAFFFC	F	–116.9	–116.6	–7.1	–6.7	0.2	0.3	68
287	FAFFFF	B	–139.1	–140.6	6.9	–1.8	–1.1	–1.5	75
288	FAFFFF	F	–141.3	–140.6	9.1	0.4	1.1	0.7	80
289	FAFFFF	D	–139.2	–140.6	7.0	–1.7	–1.0	–1.4	21
290	FAFFGk	F	–126.9	–133.0	–3.3	6.3	–4.1	–6.1	28
291	FAFFLB	B	–109.0	–111.7	–18.6	–13.4	–4.0	–2.7	41
292	FAFFLF	D	–140.7	–141.7	6.2	–1.7	–0.6	–1.0	21
293	FAFLBF	B	–139.7	–142.4	2.4	–1.7	–2.4	–2.7	41
294	FAFNAF	B	–121.8	–127.5	2.4	–2.2	–5.3	–5.7	44
295	FAFNFA	B	–98.8	–100.3	1.9	–1.9	–1.7	–1.5	44
296	FAFNFF	B	–125.6	–124.4	8.5	3.1	1.6	1.2	44
297	FAFNLA	B	–102.0	–101.5	2.8	–0.2	0.4	0.5	44
298	FAFNLF	B	–128.3	–125.5	8.9	4.3	3.2	2.8	44
299	FAFkGF	F	–137.5	–138.4	3.9	1.4	–0.7	–0.9	28
300	FAGAAA	D	–110.3	–111.4	3.6	–0.1	–0.8	–1.1	53
301	FAGAAA	H	–110.9	–111.4	4.2	0.5	–0.2	–0.5	4
302	FAGAAA	J	–110.0	–111.4	3.3	–0.4	–1.1	–1.4	4
303	FAGAAA	T	–110.1	–111.4	3.4	–0.3	–1.0	–1.3	60
304	FAGAAA	F	–110.3	–111.4	3.6	–0.1	–0.8	–1.1	63
305	FAGAAA	F	–110.4	–111.4	3.7	0.0	–0.7	–1.0	1
306	FAIAFA	F	–111.2	–109.1	4.0	0.9	1.8	2.1	1
307	FAIAIA	H	–109.2	–107.9	2.4	1.1	1.1	1.3	14
308	FAJAAA	H	–111.4	–110.2	3.5	1.9	1.2	1.2	4
309	FAJAAA	J	–110.3	–110.2	2.4	0.8	0.1	0.1	4
310	FAJAAA	T	–110.3	–110.2	2.4	0.8	0.1	0.1	60
311	FAJAAA	B	–110.9	–110.2	3.0	1.4	0.7	0.7	76
312	FAJAAA	F	–111.0	–110.2	3.1	1.5	0.8	0.8	62

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
313	FAJAAA	F	–111.0	–110.2	3.1	1.5	0.8	0.8	1
314	FAJAAA	K	–110.3	–110.2	2.4	0.8	0.1	0.1	86
315	FAJAAD	H	–131.3	–130.2	–5.1	1.1	–1.9	1.1	4
316	FAJACF	J	–131.9	–130.5	6.7	3.7	2.0	1.4	4
317	FAJAJA	H	–108.0	–106.2	4.4	4.4	1.9	1.8	14
318	FAJANA	H	–106.7	–103.7	5.5	3.5	3.2	3.0	14
319	FAJDAA	H	–133.0	–126.1	8.1	6.1	6.8	6.9	4
320	FAJFFF	A	–137.1	–136.6	6.9	0.6	1.2	0.5	12
321	FALFBF	B	–140.0	–140.4	6.4	–0.3	–0.3	–0.4	41
322	FALFFB	B	–111.5	–111.5	–16.1	–10.9	–1.7	0.0	41
323	FALNAF	B	–125.4	–128.4	3.7	–0.1	–2.9	–3.0	44
324	FAMFFF	A	–141.2	–140.1	5.8	–0.4	1.2	1.1	12
325	FAMFFF	F	–141.8	–140.1	6.4	0.2	1.8	1.7	16
326	FANAAA	D	–109.7	–110.5	4.3	0.6	–0.6	–0.8	53
327	FANAAA	H	–110.4	–110.5	5.0	1.3	0.1	–0.1	4
328	FANAAA	J	–109.5	–110.5	4.1	0.4	–0.8	–1.0	4
329	FANAAA	F	–109.6	–110.5	4.2	0.5	–0.7	–0.9	63
330	FANAAA	B	–109.7	–110.5	4.3	0.6	–0.6	–0.8	76
331	FANAAA	F	–109.7	–110.5	4.3	0.6	–0.6	–0.8	1
332	FANAAA	T	–109.8	–110.5	4.4	0.7	–0.5	–0.7	60
333	FANAAA	K	–110.6	–110.5	5.2	1.5	0.3	0.1	79
334	FANAAF	B	–135.0	–134.6	9.3	4.1	1.2	0.4	44
335	FANAAL	B	–121.9	–129.3	–8.4	–2.9	–9.1	–7.4	44
336	FANACA	H	–107.7	–106.8	5.2	1.8	1.2	0.9	14
337	FANADA	H	–111.5	–111.1	3.1	0.1	0.6	0.4	14
338	FANAFA	H	–106.4	–107.4	3.2	–1.2	–0.8	–1.0	14
339	FANAFF	B	–130.6	–131.5	7.2	1.2	–0.1	–0.9	44
340	FANAIA	H	–108.4	–106.3	5.6	3.0	2.5	2.1	14
341	FANALA	H	–109.0	–108.5	3.5	–0.1	0.7	0.5	14
342	FANAMA	H	–111.5	–110.6	5.1	3.2	1.2	0.9	14
343	FANANA	H	–105.6	–104.0	6.9	2.9	2.0	1.6	14
344	FANDAA	T	–127.4	–126.5	5.0	1.0	1.1	0.9	60
345	FANFAA	J	–114.7	–116.0	5.0	–0.9	–0.9	–1.3	4
346	FANFAF	B	–138.2	–140.0	8.2	0.7	–0.9	–1.8	44
347	FANFAL	B	–136.8	–134.7	2.2	5.4	0.5	2.1	44
348	FANFFA	B	–111.6	–112.9	4.1	–2.6	–0.9	–1.3	44
349	FANFFF	B	–138.8	–136.9	11.1	2.8	2.8	1.9	44
350	FANFFL	B	–132.5	–131.6	0.1	2.6	–0.7	0.9	44
351	FANLAF	B	–145.4	–142.9	9.4	5.3	3.2	2.5	44
352	FANLFF	B	–139.5	–139.7	5.8	0.9	0.4	–0.2	44
353	FAOFDF	E	–143.2	–143.0	4.5	–0.7	0.3	0.2	48
354	FAOFDO	E	–112.3	–112.8	–16.5	–0.2	–0.3	–0.5	48
355	FAOFFO	E	–110.0	–109.2	–13.6	1.2	1.1	0.8	48
356	FAQAAA	D	–112.7	–111.5	4.3	1.6	1.3	1.2	53
357	FAQAAA	H	–113.1	–111.5	4.7	2.0	1.7	1.6	4

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
358	FAQAAA	J	–112.0	–111.5	3.6	0.9	0.6	0.5	4
359	FAQAAA	F	–112.0	–111.5	3.6	0.9	0.6	0.5	62
360	FAQAAA	F	–112.4	–111.5	4.0	1.3	1.0	0.9	1
361	FAWFWF	H	–158.0	–147.7	12.5	7.8	9.8	10.3	31
362	FBBBBB	B	–80.3	–94.9	–52.1	–30.5	–11.1	–14.6	41
363	FBBFFF	F	–126.8	–130.9	–17.8	–13.8	–0.3	–4.1	41
364	FBBFFF	B	–125.0	–130.9	–19.6	–15.6	–2.1	–5.9	41
365	FBBFFL	B	–119.5	–127.1	–29.8	–15.0	–4.8	–7.6	41
366	FBBFLF	B	–126.9	–132.0	–20.0	–15.2	–1.3	–5.1	41
367	FBBLFF	B	–125.8	–133.7	–24.8	–17.4	–4.4	–7.9	41
368	FBFAFF	B	–125.5	–127.3	–15.7	–10.6	1.8	–1.8	41
369	FBFALF	B	–129.5	–128.4	–14.0	–8.2	4.7	1.1	41
370	FBFBFB	B	–95.4	–97.9	–38.8	–19.6	0.9	–2.5	41
371	FBFBFF	B	–125.1	–126.5	–16.0	–9.8	2.3	–1.4	41
372	FBFBLF	B	–128.3	–127.6	–15.1	–8.2	4.4	0.7	41
373	FBFFAF	B	–133.4	–135.9	–14.3	–10.8	1.3	–2.5	41
374	FBFFAL	B	–130.9	–132.1	–21.5	–7.2	1.6	–1.2	41
375	FBFFBF	D	–131.7	–131.7	–12.9	–8.9	3.9	0.0	21
376	FBFFFB	B	–102.3	–104.1	–36.3	–20.4	1.5	–1.8	41
377	FBFFFF	B	–132.7	–132.8	–12.8	–10.0	3.7	–0.1	41
378	FBFFFF	D	–132.6	–132.8	–12.9	–10.1	3.6	–0.2	21
379	FBFFGF	F	–129.4	–130.7	–12.9	–9.8	2.6	–1.3	36
380	FBFFLF	B	–135.2	–133.9	–12.6	–9.0	5.1	1.3	41
381	FBFLAF	B	–140.0	–138.7	–13.7	–6.8	4.8	1.3	41
382	FBLBFF	B	–125.4	–127.4	–18.0	–11.1	1.4	–2.0	41
383	FBLFAF	B	–132.7	–136.8	–17.3	–13.0	–0.7	–4.1	41
384	FBLFFF	B	–132.1	–133.7	–15.7	–12.1	1.8	–1.6	41
385	FCAAAF	S	–143.7	–137.1	–0.7	1.9	6.1	6.6	53
386	FCAACC	B	–106.0	–109.9	–27.3	–15.4	–4.2	–3.9	43
387	FCACAC	B	–116.6	–113.5	–19.3	–7.7	2.9	3.1	43
388	FCACAC	F	–112.6	–113.5	–23.3	–11.7	–1.1	–0.9	68
389	FCACAF	F	–133.2	–136.9	–10.9	–8.3	–4.1	–3.7	68
390	FCACCC	B	–110.0	–109.8	–23.0	–11.1	0.1	0.2	42
391	FCACCF	B	–135.5	–133.2	–5.7	–2.8	2.0	2.3	42
392	FCACFC	B	–112.6	–110.4	–21.1	–10.2	2.0	2.2	42
393	FCAFAC	F	–116.4	–119.1	–24.1	–14.8	–2.9	–2.7	68
394	FCAFAF	F	–138.2	–142.5	–10.5	–10.2	–4.7	–4.3	68
395	FCAJAF	J	–133.9	–131.1	–1.9	–0.6	2.7	2.8	4
396	FCCACC	B	–103.7	–108.0	–26.7	–14.5	–4.6	–4.3	42
397	FCCACF	B	–128.8	–131.4	–9.7	–6.6	–3.1	–2.6	42
398	FCCAFC	B	–106.7	–108.6	–24.4	–13.2	–2.3	–1.9	42
399	FCCCAF	B	–132.2	–134.9	–9.0	–6.1	–3.2	–2.7	42
400	FCCCCC	F	–108.1	–107.8	–21.9	–9.8	0.1	0.3	69
401	FCCCCF	F	–130.9	–131.2	–7.3	–4.3	–0.7	–0.3	69
402	FCCCFC	F	–109.0	–108.4	–21.8	–10.6	0.3	0.6	69

