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Research Article

Difluorobenzenes revisited: an experimental and theoretical study of spin–spin coupling constants for 1,2-, 1,3-, and 1,4-difluorobenzene

Ibon Alkorta,[a]* Fernando Blanco,[a] Janet E. Del Bene,[b] José Elguero,[a] Laura Hernández-Folgado[a] and María-Luisa Jimeno[c]

The experimental spin–spin coupling constants (SSCCs) for 1,3- and 1,4-difluorobenzene have been determined anew, and found to be consistent with previously determined values. SSCCs for 1,2-, 1,3-, and 1,4-difluorobenzene have been analyzed by comparing them with the coupling constants computed using the second-order polarization propagator approximation (SOPPA) and the equation-of-motion coupled cluster singles and doubles method (EOM-CCSD). Eighty experimental values have been analyzed using SOPPA calculations, and a subset of 40 values using both SOPPA and EOM-CCSD approaches. One-bond coupling constants $^1J(C–C)$ and $^1J(C–F)$ are better described by EOM-CCSD, whereas one-bond $^1J(C–H)$ values are better described by SOPPA. An empirical equation is presented which allows for the prediction of unknown coupling constants from computed SOPPA values. A similar approach may prove useful for predicting coupling constants in larger systems. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: ^1H; ^{13}C; ^{19}F; SOPPA; EOM-CCSD; SSCCs; difluorobenzenes

Introduction

The three difluorobenzenes, *ortho* **1**, *meta* **2**, and *para* **3**, constitute a homogeneous family of compounds for which many spin–spin coupling constants (SSCCs) have been accurately determined by various investigators.[1–8] The experimental values show remarkable consistency, as evident from Table 1. The most nearly complete set of values are those of Wray *et al.*,[1] who recorded their spectra in a 100-MHz instrument using (75%, v/v) solutions in acetone-d_6 (20%, v/v) containing internal TMS (TMS, 5%, v/v). These solutions were degassed by four freeze–pump–thaw cycles and sealed under vacuum in 5- and 10-mm sample tubes. Other authors used acetonitrile-d_3,[2] cyclohexane-d_{12},[2] or a mixture of C_6F_6 and C_6D_{12}.[5] It has been noted that coupling constants for *ortho*-difluorobenzene (**1**) are sensitive to solvent[5] and temperature effects.[2] Since **1** is the most widely studied of the difluorobenzenes, we have not recorded its spectrum, but have obtained the spectra of **2** and **3** in CDCl$_3$ to re-determine the coupling constants of these two isomers. We have also carried out a theoretical study of these isomers by computing coupling constants using the second-order polarization propagator approximation (SOPPA) and the equation-of-motion coupled cluster singles and doubles method (EOM-CCSD).

1   **2**   **3**
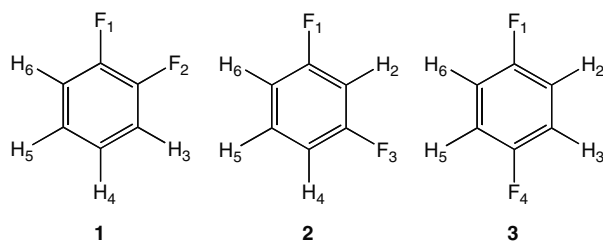
Methods

Experimental

^1H,^1H-decoupled and ^1H-coupled ^{13}C NMR spectra were recorded at room temperature on a Varian System 500 NMR spectrometer, equipped with a 5-mm HCN cold probe, operating at 499.81 MHz (^1H) and 125.69 MHz (^{13}C). ^{19}F and ^{19}F-decoupled ^{13}C NMR spectra were recorded on a Varian Inova 400 NMR spectrometer, equipped with a 5-mm QNP probe, operating at 376.16 MHz (^{19}F) and 100.54 MHz (^{13}C). Samples were dissolved in CDCl$_3$ (70 mg/0.7 ml). All NMR experiments were performed using standard Varian pulse sequences, with digital resolutions of 0.1–0.3 Hz. Most of the spectra exhibited second-order effects, and therefore spectral simulations using the program gNMR5.0[9] were required in order to obtain all of the coupling constants.

