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A SOPPA theoretical study of the spin–spin coupling constants of all fluorobenzenes $C_6H_nF_{6-n}$ ($n = 0–5$)

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ABSTRACT

The 295 experimental spin–spin coupling constants (SSCC) determined for fluorobenzenes were compared with the calculated ones using the second-order polarization propagator approximation (SOPPA). The agreement is, on the whole, good and the discrepancies were analyzed comparing couplings of the same class of coupling families.

1. Introduction

To test the performance of SOPPA calculations of SSCC [1] we have selected the whole family of fluorobenzenes (Fig. 1) because: (i) many coupling constants have been determined for these compounds; (ii) these compounds present several kinds of coupling constants: J_{HH}, J_{CH}, J_{FH}, J_{CC}, J_{CF} and J_{FF}, and (iii) SSCC involving ^{19}F atoms are amongst the most difficult to calculate theoretically [2].

2. Results and discussion

All the coupling constants (295 values) we have found are reported in Table 1. When several values were available, we selected those that offer the best guarantee of accuracy. Note, however, that all reported values are very similar. For instance, we have re-determined the SSCC of 1,3- and 1,4-difluorobenzenes obtaining almost identical values as those reported previously [3]. Several other sources have been used to build up Table 1 [4–9].

Table 1 reports six kinds of SSCC depending on the number of possible number of possible coupling constants: $^1H–^1H$, $^1H–^{19}F$ and $^{19}F–^{19}F$ have three *J*s (^3J, ^4J, ^5J); $^1H–^{13}C$ and $^{13}C–^{19}F$ have four *J*s (^1J, ^2J, ^3J, ^4J), and finally $^{13}C–^{13}C$ has three again (^1J, ^2J, ^3J). We will discuss them all together (the 296 values) and by families. Since for ^3J(C5F1) and ^4J(C4F1) of compound **2** only an average value (5.19 Hz, see below) can be determined, the actual number of coupling constants is 294 or 295 including the average value.

The linear regression corresponding to Fig. 2 is:

$$\text{Exp. (Hz)} = (2.02 \pm 0.22) + (0.918 \pm 0.003) * \text{SOPPA (Hz)}, \quad n = 294, \quad R^2 = 0.9976 \tag{1}$$

Clearly, some families of coupling constants deviate (framed in Fig. 2). We then tried a model with dummy variables (either 1 or 0) [3] for these couplings and obtained:

$$\begin{aligned}\text{Exp. (Hz)} = {} & (1.59 \pm 0.13) + (0.863 \pm 0.007) * \text{SOPPA (Hz)} \\ & + (19.64 \pm 1.21) * [^1J_{CH}] - (9.53 \pm 1.88) * [^1J_{CF}] \\ & - (6.56 \pm 0.67) * [^3J_{FF}] + (1.24 \pm 0.78) * [^1J_{CC}], \\ & n = 294, \quad R^2 = 0.9993\end{aligned} \tag{2}$$

The coefficients of Eq. (2) mean that SOPPA underestimates $^1J_{CH}$ and $^1J_{CC}$ and overestimates $^1J_{CF}$ and $^3J_{FF}$. Only taking into account the 0.863 slope it is possible to understand why ^1J(C3H3) of **2** is 163.75 (exp.) and 165.27 Hz (SOPPA), that are very close, become different when the SOPPA value is multiplied by 0.863 (142.47 Hz, difference 21.28 Hz, close to 19.64 Hz, the coefficient of [$^1J_{CH}$] in Eq. (2).

Eq. (2) predicts for ^3J(C5F1) and ^4J(C4F1) of **2**, 4.17 and 6.87 Hz. The mean of these two values (5.52 Hz) is close to the average experimental values of 5.19 Hz (the analysis of the spin

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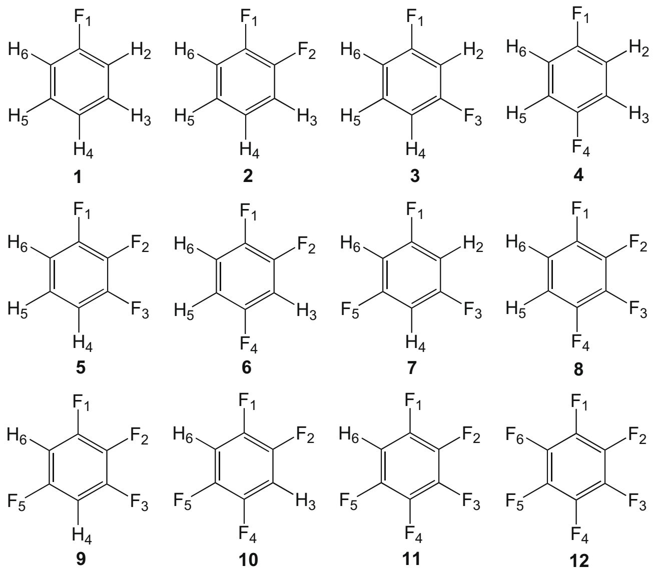

Fig. 1. The 12 fluorobenzenes.