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
403	FCCCFF	F	–130.2	–131.8	–8.7	–6.7	–2.1	–1.6	68
404	FCCCFF	F	–133.2	–131.8	–5.7	–3.7	0.9	1.4	69
405	FCCCFH	F	–131.0	–132.0	–18.4	–12.8	0.3	–1.0	68
406	FCCCHF	F	–131.5	–133.3	–10.1	–7.5	–2.4	–1.8	68
407	FCCFCC	F	–111.1	–113.4	–23.5	–13.7	–2.6	–2.3	69
408	FCCFCF	F	–135.8	–136.8	–7.0	–6.2	–1.4	–1.0	68
409	FCCFCF	F	–138.8	–136.8	–4.0	–3.2	1.6	2.0	69
410	FCCFCH	F	–135.9	–137.0	–17.4	–13.1	0.3	–1.1	68
411	FCCFFC	F	–114.3	–114.0	–21.1	–12.2	–0.1	0.3	68
412	FCCFFC	F	–117.0	–114.0	–18.4	–9.5	2.6	3.0	69
413	FCCFFF	F	–136.1	–137.4	–7.4	–7.6	–1.8	–1.3	68
414	FCCFFF	F	–138.7	–137.4	–4.8	–5.0	0.8	1.3	69
415	FCCFHC	F	–114.5	–115.5	–23.5	–14.2	–1.4	–1.0	68
416	FCCFHF	B	–135.9	–138.9	–10.3	–10.0	–3.6	–3.0	24
417	FCCMCC	B	–108.3	–111.6	–25.7	–13.0	–3.5	–3.3	43
418	FCFAFC	A	–111.7	–110.2	–20.1	–10.0	1.0	1.5	35
419	FCFAFC	B	–110.4	–110.2	–21.4	–11.3	–0.3	0.2	42
420	FCFAFC	F	–110.3	–110.2	–21.5	–11.4	–0.4	0.1	68
421	FCFAFF	A	–133.1	–133.6	–6.9	–5.8	–1.2	–0.5	35
422	FCFCCF	F	–134.2	–132.8	–4.7	–2.7	0.9	1.4	68
423	FCFCCF	F	–137.2	–132.8	–1.7	0.3	3.9	4.4	69
424	FCFCFF	F	–134.5	–133.4	–5.1	–4.1	0.5	1.1	68
425	FCFCFF	A	–134.5	–133.4	–5.1	–4.1	0.5	1.1	84
426	FCFCFF	F	–137.2	–133.4	–2.4	–1.4	3.2	3.8	69
427	FCFCHC	B	–114.1	–111.5	–20.0	–9.4	2.1	2.6	24
428	FCFCHC	B	–114.4	–111.5	–19.7	–9.1	2.4	2.9	24
429	FCFCHC	F	–112.9	–111.5	–21.2	–10.6	0.9	1.4	24
430	FCFCHC	F	–112.6	–111.5	–21.5	–10.9	0.6	1.1	68
431	FCFCHF	B	–139.0	–134.9	–3.3	–1.8	3.5	4.1	24
432	FCFCHF	F	–135.8	–134.9	–6.5	–5.0	0.3	0.9	68
433	FCFFCF	F	–140.0	–138.4	–3.5	–3.7	1.1	1.6	68
434	FCFFCF	B	–140.2	–138.4	–3.3	–3.5	1.3	1.8	70
435	FCFFCF	F	–142.4	–138.4	–1.1	–1.3	3.5	4.0	80
436	FCFFCF	F	–142.6	–138.4	–0.9	–1.1	3.7	4.2	69
437	FCFFFC	F	–118.4	–115.6	–17.7	–9.8	2.4	2.8	68
438	FCFFFC	A	–118.4	–115.6	–17.7	–9.8	2.4	2.8	84
439	FCFFFC	F	–121.0	–115.6	–15.1	–7.2	5.0	5.4	69
440	FCFFFF	A	–139.6	–139.0	–4.6	–5.9	0.0	0.6	52
441	FCFFFF	F	–140.8	–139.0	–3.4	–4.7	1.2	1.8	68
442	FCFFFF	B	–140.9	–139.0	–3.3	–4.6	1.3	1.9	75
443	FCFFFF	F	–143.0	–139.0	–1.2	–2.5	3.4	4.0	80
444	FCFFFF	F	–143.2	–139.0	–1.0	–2.3	3.6	4.2	69
445	FCFFFF	D	–141.3	–139.0	–2.9	–4.2	1.7	2.3	21
446	FCFFGF	F	–137.7	–137.0	–3.4	–4.2	0.3	0.7	36
447	FCFFHC	B	–120.6	–117.1	–18.1	–9.8	3.0	3.5	24

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
448	FCFFHC	F	−118.4	−117.1	−20.3	−12.0	0.8	1.3	68
449	FCFFHF	B	−144.6	−140.5	−2.3	−3.0	3.4	4.1	24
450	FCFFLF	B	−147.0	−140.1	0.5	0.0	6.3	6.9	25
451	FCFFOF	F	−146.6	−139.6	1.1	1.8	6.6	7.0	49
452	FCFGFC	A	−101.3	−99.6	−20.6	−8.8	1.2	1.7	35
453	FCFGFF	A	−124.0	−123.0	−6.0	−3.3	0.3	1.0	35
454	FCFJFC	B	−103.7	−104.2	−19.5	−10.6	−0.6	−0.5	70
455	FCFJFF	B	−126.2	−127.6	−5.1	−5.4	−1.7	−1.4	70
456	FCHCFF	B	−138.4	−134.9	−3.9	−2.4	2.5	3.5	24
457	FCLFLF	B	−145.2	−141.0	−3.6	−3.3	3.3	4.2	25
458	FCMCCC	B	−107.0	−108.9	−27.0	−13.4	−2.4	−1.9	43
459	FCMCFC	B	−111.3	−109.5	−23.4	−10.8	1.2	1.8	43
460	FCOFFO	F	−108.5	−108.9	−27.1	−4.9	0.2	−0.4	49
461	FCOFOO	F	−107.6	−109.4	−29.3	−5.1	−1.0	−1.8	49
462	FDFFFD	G	−159.7	−162.8	−9.3	−0.7	−6.1	−3.1	82
463	FDNFFD	G	−162.3	−159.1	−2.3	6.8	0.7	3.2	82
464	FFAAFF	D	−156.8	−158.1	6.4	−0.8	−1.4	−1.3	21
465	FFAANL	B	−150.1	−151.8	−0.5	3.4	−1.7	−1.7	44
466	FFACAF	F	−155.5	−161.0	3.2	−3.3	−5.5	−5.5	68
467	FFAFAF	D	−166.6	−166.6	9.7	1.0	0.0	0.0	21
468	FFAFAF	F	−161.5	−166.6	4.6	−4.1	−5.1	−5.1	68
469	FFAFAF	A	−165.8	−166.6	8.9	0.2	−0.8	−0.8	84
470	FFAFBF	B	−163.2	−162.5	9.4	1.1	0.8	0.7	41
471	FFAFBL	B	−158.2	−159.6	−0.2	2.2	−1.3	−1.4	41
472	FFAFCF	A	−163.5	−162.9	9.5	1.1	0.6	0.6	35
473	FFAFCF	F	−162.3	−162.9	8.3	−0.1	−0.6	−0.6	68
474	FFAFFF	B	−162.6	−163.5	7.9	−1.6	−1.0	−0.9	75
475	FFAFFF	F	−164.5	−163.5	9.8	0.3	0.9	1.0	80
476	FFAFFF	D	−162.7	−163.5	8.0	−1.5	−0.9	−0.8	21
477	FFAFFL	D	−158.4	−160.7	−0.9	0.3	−2.3	−2.3	21
478	FFAFNL	B	−157.1	−157.2	2.3	3.9	0.0	−0.1	44
479	FFAJFF	A	−149.6	−152.1	7.8	−0.7	−2.2	−2.5	12
480	FFAMFF	A	−160.7	−161.7	6.6	0.0	−1.0	−1.0	12
481	FFAMFF	F	−161.3	−161.7	7.2	0.6	−0.4	−0.4	16
482	FFANAF	B	−150.1	−150.4	8.2	2.8	−0.3	−0.3	44
483	FFANFF	B	−148.8	−147.3	9.2	3.0	1.5	1.5	44
484	FFANLF	B	−141.5	−148.4	−0.4	−5.8	−6.9	−6.9	44
485	FFAOFD	E	−159.0	−157.4	−2.2	4.3	2.1	1.6	48
486	FFAWFW	H	−167.0	−173.9	−12.1	0.0	−9.2	−6.9	31
487	FFBBFF	F	−154.4	−155.0	7.3	1.6	−0.8	−0.6	18
488	FFBBFF	B	−154.3	−155.0	7.2	1.5	−0.9	−0.7	41
489	FFBBFL	B	−150.1	−152.2	−1.7	3.3	−2.3	−2.1	41
490	FFBBLF	B	−156.2	−156.1	6.8	1.8	−0.1	0.1	41
491	FFBFAL	B	−161.8	−161.5	3.4	5.8	0.1	0.3	41
492	FFBFBF	B	−159.4	−160.2	8.7	0.9	−0.8	−0.8	41

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
493	FFBFBL	B	–156.0	–157.4	0.7	3.6	–1.4	–1.4	41
494	FFBFFF	B	–160.9	–161.3	9.4	0.3	–0.5	–0.4	41
495	FFBFFF	D	–161.2	–161.3	9.7	0.6	–0.2	–0.1	21
496	FFBFFL	B	–156.7	–158.4	0.5	2.2	–1.9	–1.7	41
497	FFBLFF	B	–161.4	–164.2	3.9	–1.8	–3.1	–2.8	41
498	FFCCCF	F	–155.3	–155.4	8.9	2.9	–0.1	–0.1	68
499	FFCCCH	F	–154.8	–157.4	–2.1	–4.5	1.0	–2.6	68
500	FFCCFF	F	–155.6	–156.0	8.5	1.5	–0.5	–0.4	68
501	FFCCFF	B	–155.9	–156.0	8.8	1.8	–0.2	–0.1	70
502	FFCCFF	F	–158.2	–156.0	11.1	4.1	2.1	2.2	69
503	FFCCFH	B	–155.2	–158.0	–2.4	–5.9	0.7	–2.8	24
504	FFCFCF	F	–160.6	–161.0	9.6	1.3	–0.4	–0.4	68
505	FFCFCF	A	–160.6	–161.0	9.6	1.3	–0.4	–0.4	84
506	FFCFCF	B	–161.0	–161.0	10.0	1.7	0.0	0.0	70
507	FFCFCF	F	–163.3	–161.0	12.3	4.0	2.3	2.3	69
508	FFCFCH	B	–161.6	–163.0	0.1	–4.6	2.2	–1.4	24
509	FFCFCH	F	–160.5	–163.0	–1.0	–5.7	1.1	–2.5	68
510	FFCFFF	A	–161.8	–161.6	10.1	0.8	0.1	0.2	52
511	FFCFFF	F	–161.5	–161.6	9.8	0.5	–0.2	–0.1	68
512	FFCFFF	B	–161.6	–161.6	9.9	0.6	–0.1	0.0	75
513	FFCFFF	F	–163.8	–161.6	12.1	2.8	2.1	2.2	80
514	FFCFFF	F	–163.9	–161.6	12.2	2.9	2.2	2.3	69
515	FFCFFF	D	–161.9	–161.6	10.2	0.9	0.2	0.3	21
516	FFCFFH	B	–163.0	–163.6	0.8	–4.9	2.9	–0.6	24
517	FFCFFL	B	–160.8	–158.7	4.4	5.9	1.9	2.1	25
518	FFCHCF	B	–165.8	–169.1	5.8	–2.2	–3.4	–3.3	24
519	FFCLFL	B	–161.0	–161.6	–1.4	3.5	–0.9	–0.6	25
520	FFDFDF	G	–169.9	–169.1	7.0	–0.3	0.0	0.8	82
521	FFDFFD	G	–163.3	–165.6	–2.7	–2.0	–2.4	–2.3	82
522	FFDFFH	M	–166.4	–167.5	–1.7	–7.0	1.8	–1.1	34
523	FFDJDF	H	–158.0	–157.7	8.0	1.7	–0.2	0.3	31
524	FFDNDF	G	–151.4	–152.8	3.6	–0.4	–2.3	–1.4	82
525	FFFAFF	B	–154.0	–157.7	5.9	–2.1	–4.0	–3.7	75
526	FFFAFF	F	–156.0	–157.7	7.9	–0.1	–2.0	–1.7	80
527	FFFAFF	D	–154.5	–157.7	6.4	–1.6	–3.5	–3.2	21
528	FFFANL	B	–158.4	–151.4	10.1	13.2	6.8	7.0	44
529	FFFBBL	B	–149.2	–153.0	–2.6	2.4	–3.9	–3.8	41
530	FFFBFF	B	–154.9	–156.9	6.9	0.0	–2.2	–2.0	41
531	FFFBFF	D	–155.2	–156.9	7.2	0.3	–1.9	–1.7	21
532	FFFBLF	B	–161.1	–158.0	10.8	4.6	2.9	3.1	41
533	FFFCFF	A	–156.3	–157.6	8.5	0.5	–1.4	–1.3	52
534	FFFCFF	B	–156.3	–157.6	8.5	0.5	–1.4	–1.3	75
535	FFFCFF	F	–156.3	–157.6	8.5	0.5	–1.4	–1.3	68
536	FFFCFF	F	–158.6	–157.6	10.8	2.8	0.9	1.0	80
537	FFFCFF	F	–158.7	–157.6	10.9	2.9	1.0	1.1	69