Computational

The geometries of the three isomers were optimized at second-order Møller–Plesset perturbation theory (MP2)[10–13] with the

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Table 1. Experimental and calculated SSCCs for difluorobenzenes (Hz)[a,b]

Coupling	Experimental 1	Experimental 2	Experimental 3	This work 4	Calcd. SOPPA	Calcd. EOM-CCSD
1,2-diFC$_6$H$_4$ (**1**)						
^3J(H3H4) ortho	8.30 [1]	8.27 [2]	8.32 [6]	–	8.16	–
^3J(H4H5) ortho	7.61 [1]	7.58 [2]	7.62 [6]	–	7.59	–
^4J(H3H5) meta	1.61 [1]	1.62 [2]	1.62 [6]	–	0.64	–
^5J(H3H6) para	0.26 [1]	0.26 [2]	0.26 [6]	–	0.64	–
^1J(C3H3)	163.75 [1]	–	–	–	165.27	–
^1J(C4H4)	163.89 [1]	–	–	–	164.59	–
^2J(C1H6)	−5.50 [1]	–	–	–	−7.63	–
^2J(C3H4)	1.52 [1]	–	–	–	−0.23	–
^2J(C4H3)	−1.05 [1]	–	–	–	−2.33	–
^2J(C4H5)	0.98 [1]	–	–	–	−0.69	–
^3J(C1H3)	7.53 [1]	–	–	–	7.87	–
^3J(C1H5)	11.55 [1]	–	–	–	11.77	–
^3J(C3H5)	9.28 [1]	–	–	–	9.56	–
^3J(C4H6)	9.25 [1]	–	–	–	9.65	–
^4J(C1H4)	−1.87 [1]	–	–	–	−2.79	–
^4J(C3H6)	−1.32 [1]	–	–	–	−2.11	–
^3J(F1H6) ortho	10.85 [1]	10.32 [2]	11.07 [6]	–	6.06	–
^4J(F1H3) meta	8.06 [1]	7.84 [2]	8.26 [6]	–	6.82	–
^4J(F1H5) meta	4.53 [1]	4.36 [2]	4.62 [6]	–	3.99	–
^5J(F1H4) para	−1.40 [1]	−1.43 [2]	−1.39 [6]	–	−2.99	–
^1J(C1C2)	82.3 [3]	82.8 [7]	–	–	90.36	86.34
^1J(C2C3)	72.3 [3]	72.3 [7]	–	–	79.72	76.22
^1J(C3C4)	57.2 [3]	57.2 [7]	–	–	64.67	61.50
^2J(C1C3)	6.6 [7]		–	–	5.25	6.61
^3J(C1C4)	7.7 [7]		–	–	9.36	7.82
^1J(C1F1)	−246.64 [1]	−248.8 [4]	–	–	−275.34	−253.45
^2J(C1F2)	12.50 [1]	14.1 [4]	–	–	15.32	13.33
^2J(C6F1)	17.02 [1]	20.5 [4]	–	–	19.42	18.36
^3J(C3F1)	0.53 [1]	−3.0 [4]	–	–	−1.62	−0.03
^3J(C5F1)[c]	5.19 av [1]	5.2 av [4]	–	–	2.99	5.02
^4J(C4F1)[c]	5.19 av [1]	5.2 av [4]	–	–	6.12	4.11
^3J(F1F2) ortho	−20.82 [1]	−20.79 [2]	−20.24 [6]	–	−17.40	−17.86
1,3-diFC$_6$H$_4$ (**2**)						
^3J(H4H5) ortho	8.43 [1]	8.41 [5]	–	8.38	8.27	–
^4J(H2H4) meta	2.44 [1]	2.43 [5]	–	2.42	1.45	–
^4J(H4H6) meta	0.87 [1]	0.89 [5]	–	0.82	0.10	–
^5J(H2H5) para	0.32 [1]	–	–	0.32	0.66	–
^1J(C2H2)	165.64 [1]	–	–	165.45	168.73	–
^1J(C4H4)	165.46 [1]	–	–	165.28	167.62	–
^1J(C5H5)	164.03 [1]	–	–	163.71	163.91	–
^2J(C1H2)	−6.02 [1]	–	–	−6.09	−7.90	–
^2J(C1H6)	−4.57 [1]	–	–	−4.62	−6.67	–
^2J(C4H5)	0.86 [1]	–	–	0.80	−0.75	–
^2J(C5H4)	−0.18 [1]	–	–	−0.20	−1.59	–
^3J(C1H5)	13.04 [1]	–	–	13.02	13.03	–
^3J(C2H4)	4.57 [1]	–	–	4.59	5.06	–
^3J(C4H2)	4.02 [1]	–	–	3.75	4.66	–
^3J(C4H6)	7.93 [1]	–	–	7.40	8.39	–
^4J(C1H4)	−1.37 [1]	–	–	−1.29	−2.18	–
^4J(C2H5)	−1.42 [1]	–	–	−1.45	−2.24	–
^4J(C5H2)	0.09 [1]	–	–	0.30	−0.86	–
^3J(F1H2) ortho	9.42 [1]	9.35 [5]	–	9.34	5.59	–
^3J(F1H6) ortho	8.43 [1]	8.34 [5]	–	8.39	5.59	–
^4J(F1H5) meta	6.63 [1]	6.57 [5]	–	6.69	5.76	–
^5J(F1H4) para	−0.81 [1]	–	–	−0.83	−2.41	–
^1J(C1C2)	73.1 [7]	–	–	–	79.98	76.67
^1J(C3C4)	71.7 [7]	–	–	–	78.54	75.13