Table 1
Experimental and calculated SSCC in fluorobenzenes (J values in Hz and K values in N A^{-2} m^{-3} × 10^{18}). The coupling constants will be reported in the following order: HH, HC, HF, CC, CF, FF.

	Molecule	Coupling	J		K	
			Experimental	Calculated	Experimental	Calculated
1	FC_6H_5 (**1**)	^3J(H2H3) *ortho*	8.34 [4]	8.16	6.94	6.79
2		^3J(H3H4) *ortho*	7.45 [4]	7.44	6.20	6.19
3		^4J(H2H6) *meta*	2.73 [4]	1.64	2.27	1.37
4		^4J(H2H4) *meta*	1.07 [4]	0.21	0.89	0.17
5		^4J(H3H5) *meta*	1.80 [4]	0.76	1.50	0.63
6		^5J(H2H5) *para*	0.42 [4]	0.74	0.35	0.62
7		^1J(C2H2)	162.55 [5]	164.71	538.05	545.20
8		^1J(C3H3)	161.14 [5]	161.85	533.39	535.74
9		^1J(C4H4)	161.37 [5]	162.58	534.15	538.15
10		^2J(C1H2)	−4.89 [5]	−6.94	−16.19	−22.97
11		^2J(C2H3)	1.10 [5]	−0.59	3.64	−1.95
12		^2J(C3H2)	−0.57 [5]	−1.86	−1.89	−6.16
13		^2J(C3H4)	1.74 [5]	0.04	5.76	0.13
14		^2J(C4H3)	0.82 [5]	−0.77	2.71	−2.55
15		^3J(C1H3)	10.95 [5]	11.17	36.25	36.97
16		^3J(C2H4)	8.29 [5]	8.60	27.44	28.47
17		^3J(C2H6)	4.11 [5]	4.66	13.60	15.42
18		^3J(C3H5)	9.02 [5]	9.33	29.86	30.88
19		^3J(C4H2)	7.57 [5]	8.11	25.06	26.84
20		^4J(C1H4)	−1.73 [5]	−2.63	−5.73	−8.71
21		^4J(C2H5)	−1.50 [5]	−2.24	−4.97	−7.41
22		^4J(C3H6)	−0.76 [5]	−1.57	−2.52	−5.20
23		^3J(F1H2) *ortho*	8.82 [4]	5.42	7.80	4.79
24		^4J(F1H3) *meta*	5.61 [4]	4.96	4.96	4.39
25		^5J(F1H4) *para*	0.23 [4]	−1.65	0.20	−1.46
26		^1J(C1C2)	70.8 [6]	78.28	931.81	1030.25
27		^1J(C2C3)	56.6 [6]	64.02	744.92	842.58
28		^1J(C3C4)	56.2 [6]	63.61	739.66	837.18
29		^2J(C2C4)	−2.9 [6]	−4.77	−38.17	−62.78
30		^3J(C1C4)	10.5 [6]	12.12	138.19	159.51
31		^3J(C2C5)	6.7 [6]	8.13	88.18	107.00
32		^1J(C1F1)	−244.70 [5]	−271.23	−860.50	−953.79
33		^2J(C2F1)	20.98 [5]	23.00	73.78	80.88
34		^3J(C3F1)	7.81 [5]	5.24	27.46	18.43
35		^4J(C4F1)	3.18 [5]	5.10	11.18	17.93
36	1,2-diFC_6H_4 (**2**)	^3J(H3H4) *ortho*	8.30 [8]	8.16	6.91	6.79
37		^3J(H4H5) *ortho*	7.61 [8]	7.59	6.34	6.32
38		^4J(H3H5) *meta*	1.61 [8]	0.64	1.34	0.53
39		^5J(H3H6) *para*	0.26 [8]	0.64	0.22	0.53
40		^1J(C3H3)	163.75 [8]	165.27	542.03	547.06
41		^1J(C4H4)	163.89 [8]	164.59	542.49	544.81
42		^2J(C1H6)	−5.50 [8]	−7.63	−18.21	−25.26
43		^2J(C3H4)	1.52 [8]	−0.23	5.03	−0.76