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
538	FFFCFF	D	–156.1	–157.6	8.3	0.3	–1.6	–1.5	21
539	FFFDDF	G	–176.4	–177.3	6.1	–0.8	–1.3	–0.9	82
540	FFFDFD	G	–173.9	–173.8	0.5	1.5	0.5	0.1	82
541	FFFDFF	B	–174.1	–173.7	9.0	0.6	0.1	0.4	75
542	FFFDFF	G	–178.3	–173.7	13.2	4.8	4.3	4.6	82
543	FFFDFF	D	–173.9	–173.7	8.8	0.4	–0.1	0.2	21
544	FFFDFH	H	–174.6	–175.7	–1.0	–5.9	2.2	–1.1	31
545	FFFDHF	M	–181.1	–175.2	13.3	5.5	5.5	5.9	34
546	FFFDJD	H	–172.5	–173.0	1.1	4.6	0.1	–0.5	31
547	FFFDND	G	–175.2	–170.4	6.2	7.7	5.4	4.8	82
548	FFFFBL	B	–156.0	–159.2	–0.2	1.5	–3.3	–3.2	41
549	FFFFDD	G	–163.8	–167.0	–2.2	–1.5	–2.7	–3.2	82
550	FFFFDF	B	–165.7	–166.8	8.1	–0.8	–1.3	–1.1	75
551	FFFFDF	G	–167.2	–166.8	9.6	0.7	0.2	0.4	82
552	FFFFDF	D	–165.5	–166.8	7.9	–1.0	–1.5	–1.3	21
553	FFFFDH	M	–170.5	–168.8	2.4	–2.9	5.1	1.7	34
554	FFFFFD	G	–163.4	–163.3	2.7	1.8	0.6	0.1	82
555	FFFFFD	B	–163.6	–163.3	2.9	2.0	0.8	0.3	75
556	FFFFFD	D	–162.9	–163.3	2.2	1.3	0.1	–0.4	21
557	FFFFFF	B	–162.6	–163.2	10.2	–0.1	–0.7	–0.6	81
558	FFFFFF	B	–162.9	–163.2	10.5	0.2	–0.4	–0.3	75
559	FFFFFF	G	–163.3	–163.2	10.9	0.6	0.0	0.1	82
560	FFFFFF	K	–163.9	–163.2	11.5	1.2	0.6	0.7	83
561	FFFFFF	B	–164.9	–163.2	12.5	2.2	1.6	1.7	85
562	FFFFFH	F	–166.3	–165.2	3.4	–3.4	4.6	1.1	69
563	FFFFFH	D	–164.1	–165.2	1.2	–5.6	2.4	–1.1	21
564	FFFFFL	B	–158.5	–160.3	1.4	1.9	–2.0	–1.8	75
565	FFFFFL	D	–158.4	–160.3	1.3	1.8	–2.1	–1.9	21
566	FFFFFW	K	–161.9	–162.6	0.5	7.3	–2.8	–0.7	83
567	FFFFFW	F	–164.5	–162.6	3.1	9.9	–0.2	1.9	69
568	FFFFFW	D	–161.9	–162.6	0.5	7.3	–2.8	–0.7	21
569	FFFFFk	H	–157.9	–159.9	4.3	11.9	1.6	–2.0	31
570	FFFFGD	G	–162.8	–161.3	5.3	4.8	2.2	1.5	36
571	FFFFGL	B	–156.2	–158.2	2.3	3.1	–2.1	–2.0	46
572	FFFFHD	M	–167.3	–164.8	3.9	3.6	2.9	2.5	34
573	FFFFHF	F	–167.8	–164.7	12.7	2.9	2.9	3.1	69
574	FFFFHF	D	–164.3	–164.7	9.2	–0.6	–0.6	–0.4	21
575	FFFFLF	B	–164.9	–164.3	10.2	0.7	0.5	0.6	75
576	FFFFLF	F	–167.0	–164.3	12.3	2.8	2.6	2.7	69
577	FFFFLF	D	–164.8	–164.3	10.1	0.6	0.4	0.5	21
578	FFFFND	G	–160.7	–159.9	4.4	4.0	1.5	0.8	82
579	FFFFNH	G	–162.0	–161.8	3.6	–2.8	3.9	0.2	34
580	FFFFNV	O	–152.1	–151.6	–15.3	–3.5	0.5	0.5	26
581	FFFFNW	O	–157.6	–159.1	0.7	7.9	–3.5	–1.5	26
582	FFFFQV	O	–155.9	–154.1	–14.4	–1.7	1.8	1.8	26

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
583	FFFFQW	O	–159.4	–161.7	–0.4	7.7	–4.2	–2.3	26
584	FFFFWF	F	–167.8	–167.6	8.7	0.4	0.0	0.2	69
585	FFFFWF	K	–165.2	–167.6	6.1	–2.2	–2.6	–2.4	83
586	FFFFWF	D	–165.2	–167.6	6.1	–2.2	–2.6	–2.4	21
587	FFFFkF	H	–165.2	–164.1	10.4	1.5	1.0	1.1	31
588	FFFFkk	B	–160.1	–160.8	4.2	13.1	3.0	–0.7	20
589	FFFFkk	B	–160.1	–160.8	4.2	13.1	3.0	–0.7	85
590	FFFGDF	G	–152.5	–150.8	9.0	4.2	1.4	1.7	36
591	FFFGFF	B	–143.4	–147.2	5.2	–1.2	–4.1	–3.8	46
592	FFFGFF	B	–143.5	–147.2	5.3	–1.1	–4.0	–3.7	75
593	FFFGFF	D	–143.1	–147.2	4.9	–1.5	–4.4	–4.1	21
594	FFFGLF	B	–146.4	–148.3	5.9	0.3	–2.1	–1.9	46
595	FFFHDF	M	–176.3	–174.9	9.7	1.1	1.1	1.4	34
596	FFFHFD	H	–168.9	–171.4	–0.8	–1.4	–2.1	–2.5	31
597	FFFHFF	F	–173.1	–171.3	11.7	1.7	1.6	1.8	69
598	FFFHFF	D	–169.2	–171.3	7.8	–2.2	–2.3	–2.1	21
599	FFFHFL	B	–172.7	–168.4	6.7	7.3	4.0	4.3	24
600	FFFIFF	B	–152.8	–155.9	3.9	–0.7	–3.5	–3.1	75
601	FFFIFF	D	–152.9	–155.9	4.0	–0.6	–3.4	–3.0	21
602	FFFJFF	B	–147.9	–151.8	8.4	–0.9	–3.7	–3.9	75
603	FFFJFF	D	–147.8	–151.8	8.3	–1.0	–3.8	–4.0	21
604	FFFLFF	B	–164.6	–166.0	6.2	–0.7	–1.8	–1.4	75
605	FFFLFF	F	–167.0	–166.0	8.6	1.7	0.6	1.0	69
606	FFFLFF	D	–164.8	–166.0	6.4	–0.5	–1.6	–1.2	21
607	FFFLFH	B	–166.0	–168.1	–2.9	–6.2	1.2	–2.1	24
608	FFFMFF	B	–159.3	–161.3	7.5	0.1	–2.2	–2.0	75
609	FFFMFF	D	–159.7	–161.3	7.9	0.5	–1.8	–1.6	21
610	FFFMFL	B	–155.0	–158.4	–1.5	1.9	–3.7	–3.4	51
611	FFFNDF	G	–151.2	–150.6	8.6	3.1	0.4	0.6	82
612	FFFNFF	B	–147.6	–146.9	10.2	3.3	0.5	0.7	46
613	FFFNFF	F	–150.1	–146.9	12.7	5.8	3.0	3.2	80
614	FFFNFF	D	–146.5	–146.9	9.1	2.2	–0.6	–0.4	21
615	FFFNHF	G	–152.4	–148.5	12.4	5.9	3.7	3.9	34
616	FFFNVF	O	–144.8	–149.4	1.8	–3.8	–4.8	–4.6	26
617	FFFNWF	O	–149.6	–151.4	5.6	0.6	–1.9	–1.8	26
618	FFFOFF	K	–157.2	–156.9	6.5	2.9	–0.1	0.3	83
619	FFFQFF	B	–159.6	–146.8	19.7	16.1	12.4	12.8	50
620	FFFQVF	O	–146.3	–149.3	0.8	–1.5	–3.4	–3.0	26
621	FFFQWF	O	–150.1	–151.3	3.6	1.9	–1.5	–1.2	26
622	FFFWFF	K	–173.1	–174.2	5.2	–0.5	–1.5	–1.1	83
623	FFFWFF	F	–175.7	–174.2	7.8	2.1	1.1	1.5	69
624	FFFWFF	D	–173.1	–174.2	5.2	–0.5	–1.5	–1.1	21
625	FFFXFF	K	–154.0	–152.3	8.1	5.0	1.3	1.7	19
626	FFFXFF	D	–153.2	–152.3	7.3	4.2	0.5	0.9	21
627	FFFdFF	K	–155.6	–157.0	7.5	1.2	–1.6	–1.4	19