Table 1. (*Continued*)

Coupling	Experimental 1	Experimental 2	Experimental 3	This work 4	Calcd. SOPPA	Calcd. EOM-CCSD
^1J(C4C5)	57.7 [7]	–	–	–	64.98	61.91
^1J(C1F1)	−247.55 [1]	−245.4 [4]	–	−248.14	−275.48	−252.86
^2J(C2F1)	25.36 [1]	25.3 [4]	–	25.36	26.57	25.70
^2J(C6F1)	21.26 [1]	21.2 [4]	–	20.94	22.97	22.12
^3J(C3F1)	11.88 [1]	12.1 [4]	–	11.88	8.13	10.03
^3J(C5F1)	9.80 [1]	9.8 [4]	–	9.76	6.73	8.33
^4J(C4F1)	3.54 [1]	3.6 [4]	–	3.59	5.33	3.53
^4J(F1F3) *meta*	6.52 [1]	6.54 [5]	–	6.10	1.61	4.13
1,4-diFC$_6$H$_4$ (**3**)						
^3J(H2H3) *ortho*	9.09 [1]	9.06 [5]	–	9.06	8.79	7.85
^4J(H2H6) *meta*	3.24 [1]	3.28 [5]	–	3.28	2.00	1.86
^5J(H2H5) *para*	0.34 [1]	0.33 [5]	–	0.33	0.72	0.27
^1J(C2H2)	164.88 [1]	–	–	164.76	166.49	154.77
^2J(C1H2)	−5.13 [1]	–	–	−5.21	−7.31	−5.61
^2J(C2H3)	−0.68 [1]	–	–	−0.73	−2.06	−0.93
^3J(C1H3)	10.65 [1]	–	–	10.70	11.15	10.01
^3J(C2H6)	5.11 [1]	–	–	5.22	5.64	5.01
^4J(C2H5)	−1.21 [1]	–	–	−1.19	−2.00	−1.44
^3J(F1H2) *ortho*	8.09 [1]	7.99 [5]	–	7.95	4.46	5.68
^4J(F1H3) *meta*	4.16 [1]	4.13 [5]	–	4.12	3.91	3.45
^1J(C1C2)	72.5 [3]	72.5 [7]	–	–	79.76	76.38
^1J(C2C3)	–	–	–	–	65.73	62.98
^1J(C1F1)	−240.89 [1]	−242.0 [4]	–	−241.22	−267.13	−246.60
^2J(C2F1)	24.36 [1]	24.3 [4]	–	23.23	25.54	24.52
^3J(C3F1)	8.52 [1]	8.5 [4]	–	9.33	5.05	7.05
^4J(C4F1)	2.42 [1]	3.8 [4]	–	2.47	4.91	2.82
^5J(F1F4) *para*	17.65 [1]	17.5 [5]	–	17.61	17.95	14.21