44		^2J(C4H3)	−1.05 [8]	−2.33	−3.48	−7.71
45		^2J(C4H5)	0.98 [8]	−0.69	3.24	−2.28
46		^3J(C1H3)	7.53 [8]	7.87	24.92	26.05
47		^3J(C1H5)	11.55 [8]	11.77	38.23	38.96
48		^3J(C3H5)	9.28 [8]	9.56	30.72	31.64
49		^3J(C4H6)	9.25 [8]	9.65	30.62	31.94
50		^4J(C1H4)	−1.87 [8]	−2.79	−6.19	−9.24
51		^4J(C3H6)	−1.32 [8]	−2.11	−4.37	−6.98
52		^3J(F1H6) *ortho*	10.85 [8]	6.06	9.60	5.36
53		^4J(F1H3) *meta*	8.06 [8]	6.82	7.13	6.03
54		^4J(F1H5) *meta*	4.53 [8]	3.99	4.01	3.53
55		^5J(F1H4) *para*	−1.40 [8]	−2.99	−4.37	−2.64
56		^1J(C1C2)	82.3 [7]	90.36	1083.16	1189.24
57		^1J(C2C3)	72.3 [7]	79.72	951.55	1049.21
58		^1J(C3C4)	57.2 [7]	64.67	752.82	851.13
59		^2J(C1C3)	6.8 [9]	5.25	89.50	69.10
60		^3J(C1C4)	7.7 [9]	9.36	101.34	123.19
61		^1J(C1F1)	−246.64 [8]	−275.34	−867.32	−968.25
62		^2J(C2F1)	12.50 [8]	15.32	43.96	53.87
63		^2J(C6F1)	17.02 [8]	19.42	59.85	68.29
64		^3J(C3F1)	0.53 [8]	−1.62	1.86	−5.70
65		^3J(C5F1)[a]	5.19[a] [8]	2.99	18.25	10.51
66		^4J(C4F1)[a]	5.19[a] [8]	6.12	18.25	21.52
67		^3J(F1F2) *ortho*	−20.82 [8]	−17.40	−19.56	−16.35
68	1,3-diFC_6H_4 (**3**)	^3J(H4H5) *ortho*	8.43 [3]	8.27	7.02	6.88
69		^4J(H2H4) *meta*	2.44 [3]	1.45	2.03	1.21
70		^4J(H4H6) *meta*	0.87 [3]	0.10	0.72	0.08
71		^5J(H2H5) *para*	0.32 [3]	0.66	0.27	0.55
72		^1J(C2H2)	165.45 [3]	168.73	547.65	558.51
73		^1J(C4H4)	165.28 [3]	167.62	547.09	554.84
74		^1J(C5H5)	163.71 [3]	163.91	541.89	542.56
75		^2J(C1H2)	−6.09 [3]	−7.90	−20.16	−26.15
76		^2J(C1H6)	−4.62 [3]	−6.67	−15.29	−22.08
77		^2J(C4H5)	0.80 [3]	−0.75	2.65	−2.48
78		^2J(C5H4)	−0.20 [3]	−1.59	−0.66	−5.26
79		^3J(C1H5)	13.02 [3]	13.03	43.10	43.13
80		^3J(C2H4)	4.59 [3]	5.06	15.19	16.75
81		^3J(C4H2)	3.75 [3]	4.66	12.41	15.42
82		^3J(C4H6)	7.40 [3]	8.39	24.49	27.77
83		^4J(C1H4)	−1.29 [3]	−2.18	−4.27	−7.22
84		^4J(C2H5)	−1.45 [3]	−2.24	−4.80	−7.41
85		^4J(C5H2)	0.30 [3]	−0.86	0.99	−2.85
86		^3J(F1H2) *ortho*	9.34 [3]	5.59	8.26	4.94
87		^3J(F1H6) *ortho*	8.39 [3]	5.59	7.42	4.94
88		^4J(F1H5) *meta*	6.69 [3]	5.76	5.92	5.09
89		^5J(F1H4) *para*	−0.83 [3]	−2.41	−0.73	−2.13
90		^1J(C1C2)	73.1 [9]	79.98	962.08	1052.63
91		^1J(C3C4)	71.7 [9]	78.54	943.65	1033.67
92		^1J(C4C5)	57.7 [9]	64.98	759.40	855.21