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
628	FFFeFF	F	–156.8	–160.6	7.4	–0.6	–3.6	–3.8	78
629	FFFeFF	D	–157.0	–160.6	7.6	–0.4	–3.4	–3.6	21
630	FFFkFF	H	–165.2	–163.0	8.2	3.7	1.7	2.2	31
631	FFFkFk	B	–159.3	–159.8	1.1	14.5	2.8	–0.5	20
632	FFFkkF	B	–166.9	–163.9	7.5	4.4	2.6	3.0	20
633	FFGDFF	G	–177.4	–170.8	15.5	7.5	6.8	6.6	36
634	FFGFCF	A	–161.7	–159.7	13.2	4.3	2.5	2.0	35
635	FFGFFD	G	–163.7	–160.4	6.2	5.7	4.3	3.3	36
636	FFGFFF	B	–163.5	–160.3	14.3	4.3	3.6	3.2	46
637	FFGFFF	B	–159.2	–160.3	10.0	0.0	–0.7	–1.1	75
638	FFGFFF	D	–158.9	–160.3	9.7	–0.3	–1.0	–1.4	21
639	FFGFFV	O	–150.4	–152.1	–18.2	–6.5	–1.4	–1.7	26
640	FFGFFW	O	–161.1	–159.7	2.9	10.1	–0.2	1.4	26
641	FFGGFF	D	–143.5	–144.3	8.5	2.5	–0.5	–0.8	21
642	FFGGFF	D	–143.8	–144.3	8.8	2.8	–0.2	–0.5	21
643	FFGGFF	B	–141.6	–144.3	6.6	0.6	–2.4	–2.7	46
644	FFGLFF	B	–162.8	–163.1	7.6	1.1	–0.2	–0.3	46
645	FFHFDF	H	–169.8	–168.3	9.5	1.2	0.9	1.5	31
646	FFHFFD	M	–165.4	–164.8	2.0	1.7	0.7	0.6	34
647	FFHFFL	B	–161.2	–161.8	1.5	2.4	–1.3	–0.6	24
648	FFIFFF	B	–159.9	–161.1	7.9	–0.6	–1.4	–1.2	75
649	FFIFFF	D	–159.9	–161.1	7.9	–0.6	–1.4	–1.2	21
650	FFIIFF	F	–152.1	–153.9	3.6	0.8	–2.2	–1.8	21
651	FFIIFF	D	–151.5	–153.9	3.0	0.2	–2.8	–2.4	21
652	FFJAFF	A	–153.3	–153.7	7.2	1.6	–0.4	–0.4	12
653	FFJFCF	B	–160.8	–158.5	11.1	4.2	2.4	2.3	70
654	FFJFFF	B	–160.6	–159.1	10.2	2.3	1.6	1.5	75
655	FFJFFF	D	–160.5	–159.1	10.1	2.2	1.5	1.4	21
656	FFJFFL	B	–157.0	–156.3	2.0	4.8	0.8	0.7	51
657	FFJFFV	O	–151.2	–151.0	–18.6	–4.9	0.3	0.2	26
658	FFJFFW	O	–162.0	–158.5	2.7	11.8	1.6	3.5	26
659	FFJJFF	A	–145.4	–147.7	7.9	1.0	–1.9	–2.3	12
660	FFJLFF	B	–162.0	–162.0	5.6	1.1	–0.1	0.0	51
661	FFLFFH	B	–166.0	–166.1	0.8	–5.2	3.0	–0.1	24
662	FFLFHF	B	–166.0	–165.6	8.6	–0.4	–0.1	0.4	24
663	FFMAFF	A	–157.6	–157.3	6.3	0.7	–0.1	0.3	12
664	FFMAFF	F	–158.3	–157.3	7.0	1.4	0.6	1.0	16
665	FFMFFF	B	–164.3	–162.7	8.7	0.9	1.2	1.6	75
666	FFMFFF	D	–164.4	–162.7	8.8	1.0	1.3	1.7	21
667	FFMFFL	B	–159.5	–159.8	–0.8	2.1	–0.7	–0.3	51
668	FFMFLF	B	–166.0	–163.8	8.1	1.0	1.9	2.2	51
669	FFMMFF	A	–161.9	–160.8	6.9	1.9	0.7	1.1	12
670	FFMMFF	E	–162.0	–160.8	7.0	2.0	0.8	1.2	16
671	FFNAAF	B	–155.9	–157.1	10.0	3.2	–1.0	–1.2	44
672	FFNAAL	B	–155.0	–154.3	4.4	8.3	0.9	0.7	44

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
673	FFNAFF	B	–154.2	–154.0	10.5	2.9	0.4	0.2	44
674	FFNAFL	B	–150.3	–151.2	2.0	5.1	–0.7	–0.9	44
675	FFNDFD	G	–173.1	–170.1	4.1	5.6	3.9	3.0	82
676	FFNDFF	G	–176.9	–170.0	16.3	8.3	7.1	6.9	82
677	FFNFAF	B	–163.5	–162.6	13.3	4.2	1.3	0.9	44
678	FFNFAL	B	–161.5	–159.7	6.7	8.3	2.1	1.8	44
679	FFNFFD	G	–163.1	–159.6	6.8	6.4	4.5	3.5	82
680	FFNFFF	B	–158.6	–159.5	10.7	0.8	–0.5	–0.9	46
681	FFNFFF	F	–161.2	–159.5	13.3	3.4	2.1	1.7	80
682	FFNFFF	D	–158.8	–159.5	10.9	1.0	–0.3	–0.7	21
683	FFNFFH	G	–163.0	–161.5	4.6	–1.8	5.5	1.5	34
684	FFNFFV	O	–151.6	–151.3	–15.8	–4.0	0.6	0.3	26
685	FFNFFW	O	–162.4	–158.9	5.5	12.7	1.9	3.5	26
686	FFNHFF	G	–171.1	–167.6	14.2	4.5	3.8	3.5	34
687	FFNHFH	G	–169.6	–169.6	2.2	–3.9	3.9	0.0	34
688	FFNVFF	O	–161.9	–170.6	–4.0	–7.2	–8.8	–8.7	26
689	FFNWFF	O	–173.9	–170.5	10.4	5.2	3.5	3.4	26
690	FFOFFF	K	–164.4	–162.0	10.7	2.4	2.1	2.4	83
691	FFOFFH	F	–161.7	–164.0	–2.5	–7.3	1.0	–2.3	49
692	FFOFFL	F	–156.9	–159.1	–1.5	1.0	–2.6	–2.2	49
693	FFQFFF	B	–164.1	–160.4	13.2	4.3	3.9	3.7	50
694	FFQFFV	O	–152.3	–152.3	–18.0	–5.3	0.2	0.0	26
695	FFQFFW	O	–162.6	–159.8	2.8	10.9	1.0	2.8	26
696	FFQVFF	O	–161.9	–171.6	–6.9	–9.2	–9.9	–9.7	26
697	FFQWFF	O	–177.2	–171.4	10.8	6.5	5.7	5.8	26
698	FFXFFF	K	–162.3	–161.2	8.8	0.9	0.9	1.1	19
699	FFXFFF	D	–161.4	–161.2	7.9	0.0	0.0	0.2	21
700	FFdFFF	K	–163.1	–162.0	8.4	0.6	0.9	1.1	19
701	FFeFFF	F	–163.8	–159.9	9.4	3.7	3.4	3.9	78
702	FFeFFF	D	–163.9	–159.9	9.5	3.8	3.5	4.0	21
703	FFkFFk	B	–159.4	–160.3	3.5	12.4	2.4	–0.9	20
704	FFkFkF	B	–166.9	–164.4	9.8	2.2	2.1	2.5	20
705	FGAAAA	F	–107.3	–108.2	–4.2	–1.0	–2.9	–0.9	13
706	FGAAAA	D	–107.3	–108.2	–4.2	–1.0	–2.9	–0.9	53
707	FGAAAA	H	–108.6	–108.2	–2.9	0.3	–1.6	0.4	4
708	FGAAAA	J	–107.9	–108.2	–3.6	–0.4	–2.3	–0.3	4
709	FGAAAA	T	–107.9	–108.2	–3.6	–0.4	–2.3	–0.3	60
710	FGDFFF	G	–139.4	–136.2	2.6	1.9	0.8	3.2	36
711	FGFAAA	H	–105.9	–107.8	–3.4	–0.9	–4.1	–1.9	4
712	FGFCFC	A	–106.3	–107.4	–12.5	–3.3	–0.3	–1.1	35
713	FGFCFF	A	–129.5	–128.3	2.6	2.6	–0.6	1.2	35
714	FGFFBF	F	–131.7	–132.9	1.0	0.1	–2.8	–1.2	36
715	FGFFCF	F	–132.3	–133.3	1.5	0.3	–2.7	–1.0	36
716	FGFFDF	G	–140.8	–137.6	4.0	3.3	1.4	3.2	36
717	FGFFFC	A	–112.1	–113.0	–11.3	–4.4	–0.1	–0.9	35

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
718	FGFFFF	B	–131.9	–133.9	0.4	–1.8	–3.8	–2.0	46
719	FGFFFF	B	–132.5	–133.9	1.0	–1.2	–3.2	–1.4	75
720	FGFFFF	D	–132.2	–133.9	0.7	–1.5	–3.5	–1.7	21
721	FGFFGF	D	–130.6	–131.9	2.2	0.4	–2.9	–1.3	21
722	FGFFGF	B	–129.2	–131.9	0.8	–1.0	–4.3	–2.7	46
723	FGFFIF	F	–132.0	–132.8	0.9	0.5	–2.4	–0.8	36
724	FGFFVF	O	–135.5	–136.4	–1.7	–2.5	–2.7	–0.9	26
725	FGFFWF	O	–136.6	–138.4	–1.6	–1.8	–3.5	–1.8	26
726	FGGFFF	D	–127.9	–131.1	–0.5	–2.3	–4.4	–3.2	21
727	FGGFFF	B	–126.3	–131.1	–2.1	–3.9	–6.0	–4.8	46
728	FGGFFF	Q	–130.0	–131.1	1.6	–0.2	–2.3	–1.1	77
729	FGLFFF	B	–134.0	–134.8	0.2	–1.2	–2.9	–0.8	46
730	FGkFAF	F	–132.9	–137.4	–3.2	–3.3	–6.6	–4.5	28
731	FHFFFD	H	–160.9	–155.5	–10.3	–7.6	–10.5	5.4	31
732	FHNFFH	G	–162.7	–153.4	–6.2	–9.0	–3.4	9.3	34
733	FIFFFF	B	–119.3	–116.4	–26.5	–16.0	–1.9	2.9	75
734	FIFFFF	D	–119.7	–116.4	–26.1	–15.6	–1.5	3.3	21
735	FIFFGF	F	–116.7	–114.4	–25.9	–15.0	–2.2	2.3	36
736	FIIFFF	F	–107.2	–114.4	–38.1	–25.9	–12.0	–7.2	18
737	FIIFFF	D	–104.1	–114.4	–41.2	–29.0	–15.1	–10.3	21
738	FJAAAA	H	–115.8	–114.3	6.1	12.6	1.9	1.5	4
739	FJAAAA	J	–115.4	–114.3	5.7	12.2	1.5	1.1	4
740	FJACAC	B	–111.5	–116.0	–9.9	4.0	–2.1	–4.5	70
741	FJADAA	H	–129.0	–130.2	2.4	8.5	–0.9	–1.2	4
742	FJAFFF	A	–139.5	–140.0	7.6	9.4	–0.2	–0.5	12
743	FJFCFC	B	–111.1	–112.6	–5.8	6.5	0.8	–1.5	70
744	FJFFFF	B	–140.0	–139.6	10.3	11.3	0.5	0.4	75
745	FJFFFF	D	–140.1	–139.6	10.4	11.4	0.6	0.5	21
746	FJFFLF	B	–142.4	–140.7	10.4	12.2	1.9	1.7	51
747	FJFFVF	O	–142.5	–142.1	7.2	9.6	0.6	0.4	26
748	FJFFWF	O	–143.1	–144.0	6.7	9.8	–0.8	–0.9	26
749	FJJFFF	A	–132.3	–135.6	4.6	8.1	–2.9	–3.3	12
750	FLCFFL	B	–153.6	–154.8	–7.4	4.8	3.2	–1.2	25
751	FLFFFH	B	–160.1	–162.1	–7.4	–3.5	6.9	–2.0	24
752	FMAFFF	A	–145.5	–144.7	6.2	9.3	–0.6	0.8	12
753	FMAFFF	F	–143.8	–144.7	4.5	7.6	–2.3	–0.9	16
754	FMAMAM	T	–128.1	–126.0	2.6	22.0	4.9	2.1	60
755	FMCCCC	B	–110.0	–111.5	–12.8	2.9	–4.3	–1.5	43
756	FMFCCC	B	–112.1	–113.1	–11.4	3.2	–3.9	–1.0	43
757	FMFFFF	B	–144.0	–144.3	7.0	9.3	–1.9	–0.3	75
758	FMFFFF	D	–144.1	–144.3	7.1	9.4	–1.8	–0.2	21
759	FMFFFL	B	–137.8	–139.7	–3.9	9.2	–5.2	–1.9	51
760	FMFFLF	B	–145.8	–145.4	6.5	9.6	–1.1	0.4	51
761	FMFLFF	B	–145.8	–147.2	2.8	8.5	–3.1	–1.4	51
762	FMMFFF	A	–143.9	–143.8	3.7	8.5	–1.7	0.1	12