[a] SSCCs are given in the order HH, HC, HF, CC, CF, FF. References for experimental data are given in square brackets.
[b] Only one-bond C–C couplings ^1J(CC) are reported.
[c] Only the average experimental value was reported for these two coupling constants.

aug'-cc-pVTZ basis set, which is the aug-cc-pVTZ basis without diffuse functions on H.[14,15] Vibrational frequencies were computed to confirm that these structures correspond to minima on their potential surfaces. The optimization and frequency calculations were carried out with the Gaussian 03 suite of programs.[16]

SSCCs involving ^{1}H, ^{13}C, and ^{19}F were computed using SOPPA[17–21] and EOM-CCSD in the configuration interaction (CI)-like approximation,[22,23] with all electrons correlated. Both SOPPA and EOM-CCSD explicitly treat electron correlation effects. SOPPA does this at second order. Because of its exponential ansatz, EOM-CCSD introduces higher order terms as products of singles and doubles and thereby provides an improved treatment of electron correlation.

For the SOPPA calculations, the Ahlrichs[24] qzp basis set was placed on ^{13}C and ^{19}F, and the qz2p basis set on ^{1}H. Since **3** has high computational symmetry, the same basis set was used for the EOM-CCSD calculation on this isomer. However, because of the computational demands of EOM-CCSD, these calculations were feasible for **1** and **2** only with the Dunning cc-pVDZ basis set on H. As a result, no EOM-CCSD coupling constants involving H are reported for **1** and **2**. Coupling constants involving atoms other than H are essentially insensitive to the nature of the basis set on H.[25] Thus, the levels of theory may be represented as EOM-CCSD/(qzp,qz2p)//MP2/aug'-cc-pVTZ and SOPPA/(qzp,qz2p)//MP2/aug'-cc-pVTZ. In the Ramsey

approximation,[26] the total coupling constant (*J*) is a sum of four contributions: the paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi contact (FC), and spin–dipole (SD). All terms have been computed for all molecules. SOPPA calculations were performed using Dalton-2[27] on the IQM computers, and the EOM-CCSD calculations were done with ACES II[28] on the IBM cluster 1350 (Glenn) at the Ohio Supercomputer Center.

Results and Discussion

Experimental values

The experimental values of coupling constants determined for **2** and **3** in CDCl$_3$ are reported in Table 1, and are almost identical to those reported by Wray *et al.* in acetone-d_6.[1] The largest differences are observed for isomer **3**: 1.13 Hz for ^2J(C2F1) and −0.81 Hz for ^3J(C3F1). Given this consistency for isomers **2** and **3** and the values for **1** given by Wray *et al.*, we will use Wray's values which are listed in the first column of Table 1 and labeled Experimental 1, for comparison with the computed values.

SOPPA *versus* EOM-CCSD

In previous studies we have compared SOPPA and EOM-CCSD C–C, C–H, C–F, and F–F coupling constants in nonaromatic

molecules with single, double, and triple bonds.[29] We observed that computed SOPPA $^1J(C-F)$ and $^nJ(F-F)$ values are usually significantly in error compared to EOM-CCSD and experiment. However, for coupling involving the less electronegative atoms C and H, SOPPA $^1J(C-C)$ values are reasonable, and $^1J(C-H)$ coupling constants are in better agreement with experiment than EOM-CCSD, with the latter underestimating the experimental values by about 10 Hz. We can now compare coupling constants computed using these two methods with each other and with experiment for coupling arising in these three aromatic rings.

The SOPPA and EOM-CCSD coupling constants for the difluorobenzenes are also reported in Table 1. The linear regression obtained for computed SOPPA *versus* EOM-CCSD coupling constants is given by Eqn (1).

$$J(SOPPA) = -(0.86 \pm 0.24) + (1.079 \pm 0.003) \times J(EOM\text{-}CCSD);$$
$$n = 40,\ R^2 = 0.9997 \tag{1}$$

The two points that show the largest deviation statistically correspond to $^4J(F1F3)$ for **2** and $^5J(F1F4)$ for **3,** for which the residuals are -1.93 and $+3.53$ Hz, respectively. However, these are not the couplings that show the largest differences between the two methods, since the slope of the trendline of Eqn (1) is not 1. Rather, the greatest differences between the two methods are found for $^1J(CH)$ (SOPPA $-$ EOM-CCSD $= +11.7$ Hz, average) and $^1J(CF)$ (SOPPA $-$ EOM-CCSD $= -21.7$ Hz, average). These results are in agreement with our previous studies which found that SOPPA one-bond C–H coupling constants are about 10 Hz greater than EOM-CCSD values and in better agreement with experimental ones, while one-bond SOPPA C–F coupling constants have absolute values which are much too large relative to EOM-CCSD and experimental values.