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
763	FMMFFF	E	–144.5	–143.8	4.3	9.1	–1.1	0.7	16
764	FNAAAA	F	–118.4	–118.6	3.4	7.7	–1.1	–0.2	13
765	FNAAAA	H	–119.7	–118.6	4.7	9.0	0.2	1.1	4
766	FNAAAA	J	–119.0	–118.6	4.0	8.3	–0.5	0.4	4
767	FNAAAA	T	–118.7	–118.6	3.7	8.0	–0.8	0.1	60
768	FNAAFA	B	–111.9	–115.4	–0.9	2.7	–4.5	–3.5	44
769	FNAAFF	B	–137.5	–140.2	4.5	6.5	–2.4	–2.7	44
770	FNAALA	B	–113.4	–116.6	–1.7	2.7	–4.0	–3.2	44
771	FNAALF	B	–140.6	–141.3	5.3	8.1	–0.3	–0.7	44
772	FNADAA	T	–134.7	–134.5	2.7	6.7	–0.7	0.2	60
773	FNAFAA	J	–123.5	–124.0	4.2	6.3	–1.3	–0.5	4
774	FNAFAF	B	–147.8	–148.7	8.3	8.7	–0.5	–0.9	44
775	FNAFFA	B	–117.6	–120.9	0.5	1.8	–4.1	–3.3	44
776	FNAFFF	B	–145.1	–145.6	7.8	7.5	–0.1	–0.5	44
777	FNAFLA	B	–117.6	–122.0	–1.8	0.3	–5.2	–4.4	44
778	FNAFLF	B	–145.7	–146.7	6.1	6.6	–0.6	–1.0	44
779	FNAJAN	H	–120.4	–116.5	11.1	21.8	2.7	3.9	4
780	FNAJAN	J	–119.0	–116.5	9.7	20.4	1.3	2.5	4
781	FNANAA	T	–107.7	–107.8	3.4	8.9	–0.9	–0.1	60
782	FNDFDF	G	–150.0	–151.1	4.5	6.4	–1.6	–1.1	82
783	FNDFFF	G	–148.0	–147.5	7.7	8.1	0.1	0.5	82
784	FNFAFA	B	–115.3	–115.1	4.8	7.6	–0.9	0.2	44
785	FNFAFF	B	–141.0	–139.8	10.2	11.4	1.3	1.2	44
786	FNFALA	B	–117.0	–116.2	4.2	7.7	–0.2	0.8	44
787	FNFALF	B	–142.8	–140.9	9.7	11.7	2.1	1.9	44
788	FNFFDF	G	–149.9	–148.9	9.6	10.0	1.2	1.0	82
789	FNFFFA	B	–128.8	–120.5	14.0	14.5	7.3	8.3	44
790	FNFFFF	B	–146.4	–145.2	11.3	10.3	1.4	1.2	46
791	FNFFFF	F	–148.8	–145.2	13.7	12.7	3.8	3.6	80
792	FNFFFF	D	–145.8	–145.2	10.7	9.7	0.8	0.6	21
793	FNFFHF	G	–151.0	–146.8	13.3	12.7	4.4	4.2	34
794	FNFFLA	B	–118.9	–121.6	1.8	3.1	–3.7	–2.7	44
795	FNFFVF	O	–145.0	–147.7	4.3	4.6	–2.4	–2.7	26
796	FNFFWF	O	–148.7	–149.6	7.0	7.9	–0.7	–0.9	26
797	FNHFFF	G	–151.4	–146.8	13.7	13.1	4.5	4.6	34
798	FNHFHF	G	–150.8	–148.3	10.5	10.4	2.3	2.5	34
799	FNLAFA	B	–119.7	–116.0	6.9	10.4	2.3	3.7	44
800	FNLFFA	B	–126.0	–121.4	8.9	10.2	3.3	4.6	44
801	FNOFOF	F	–149.8	–144.6	12.1	15.1	5.5	5.2	49
802	FNOFOO	F	–122.0	–118.6	–5.7	18.7	8.0	3.4	49
803	FNVFFF	O	–149.6	–148.1	8.9	9.2	0.9	1.5	26
804	FNWFFF	O	–146.4	–148.0	4.7	5.6	–2.1	–1.6	26
805	FOAFFD	E	–135.9	–132.6	–17.1	4.3	–0.2	3.3	48
806	FOAFOD	E	–137.8	–133.2	–16.5	6.9	1.4	4.6	48
807	FOAFOF	E	–139.9	–135.0	–6.1	7.8	2.9	4.9	48

(*continued*)

TABLE 1 (*continued*)

No.	Sort code and solvent		^{19}F NMR signal position		Model residuals				Ref.
			Obs.	Pred.	F	G	J	K	
808	FOCFOO	F	–99.4	–103.0	–33.8	1.9	–5.5	–3.6	49
809	FODFOF	F	–135.7	–136.9	–13.3	1.4	–4.0	–1.2	49
810	FOFAOF	E	–128.9	–129.2	–10.6	4.9	–2.6	–0.3	48
811	FOFDAF	E	–142.1	–147.8	–15.3	–1.5	–8.1	–5.7	48
812	FOFDOF	F	–146.2	–145.2	–10.3	4.8	–1.2	1.0	49
813	FOFFAD	E	–133.9	–135.4	–19.1	2.3	–5.1	–1.5	48
814	FOFFCF	F	–134.3	–133.5	–7.5	4.7	–1.4	0.8	49
815	FOFFFF	K	–135.8	–134.1	–6.7	4.5	–0.6	1.7	83
816	FOFFHF	F	–134.7	–135.7	–10.4	1.3	–3.3	–1.0	49
817	FOFFLF	F	–135.2	–135.2	–9.6	2.4	–2.3	0.0	49
818	FOFFOD	F	–132.8	–132.8	–19.3	3.3	–3.4	0.0	49
819	FOFONF	F	–126.8	–124.4	–9.5	8.7	0.1	2.4	49
820	FONFFO	F	–100.1	–100.3	–28.0	5.1	–1.8	–0.2	49
821	FONFOO	F	–100.3	–100.8	–29.1	6.0	–2.0	–0.5	49
822	FOOFHO	F	–100.4	–104.3	–36.1	–0.9	–6.3	–3.9	49
823	FOOFOH	F	–129.9	–133.8	–25.7	–7.0	–4.2	–3.9	49
824	FQAAAA	D	–110.3	–112.5	1.9	13.8	2.9	–2.2	53
825	FQAAAA	H	–110.6	–112.5	2.2	14.1	3.2	–1.9	4
826	FQAAAA	J	–110.0	–112.5	1.6	13.5	2.6	–2.5	4
827	FQFFFF	B	–154.0	–137.5	25.6	32.1	21.1	16.5	50
828	FQFFVF	O	–141.9	–140.0	7.8	15.7	6.6	1.9	26
829	FQFFWF	O	–141.9	–141.9	6.8	15.3	4.6	0.0	26
830	FQVFFF	O	–144.5	–140.4	10.4	18.3	7.9	4.1	26
831	FQWFFF	O	–132.7	–140.2	–2.4	6.1	–3.7	–7.5	26
832	FSFAFF	F	–132.1	–126.3	–0.2	27.6	10.7	5.8	68
833	FWAFFW	H	–140.0	–150.3	–32.6	–7.9	7.3	–10.3	31
834	FXFFFF	K	–143.3	–146.7	11.8	23.8	8.4	–3.4	19
835	FXFFFF	D	–142.5	–146.7	11.0	23.0	7.6	–4.2	21
836	FdFFFF	K	–145.0	–143.1	12.8	17.1	1.9	1.9	19
837	FeFFFF	F	–144.3	–144.0	7.8	21.6	–2.8	0.3	78
838	FeFFFF	D	–143.8	–144.0	7.3	21.1	–3.3	–0.2	21
839	FkFFFk	B	–151.3	–128.3	–3.5	22.1	10.4	23.0	20

For three compounds, signals in two positions were switched because of the high probability that they were misinterpreted. In this table, they appear as numbers: 1) 599 and 662, 2) 801 and 819, 3) 293 and 383.

established in which a compound is identified in the computer programs by its six letter sort code, the key to which is given in Table 2. The letters of the sort code tell the program which group is in each position and allows the program to look up the parameter values for that group. The fluorine atom whose signal is being predicted must be in position 1. Fluoroarenes with more than one signal are encoded separately for each signal. Thus, for example, a fluoroarene which gives three signals is in the compound list three times with three different sort codes. For models J and K it is necessary to define a clockwise direction around the ring, and all sort codes in Table

TABLE 2

Sort code, field ($\mathscr{F}$), resonance ($\mathscr{R}$), Charton steric parameter (ν) and molar refractivity (MR) for substituents used in Table 1[a]

Sort code	Group	$\mathscr{F}$	$\mathscr{R}$	ν	MR
A	H	0.00	0.00	0.00	0.00
B	Br	0.44	−0.17	0.65	8.88
C	Cl	0.41	−0.15	0.55	6.03
D	NH_2	0.02	−0.68	0.35	5.42
E	CH_2CH_3	−0.05	−0.10	0.56	10.30
F	F	0.43	−0.34	0.27	0.92
G	CN	0.51	0.19	0.40	6.33
H	OH	0.29	−0.64	0.32	2.85
I	I	0.40	−0.19	0.78	13.94
J	CF_3	0.38	0.19	0.91	5.02
L	OCH_3	0.26	−0.51	0.36	7.87
M	CH_3	−0.04	−0.13	0.52	5.65
N	NO_2	0.67	0.16	0.59	7.36
O	SCH_3	0.20	−0.18	0.64	13.82
Q	$COCH_3$	0.32	0.20	0.50	11.18
R	$CH(CH_3)_2$	−0.05	−0.10	0.76	14.96
S	$C(CH_3)_3$	−0.07	−0.13	1.24	19.62
V	$N(CH_3)_2$	0.10	−0.92	0.43	15.55
W	$NHCH_3$	−0.11	−0.74	0.39	10.33
X	CH_2Br	0.10	0.05	0.64	13.39
d	CH_2OH	0.00	0.00	0.53	7.19
e	$CH{=}CH_2$	0.07	−0.08	1.31	10.99
k	OCH_2CH_3	0.22	−0.44	0.48	12.47
n	$NHCH_2CH_3$	−0.11	−0.51	0.59	14.98

[a]This table is part of a larger table and lists only groups used in this study, and thus not all letters have been used.

1 are the clockwise sort codes. The meaning of clockwise in this context is explained in the section on models J and K.

Table 1 is sorted alphabetically in terms of the sort codes assigned in order to facilitate looking up a given compound or signal. Groups not used in this study were deleted from the parameters table (Table 2) and thus some of the letters are missing. Note also that lower case letters are treated as different from capital letters. The computer program treats all capital letters as coming before all lower case letters in lexicographic order.

Statistical analysis

It was shown some 30 years ago that, for fluoroarenes with a single *para* substituent, the ^{19}F NMR signal was highly correlated [2] with the field $\mathscr{F}$ and resonance $\mathscr{R}$ parameters. For the 111 such resonances in Table 1, we found this to be correct. From these data we computed model A,

$$\Delta^F = 9.5\mathscr{F} + 22.0\mathscr{R} - 114.7 \qquad (r = 0.98,\ s = 1.7,\ n = 111)\ \text{[model A]}$$

This model will predict the signal with an average error of about 1.1 ppm, since the average error of prediction (residual) is about two-thirds of a standard deviation. This follows from the fact that 50% of the area under a normal curve is within 0.67 standard deviations of the mean, and thus two-thirds of a standard deviation is a good approximation to the average error of prediction. This error increases, however, to the 4–5 ppm range when the substituent is a bulky or easily polarizable group.

For the 95 signals from fluoroarenes having a single *meta* substituent the analogous model is:

$\Delta^{F} = 6.5\mathscr{F} - 113.8 \quad (r = 0.91, s = 0.7, n = 95)$ [model B]

The $\mathscr{R}$ term was removed from this model as it was not statistically significant. Although the correlation coefficient is less than that for *para* compounds, due to the narrow range of ^{19}F NMR values in the *meta* compounds, the prediction is actually more accurate in an absolute (though not relative) sense. The average error of prediction was about 0.5 ppm.

It has long been known that simple linear models using the field and resonance parameters produce poor results with fluoroarenes containing *ortho* substituents [3]. Using 64 resonances of compounds containing a single *ortho* substituent, we derived the following model, which had a lower correlation coefficient and higher standard deviation than either of the models for the *meta* or *para* compounds.

$\Delta^{F} = 35.5\mathscr{R} - 114.3 \quad (r = 0.72, s = 9.2, n = 64)$ [model C]

In this case, the $\mathscr{F}$ term has been removed from the model because it was not statistically significant. Model C had an average error of prediction of about 6 ppm with the most extreme cases being about 30 ppm.

From an inspection of the $\mathscr{F}$ and $\mathscr{R}$ values for various groups, for example, the halogens, it is seen that it is clearly impossible to predict the spectra of fluoroarenes containing iodo, bromo or chloro substituents in the *ortho* position using a model with only $\mathscr{F}$ and $\mathscr{R}$, because all three of these substituents have nearly the same $\mathscr{F}$ and $\mathscr{R}$ values but give significantly different NMR signals. This realization, together with the success we have had modeling fluoroarenetricarbonylchromium complexes [8] using $\mathscr{F}$ and $\mathscr{R}$ together with the Charton steric factor ν and molar refractivity *MR* prompted us to try a linear model containing all four of these parameters. Using this approach, we derived model D which gave a much higher correlation coefficient and smaller standard deviation than model C.

$$\Delta^{F} = -15.3\mathscr{F} + 34.9\mathscr{R} + 1.61MR - 118.6$$

$(r = 0.85, s = 7.0, n = 64)$ [model D]

It appears from our work and that of others that it is impossible to accurately model the *ortho* effect using linear models. The difficulty with nonlinear models is that there is an infinite variety of nonlinear terms that may be used in a model and these must be found empirically. At this stage we could not use interaction terms because of the small data set and had hoped to limit ourselves to quadratic terms. However, we found that cubic terms seemed to be necessary in modeling the nonlinearity of the *ortho* effect. This nonlinearity has been noted before by others [3]. The following cubic model has an improved correlation coefficient and standard deviation. The average residual for this model is about 1.7 ppm. Two terms, $\mathscr{R}^2$ and $\mathscr{R}^3$, were removed from the model as they were found not to be statistically significant. Though this model has good predictive power, it is in general true with nonlinear models that it becomes difficult or impossible to give any explanation of what the coefficients actually mean.

$$\begin{aligned}\Delta^{\mathrm{F}} = {} & -143.0\mathscr{F} + 16.32\mathscr{R} - 260.1\nu + 12.15MR + 704.4\mathscr{F}^2 + 500.6\nu^2 \\ & - 1.512MR^2 - 739.8\mathscr{F}^3 - 292.7\nu^3 + 0.06376MR^3 - 113.1 \\ & \qquad (r = 0.98,\ s = 2.5,\ n = 64)\ [\text{model E}]\end{aligned}$$

While it is doubtful that the parameters themselves are exactly linear measurements, the fact that linear models work so well for *meta* and *para* compounds indicates that they must be fairly close to linear. However, they appear to have a nonlinear effect when substituents are in the *ortho* position. While the coefficients themselves appear to be uninterpretable, it is to some extent possible to assess the effect of parameters on the NMR signal of a compound. Because ν and MR are highly correlated ($r = 0.77$) for the 64 *ortho* compounds, it is not really possible to separate their effects, and the combined effect is called here 'the steric/polarization effect'. Let us take compound No. 43, *o*-fluoroanisole, as an example:

Field effect:

$-143.9(0.26) + 704.4(0.26)^2 - 739.8(0.26)^3 \quad = \quad -2.6$

Resonance:

$16.32(-0.51) \quad = \quad -8.3$

Steric/polarization effect:

$-260.1(0.36) + 500.6(0.36)^2 - 292.7(0.36)^3 \quad = \quad -9.4$

$+12.15(7.87) - 1.512(7.87)^2 + 0.06376(7.87)^3$

Constant effect: $\quad = -113.1$

Δ^{F} (pred.) $= -133.4$

Δ^{F} (obs.) $= -135.3$

Error of prediction $=$ 1.9

Although this is purely a statistical interpretation, some 46% of the change in the constant effect to give the new value is provided by the steric/polarization effect. Similar calculations for the halogens illustrate the very significant nature of these steric/polarization effects.

Halogen	$\mathscr{F}$ effect	$\mathscr{R}$ effect	v/MR effect	Δ^F(obs.)	Δ^f(pred.)	Residual
F	9.96	−5.55	−29.54	−138.0	−138.2	−0.2
Cl	8.81	−2.45	−8.08	−115.3	−114.8	0.5
Br	10.46	−2.77	−4.69	−107.0	−110.1	−3.1
I	8.18	−3.10	10.94	−93.2	−97.0	−3.8

We can therefore infer that simple $\mathscr{F}$ and $\mathscr{R}$ models for the ^{19}F NMR signal positions of *polysubstituted* fluoroarenes would not be successful. Indeed for the simplest such model we tried, using the entire data set of 839 signals the correlation coefficient was almost 0.9, but the average residual was quite high at about 6.5 and a number of compounds had residuals as high as 30 ppm.

$$\Delta^F = -14.20\mathscr{F}_o + 41.55\mathscr{R}_o + 8.902\mathscr{F}_m + 4.660\mathscr{R}_m + 10.01\mathscr{F}_p$$

$$+25.28\mathscr{R}_p - 112.1 \qquad (r=0.89, s=9.7, n=839) \text{ [model F]}$$

In this model we defined $\mathscr{F}_i$ as the $\mathscr{F}$ value of the substituent in the *i*th position or the sum of the $\mathscr{F}$ values if there are two substituents in that position for $i=o$, m, p: $\mathscr{R}_i$ is defined similarly. This model makes the assumption that parameters are summable across *ortho* and *meta* positions. Figure 1 illustrates the plot of observed versus predicted values. Note that in the figures, B means two data points coinciding on the graph, C means three data points, etc.

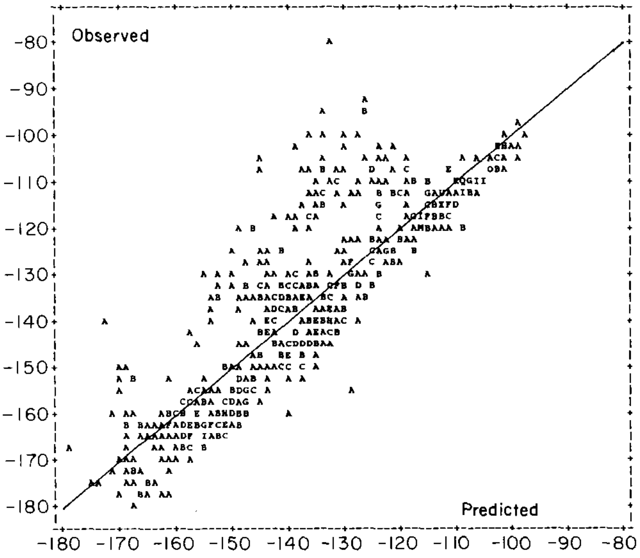

Fig. 1. Model F correlation.

From the work with *ortho* compounds, one would expect models using ν and MR in addition to $\mathcal{F}$ and $\mathcal{R}$ to be more successful. For the $\mathcal{F}$, $\mathcal{R}$, ν and MR linear model below, as expected, r is considerably higher than for model F. While the majority of compounds are predicted well, there are a number of compounds which still have quite large residuals. These compounds are, as one might expect, the ones with bulky groups in the *ortho* position(s). The average error of prediction for model G was about 4.5 ppm. This can be seen by inspection of the model G residuals given in Table 1.

$$\Delta^{F} = -23.57\mathcal{F}_{o} + 43.53\mathcal{R}_{o} + 7.187\nu_{o} + 1.269MR_{o} + 5.504\mathcal{F}_{m} + 5.109\mathcal{R}_{m} + 3.099\nu_{m} + 8.549\mathcal{F}_{p} + 28.08\mathcal{R}_{p} - 4.592\nu_{p} + 0.5843MR_{p} - 115.4$$

$$(r = 0.95,\ s = 6.6,\ n = 839)\ \text{[model G]}$$

In model G, ν_i and MR_i are defined similarly to $\mathcal{F}_i$ and $\mathcal{R}_i$, $i = o, m, p$. The term MR_m has been removed from this model because it was not statistically significant. This model is shown graphically in Fig. 2.

In the above model, $r^2 = 0.90$, which may be interpreted as implying that 90% of the variation in Δ^F is explained by the model and the other 10% is unexplained. The unexplained 10% may be due to a number of causes: nonlinearity, failure of *ortho* additivity, errors of measurement, solvent effects, restricted rotation of groups and other effects not accounted for by the four parameters $\mathcal{F}$, $\mathcal{R}$, ν and MR. The variation due to solvent effects has been studied and will be discussed presently.

Of the 10% unexplained variation, the part due to nonlinear effects can be modeled, though as already stated, the variety of nonlinear terms which may be added to the model is great. It should be noted that nonlinear effects

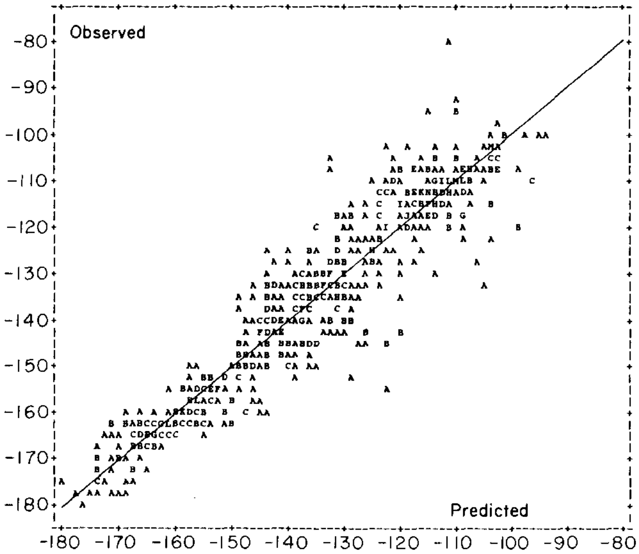

Fig. 2. Model G correlation.

show up in simple regression as a curvature in the pattern of points on the scatter diagram. But for multivariate regression, nonlinearity is not easy to detect graphically. Because the plot of Δ^{F}(obs.) versus Δ^{F}(pred.) is only a two-dimensional projection of a multidimensional graph, nonlinearity may show up only as additional scatter in the graph. The simplest nonlinear terms to be added to a regression model are the quadratic terms. Adding $\mathcal{F}_o^2$, $\mathcal{R}_o^2$, ν_o^2 and MR_o^2 to the above model, produces a model for which r is only marginally larger than for the linear model G above. The next model we tried contained cubic terms in order to try to model the *ortho* effect. Adding $\mathcal{F}_o^3$, $\mathcal{R}_o^3$, ν_o^3 and MR_o^3 to this model produced model H below. The average residual is about 3.8 ppm.

$$\begin{aligned}\Delta^{F} = {} & -15.41\mathcal{F}_o + 18.12\mathcal{R}_o - 56.32\nu_o + 1.906MR_o + 4.547\mathcal{F}_m + 5.803\mathcal{R}_m \\ & + 1.744\nu_m + 4.761\mathcal{F}_p + 28.74\mathcal{R}_p \\ & + 0.2914MR_p + 40.05\mathcal{F}_o^2 - 51.27\mathcal{R}_o^2 \\ & + 85.77\nu_o^2 - 0.02449MR_o^2 - 39.87\mathcal{F}_o^3 - 27.39\mathcal{R}_o^3 - 35.27\nu_o^3 \\ & - 113.3 \qquad (r=0.96,\ s=5.7,\ n=839)\ [\text{model H}]\end{aligned}$$

The variables MR_m, ν_p and MR_o^3 were removed because they were not statistically significant.