SOPPA and EOM-CCSD *versus* experiment

There are 40 experimental SSCCs in the difluorobenzene series for which both SOPPA and EOM-CCSD couplings constants have been evaluated. The experimental values have been plotted against these in Fig. 1. A reference trendline with a slope of 1 and an intercept of 0.00 Hz is also shown for comparison. The equations of the trendlines are given below.

$$J(Exp) = (1.16 \pm 0.45) + (0.909 \pm 0.005) \times J(SOPPA);$$
$$n = 40,\ R^2 = 0.9987 \tag{2}$$
$$J(Exp) = (0.37 \pm 0.42) + (0.981 \pm 0.005) \times J(EOM\text{-}CCSD);$$
$$n = 40,\ R^2 = 0.9989 \tag{3}$$

A comparison of Eqns (2) and (3) indicates that EOM-CCSD coupling constants are in better agreement with experiment than SOPPA, since the EOM-CCSD trendline has an intercept closer to 0.00 Hz (actually, not statistically different) and a slope closer to 1.00. The largest differences between SOPPA and experimental coupling constants are -7.6 Hz for $^1J(CC)$ (average of four values) and 27.6 Hz for $^1J(CF)$ (average of three values). By comparison, the differences between EOM-CCSD values of $^1J(CC)$ and $^1J(CF)$ are 4.0 Hz (average of four values) and 5.9 Hz (average of three values), respectively. However, the computed SOPPA $^1J(CH)$ coupling constant for **3** is closer to the experimental value than the EOM-CCSD value, with differences of -1.6 and 10.1 Hz, respectively. These observations are consistent with our previous studies, as noted above.

SOPPA *versus* experiment for all couplings

Figure 2 presents a plot of the set of 80 computed SOPPA coupling constants *versus* the experimental coupling constants for all three isomers. The equation of the trendline is:

$$J(Exp) = (1.68 \pm 0.38) + (0.932 \pm 0.005) \times J(SOPPA);$$
$$n = 80,\ R^2 = 0.9976 \tag{4}$$

However, it should be emphasized that different SSCCs behave differently, that is, the differences between experimental and computed values are not random. Since the range of coupling constants in the difluorobenzenes is large at about 500 Hz, it is not possible to see in Fig. 2 what these differences are. This is illustrated in Fig. 3 in which the three experimental coupling constants $^1J(CF)$ are plotted against the SOPPA and EOM-CCSD values. The equations of the trendlines are:

$$^1J(C-F)\ (Exp) = -(40 \pm 23) + (0.75 \pm 0.08)$$
$$\times\ ^1J(C-F)\ (SOPPA);\ n = 3,\ R^2 = 0.988 \tag{5}$$
$$^1J(C-F)\ (Exp) = -(11 \pm 48) + (0.93 \pm 0.19)$$
$$\times\ ^1J(C-F)\ (EOM\text{-}CCSD);\ n = 3,\ R^2 = 0.959 \tag{6}$$

It is apparent that SOPPA $^1J(C-F)$ values for the difluorobenzenes are significantly in error since the slope of Eqn (5) is significantly less than 1 and its intercept is far from 0 Hz. A similar graph can be constructed for $^1J(C-C)$ which yields the following equations for the trendlines:

$$^1J(C-C)\ (Exp) = -(6.3 \pm 1.5) + (0.99 \pm 0.02)$$
$$\times\ ^1J(C-C)\ (SOPPA);\ n = 7,\ R^2 = 0.9981 \tag{7}$$
$$^1J(C-C)\ (Exp) = -(5.2 \pm 1.0) + (1.02 \pm 0.01)$$
$$\times\ ^1J(C-C)\ (EOM\text{-}CCSD);\ n = 7,\ R^2 = 0.9991 \tag{8}$$

Similar graphs can be constructed for the various pairs of coupled atoms, and a summary of the performance of the two methods can be obtained by examining the slopes and intercepts of the corresponding trendlines, the correlation coefficients, and the location of the trendlines relative to the reference trendline. This summary is given in Table 2.