An alternative to the cubic model above is a quadratic model which includes cross product or interaction terms in order to again try to model the *ortho* effects. Statistically, model I has a slightly higher correlation coefficient, lower standard deviation but has two more variables than model H.

$$\begin{aligned}\Delta^{F} = {} & -17.88\mathcal{F}_o + 50.86\mathcal{R}_o + 1.115MR_o + 5.056\mathcal{F}_m + 4.950\mathcal{R}_m \\ & + 1.499\nu_m + 8.238\mathcal{F}_p + 27.30\mathcal{R}_p - 4.677\nu_p + 0.4216MR_p \\ & - 55.70\mathcal{F}_o^2 - 19.35\mathcal{F}_o\mathcal{R}_o + 142.8\mathcal{F}_o\nu_o - 6.330\mathcal{F}_oMR_o + 18.15\mathcal{R}_o\nu_o \\ & - 1.366\mathcal{R}_oMR_o - 95.82\nu_o^2 + 10.50\nu_oMR_o - 0.2736MR_o^2 - 113.2 \\ & \qquad (r=0.97,\ s=5.1,\ n=839)\ [\text{model I}]\end{aligned}$$

The variables ν_o, MR_m and $\mathcal{R}_o^2$ were removed because they were not statistically significant.

Our best modeling results were obtained when we began using models which did not assume *ortho* additivity. Even though the *meta* substituents have only small effects, for consistency we similarly abandoned the *meta* additivity assumption. However, to construct models which do not include these assumptions, it was necessary to define a direction around the ring so that position 2 can be distinguished from position 6. We decided that since $\mathcal{R}$ usually has the largest effect of all the parameters on signals from *ortho* substituents, it was reasonable to define a clockwise direction so that position 2 had the substituent with the highest $\mathcal{R}$ value compared with position 6. In case of a tie in the *ortho* positions, position 3 is defined as having the substituent with the highest $\mathscr{R}$ value as compared with position 5. In case of a tie in the *meta* positions also, the symmetry of the molecule makes it unnecessary to distinguish a clockwise direction. Thus all compounds in Table 1 are encoded in the clockwise direction according to this convention.

We now define $\mathscr{F}_i$ to be the $\mathscr{F}$ value of the substituent in position i for $i=2, 3, 4, 5, 6$; $\mathscr{R}_i$, ν_i and MR_i are similarly defined. This has the effect of breaking $\mathscr{F}_o$ up into two parts, $\mathscr{F}_2$ and $\mathscr{F}_6$. The other parameters are separated in a similar manner. Numerous models were tested and rejected either because the correlation coefficient was not much higher than that for models H and I, or in some cases, because the number of variables became too large to be practical. We report here two models; the first contains cubic terms in the *ortho* positions and the second uses quadratic and interaction terms in the *ortho* positions. The two models J and K are about equally effective in the prediction of the spectra. However, the cubic model has six fewer variables than the quadratic model. Both models predict the ^{19}F NMR line position with an average error of about 2 ppm.

$$\begin{aligned}\Delta^{F} = {} & -103.8\mathscr{F}_2+22.98\mathscr{F}_6+7.293\mathscr{R}_2+82.06\mathscr{R}_6 \\ & -168.7\nu_2+5.747MR_2+3.117\mathscr{F}_3 \\ & +8.489\mathscr{F}_5+5.354\mathscr{R}_3+1.900\mathscr{R}_5+2.529\nu_3 \\ & +0.09904MR_5+9.343\mathscr{F}_4+25.03\mathscr{R}_4 \\ & -4.651\nu_4+0.4591MR_4+570.9\mathscr{F}_2^{2}-110.8\mathscr{R}_2^{2} \\ & +44.80\mathscr{R}_6^{2}+256.0\nu_2^{2}-0.1835MR_2^{2} \\ & -623.3\mathscr{F}_2^{3}-168.0\mathscr{F}_6^{3}-123.4\mathscr{R}_2^{3}-26.78\mathscr{R}_6^{3}-115.8\nu_2^{3}+83.30\nu_6^{3} \\ & -0.001962MR_6^{3}-114.7 \qquad (r=0.99,\ s=2.9,\ n=839)\ [\text{model J}]\end{aligned}$$

The variables ν_6, MR_6, ν_5, MR_3, $\mathscr{F}_6^2$, ν_6^2, MR_6^2 and MR_2^3 were removed from the model where they were not statistically significant. Residuals for this model are listed in Table 1 and it is illustrated in Fig. 3.

The final model K is the best in the sense it has the smallest average residual though model J has fewer variables:

$$\begin{aligned}\Delta^{F} = {} & -40.22\mathscr{F}_2+280.4\mathscr{R}_2-73.70\mathscr{R}_6+100.5\nu_2 \\ & -76.03\nu_6-6.687MR_2+2.476\mathscr{F}_3 \\ & +8.409\mathscr{F}_5+4.360\mathscr{R}_3+1.706\mathscr{R}_5+2.890\nu_3 \\ & +0.08680MR_5+9.354\mathscr{F}_4+24.95\mathscr{R}_4 \\ & -5.308\nu_4+0.4967MR_4-112.6\mathscr{F}_2\mathscr{R}_2+47.41\mathscr{F}_2\nu_2 \\ & +1.922\mathscr{F}_2MR_2-13.61\mathscr{F}_2\nu_6+165.0\mathscr{R}_2^{2} \\ & -383.0\mathscr{R}_2\nu_2-3.646\mathscr{R}_2MR_2-32.40\mathscr{R}_2\mathscr{R}_6-38.18\nu_2^{2} \\ & -5.021\nu_2MR_2+0.4288MR_2^{2}-182.8\mathscr{F}_6^{2} \\ & +214.3\mathscr{F}_6\nu_6-6.572\mathscr{F}_6MR_6+351.2\mathscr{R}_6\nu_6-4.947\mathscr{R}_6MR_6+191.5\nu_6^{2} \\ & -1.207\nu_6MR_6-114.6 \qquad (r=0.99,\ s=2.8,\ \mathrm{n}=839)\ [\text{model K}]\end{aligned}$$

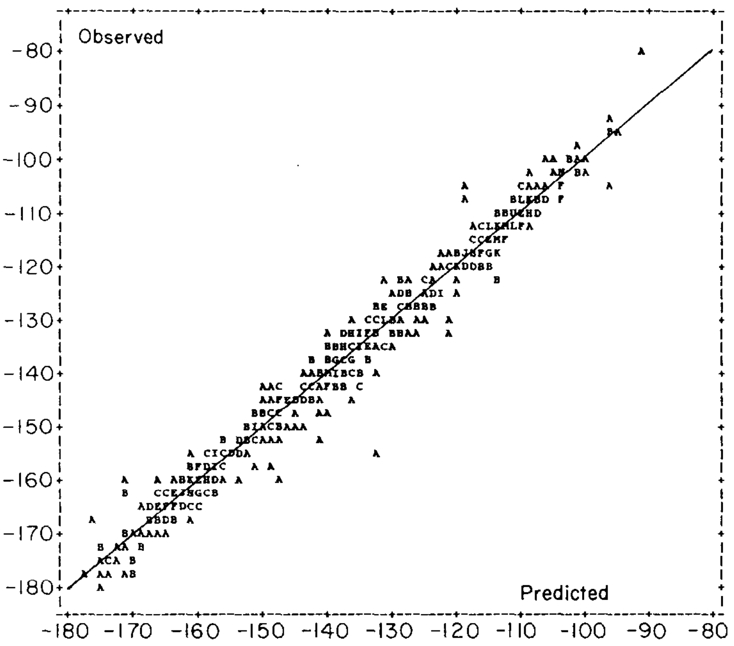

Fig. 3. Model J correlation.

The variables $\mathcal{F}_6$, MR_6, ν_5, MR_3, $\mathcal{F}_2{}^2$, $\mathcal{F}_2\mathcal{F}_6$, $\mathcal{F}_2\mathcal{R}_6$, $\mathcal{F}_2MR_6$, $\mathcal{R}_2\mathcal{F}_6$, $\mathcal{R}_2\nu_6$, $\mathcal{R}_2MR_6$, $\nu_2\mathcal{F}_6$, $\nu_2\mathcal{R}_6$, $\nu_2\nu_6$, ν_2MR_6, $MR_2\mathcal{F}_6$, $MR_2\mathcal{R}_6$, $MR_2\nu_6$, MR_2MR_6, $\mathcal{F}_6\mathcal{R}_6$, $\mathcal{R}_6{}^2$ and $MR_6{}^2$ were deleted from the model because they were not statistically significant. The residuals for model K are listed in Table 1 and it is illustrated in Fig. 4. While this model is a little large for hand calculators, a very simple computer program using this equation facilitates its use. It is helpful to write the program so that it can read the parameter values from the parameter table (Table 2) using the sort code for that compound. It is necessary that a compound be oriented clockwise before using models J or K to compute the predicted NMR signal.

Of the eight fluorine signals that have a model J residual greater than 10 ppm in Table 1, No. 39, although a compound containing *ortho*-iodo substitution, it is nevertheless predicted very well in other solvents but *not* in DMSO-d_6. This presumably means that there is a solvent interaction between this solvent and arenes containing the iodo group. The signals for the diiodo compounds Nos. 736 and 737, as noted before, are very difficult to predict and we concur with the previous findings [21, 89]. The signals from Nos. 362, 619, 827, 832 and 839 probably have high residuals due to restricted rotation which is known to greatly influence NMR spectra [94].

The situation for model K is little different except that there are now six residuals greater than 10 ppm, signal Nos. 736 and 832 no longer being on the list.

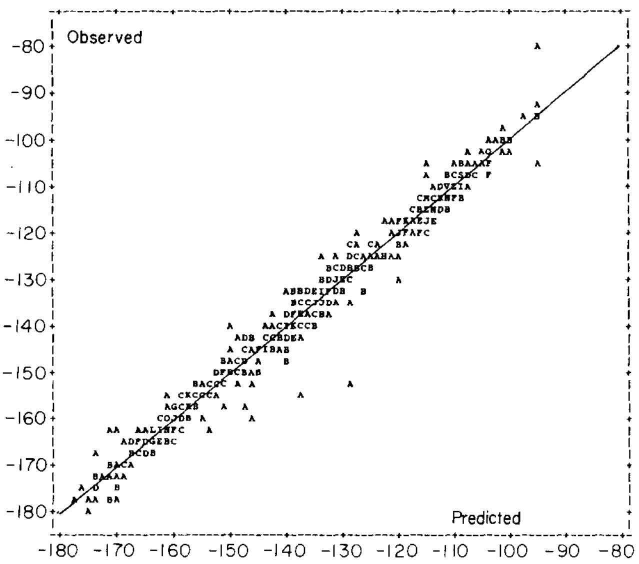

Fig. 4. Model K correlation.

TABLE 3

Comparison of models A–K with and without solvent effect variables giving correlation coefficient r and standard deviation s

Model	Sample size	Without solvent effect variables		With solvent effect variables	
		r	s	r	s
A	111	0.977	1.70	0.978	1.70
B	95	0.906	0.68	0.912	0.66
C	64	0.716	9.24	0.716	9.24
D	64	0.853	7.01	0.853	7.01
E	64	0.984	2.53	[a]	[a]
F	839	0.889	9.82	0.895	9.48
G	839	0.951	6.58	0.955	6.33
H	839	0.964	5.71	0.965	5.58
I	839	0.971	5.11	0.972	5.07
J	839	0.991	2.94	0.991	2.94
K	839	0.992	2.77	0.992	2.69

[a] Not determined due to small sample size.

Solvent effects

The previous discussion described the various mathematical models which were tried. However, none of the above equations took into account solvent effects.

In our data set we were particularly careful to select data where the solvent was clearly given. We did not use data where no solvent was given or mixed solvents were used in the determination of the spectrum.

TABLE 4

Solvent code and dielectric constant (ϵ)[a] for solvents

Solvent code	Solvent	Dielectric constant
A	neat	–
B	$CFCl_3$	2.3
C	CH_2Cl_2	9.1
D	$CHCl_3$	4.8
E	$CDCl_3$	4.8
F	CCl_4	2.2
G	Me_2CO	20.7
H	$(CD_3)_2CO$	20.7
I	DMSO	46.6
J	DMSO-d_6	46.6
K	C_6H_6	2.3
L	C_6D_6	2.3
M	C_2H_5OH	24.3
N	Et_2O	4.3
O	DMF	36.7
P	$MeNO_2$	35.9
Q	THF	7.6
R	THF-d_8	7.6
S	n-hexane	1.9
T	nitrobenzene	34.8
U	*p*-dioxan	2.2

[a] Dielectric constants taken from *The Handbook of Chemistry and Physics*, 66th edn., The Chemical Rubber Company, Cleveland, OH, 1985/86.

Table 3 illustrates the use of solvent effect variables on the various models. It did not seem likely that solvent effects could be modeled using a single variable because the solvent interacts separately with each of the groups on the ring. Interaction of variables u and v is usually modeled using a product of powers of the variables $u^k v^l$. Because this was clearly going to introduce a large number of variables into our model, we chose to use only the first-order interactions. Thus to model solvent effects we used variables ϵ, $\mathcal{F}_i\epsilon$, $\mathcal{R}_i\epsilon$, $\nu_i\epsilon$, $MR_i\epsilon$, $i=2, 3, 4, 5, 6$, where ϵ is the dielectric constant of the solvent (see Table 4). In models F to K, this results in the introduction of 21 new variables. It will be noted in Table 3 that the correlation coefficient does increase slightly when the solvent effect variables were used, but the average error of prediction was decreased only slightly. Solvent effects are probably of the same magnitude as systematic errors such as spectra being run on different instruments, different concentrations, temperatures, etc. That solvent effects are small has been noted by other workers [4, 21, 89].

It will be noted from Table 3, which gives a comparison of models without solvent effect variables and models with solvent effect variables, that

TABLE 5

Sort codes, observed and model K predicted values for some previously uninterpreted literature and new spectra (new compounds are nos. 10, 11 and 12)

No.	Sort code	Substituents and positions on the aromatic ring						^{19}F NMR signal position		Ref.
		1	2	3	4	5	6	Obs.	Pred.	
1	FFBFFk	F	F	Br	F	F	OEt	−156.0	−158.1	28
	FBFFkF	F	Br	F	F	OEt	F	−135.5	−133.7	
2	FFQFFk	F	F	COMe	F	F	OEt	−156.2	−157.2	28
	FQFFkF	F	COMe	F	F	OEt	F	−141.8	−138.4	
3	FCCMFC	F	Cl	Cl	Me	F	Cl	−111.9	−112.2	43
	FMCCFC	F	Me	Cl	Cl	F	Cl	−114.0	−112.1	
4	FFdFFH	F	F	CH_2OH	F	F	OH	−164.0	−164.1	91
	FdFFHF	F	CH_2OH	F	F	OH	F	−148.6	−144.6	
5	FQAFFF	F	COMe	H	F	F	F	−136.9	−137.9	92
	FFQAFF	F	F	COMe	H	F	F	−155.5	−155.0	
	FFAQFF	F	F	H	COMe	F	F	−148.8	−147.2	
	FAQFFF	F	H	COMe	F	F	F	−138.3	−137.9	
6	FAAFAB	F	H	H	F	H	Br	−114.1	−114.1	93
	FAAFBA	F	H	H	F	Br	H	−117.6	−115.9	
7	FAAFAC	F	H	H	F	H	Cl	−122.1	−120.0	93
	FAAFCA	F	H	H	F	Cl	H	−117.5	−116.3	
8	FAAFAD	F	H	H	F	H	NH_2	−141.7	−140.0	93
	FAAFDA	F	H	H	F	NH_2	H	−119.0	−120.6	
9	FGAFAA	F	CN	H	F	H	H	−112.8	−113.6	93
	FAGFAA	F	H	CN	F	H	H	−116.2	−116.8	
10	FAFAAD	F	H	F	H	H	NH_2	−131.4	−134.2	[a]
	FAADFA	F	H	H	NH_2	F	H	−124.7	−127.5	
11	FFAAAD	F	F	H	H	H	NH_2	−161.7	−161.4	[a]
	FAAADF	F	H	H	H	NH_2	F	−140.1	−139.2	
12	FAAFAD	F	H	H	F	H	NH_2	−142.2	−140.0	[a]
	FAAFDA	F	H	H	F	NH_2	H	−119.4	−118.0	
13	FQAFAA	F	COMe	H	F	H	H	−118.0	−118.0	93
	FAQFAA	F	H	COMe	F	H	H	−115.4	−116.9	
14	FAdFFF	F	H	CH_2OH	F	F	F	−139.8	−139.4	92
	FFAdFF	F	F	H	CH_2OH	F	F	−157.9	−157.3[b]	
	FFdAFF	F	F	CH_2OH	H	F	F	−157.0	−156.6[b]	
	FdAFFF	F	CH_2OH	H	F	F	F	−146.3	−143.5	
15	FdFFHF	F	CH_2OH	F	F	OH	F	−148.6	−144.7	91
	FFdFFH	F	F	CH_2OH	F	F	OH	−164.0	−164.1	

[a] This work.
[b] May be interchanged.

the slight increase in correlation coefficient hardly warrants the use of a large number of extra variables in view of the small advantage gained in a very slightly more precise predicted value.

Interpretation of new and existing spectra

As a test of the predictive capabilities of model K, we have used this model to interpret a number of spectra which were reported but not interpreted

TABLE 6

Variables, coefficients, standard error of estimates of coefficients, F statistic and p values for model K

Variable	Coefficient	Standard error	F	p
$\mathcal{F}_2$	−40.22	3.21	157.32	<0.0001
$\mathcal{R}_2$	280.4	10.9	666.59	<0.0001
$\mathcal{R}_6$	−73.70	12.0	37.85	<0.0001
ν_2	100.5	8.80	130.20	<0.0001
ν_6	−76.03	6.41	140.82	<0.0001
MR_2	−6.687	0.662	102.15	<0.0001
$\mathcal{F}_3$	2.476	0.633	15.29	<0.0001
$\mathcal{F}_5$	8.409	0.583	207.88	<0.0001
$\mathcal{R}_3$	4.360	0.608	51.38	<0.0001
$\mathcal{R}_5$	1.706	0.537	10.11	0.0015
ν_3	2.890	0.570	25.74	<0.0001
MR_5	0.08680	0.0238	9.35	0.0023
$\mathcal{F}_4$	9.354	0.641	213.12	<0.0001
$\mathcal{R}_4$	24.95	0.47	2835.32	<0.0001
ν_4	−5.308	0.877	36.60	<0.0001
MR_4	0.4967	0.0496	100.20	<0.0001
$\mathcal{F}_2\mathcal{R}_2$	−112.6	10.9	106.25	<0.0001
$\mathcal{F}_2\nu_2$	47.41	13.8	11.77	0.0006
$\mathcal{F}_2MR_2$	1.922	0.932	4.26	0.0394
$\mathcal{F}_2\nu_6$	−13.61	3.21	17.93	<0.0001
$\mathcal{R}_2^2$	165.0	9.20	322.09	<0.0001
$\mathcal{R}_2\nu_2$	−383.0	24.9	237.30	<0.0001
$\mathcal{R}_2MR_2$	−3.646	0.706	26.69	<0.0001
$\mathcal{R}_2\mathcal{R}_6$	−32.40	6.46	25.13	<0.0001
ν_2^2	−38.18	7.95	23.05	<0.0001
ν_2MR_2	−5.021	1.125	19.91	<0.0001
MR_2^2	0.4288	0.0508	71.12	<0.0001
$\mathcal{F}_6^2$	−182.8	14.5	160.03	<0.0001
$\mathcal{F}_6\nu_6$	214.3	21.3	100.88	<0.0001
$\mathcal{F}_6MR_6$	−6.572	0.813	65.36	<0.0001
$\mathcal{R}_6\nu_6$	351.2	41.1	72.90	<0.0001
$\mathcal{R}_6MR_6$	−4.947	0.412	144.49	<0.0001
ν_6^2	191.5	15.2	158.31	<0.0001
ν_6MR_6	−1.207	0.452	7.12	0.0078
intercept	−114.6	0.300	187836	<0.0001

in the literature. We also report and interpret the spectra of several isomers of difluoroaniline.

It may be seen from Table 5 that model K can interpret most of these spectra with ease. The exceptions are obviously where the signals are very similar and interpretation is not therefore possible.

Experimental

The new data for the isomeric difluoroaniline were determined by Spectral Data Services, Champaign, IL using a Nicolet NT360 spectrometer operating at 338.7 MHz with Freon-11 as the external standard and chloroform-*d* as the solvent.

Statistical computations were done using programs written in FORTRAN and SAS (Statistical Analysis System) running on a Microvax model 3900. The words 'statistically significant' are used in this paper to mean 'statistically significant at the 5% level of significance'. All variables remaining in the models are significant at at least the 5% level, but most are very highly significant at about the 0.0001 level. This can be seen for example in Table 6 for model K, which shows in addition to the significance level for the variables the standard error for the estimated regression coefficients.

Coefficients in the models estimated from the data are accurate in most cases to about two significant digits. However, because of the large amount of computations involved in the larger models (F to K), it is necessary to use four digits to avoid excessive roundoff error.

Conclusions

1. It is now possible to predict the ^{19}F NMR spectra for free arenes using mathematical modeling techniques. Model K seems to give the most accurate prediction. Even signals from compounds containing *ortho* substituents, although requiring more terms in the modeling equations, can now be predicted with a high degree of accuracy.
2. Interpretation of the ^{19}F NMR signals from polyfluoroarenes can now be done quickly and reliably in the vast majority of cases.
3. It is possible to solvent-correct the majority of the above models but this does not greatly enhance the models' predictive abilities.
4. Solvent effects appear to be in the range 0.5–2 ppm, except for some compounds containing iodine. The variation in different solvents does not severely impair the predictive ability of model K even if solvent effect variables are not used.

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