Although EOM-CCSD coupling constants are usually in better agreement with experiment than SOPPA coupling constants except for $^1J(CH)$, the computational cost of EOM-CCSD restricts its application to rather small systems and/or systems with high computational symmetry. SOPPA does not have such a high computational cost, and as a result, it has much wider applicability. Therefore, at this point it is appropriate to ask whether there is an empirical model based on SOPPA coupling constants that can reliably reproduce experimental coupling constants and could then be used to predict unknown ones. We offer Eqn (9) as a simple model which is consistent with most of the coupling constants in Table 1, provided that an adjustment is made for $^1J(C-C)$ and $^1J(C-F)$. This model is based on the Free–Wilson or 'presence–absence' model which involves the addition of adjustable dummy variables,[30–32] in this case specifically for $^1J_{CC}$ and $^1J_{CF}$. Since only a single value is available for each of the couplings $^3J(F-F)$, $^4J(F-F)$, and $^5J(F-F)$, dummy variables for $^nJ(F-F)$ were not included despite the fact that it is well known that SOPPA does not generally handle such couplings very well.[29]
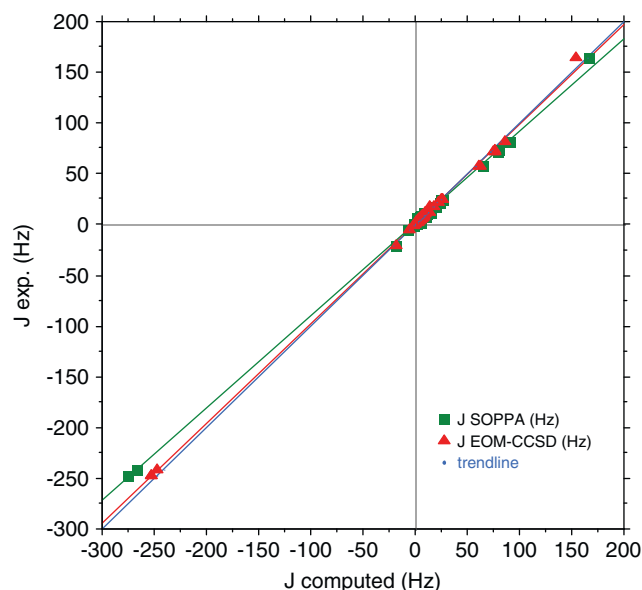
Figure 1. Experimental coupling constants *versus* computed EOM-CCSD (▲) and SOPPA (■) values. The reference trendline (blue) has a slope of 1 and an intercept of 0.00 Hz.
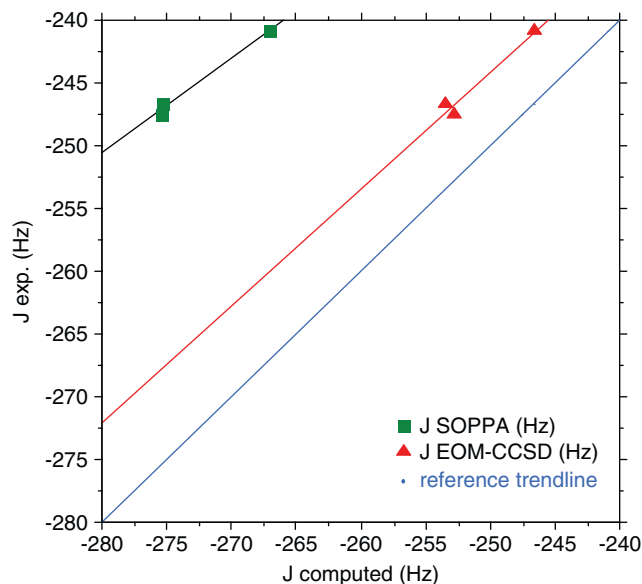

Figure 3. Experimental *versus* computed EOM-CCSD (▲) and SOPPA (■) values of $^1J(C-F)$. The reference trendline (blue) has a slope of 1 and an intercept of 0.00 Hz.
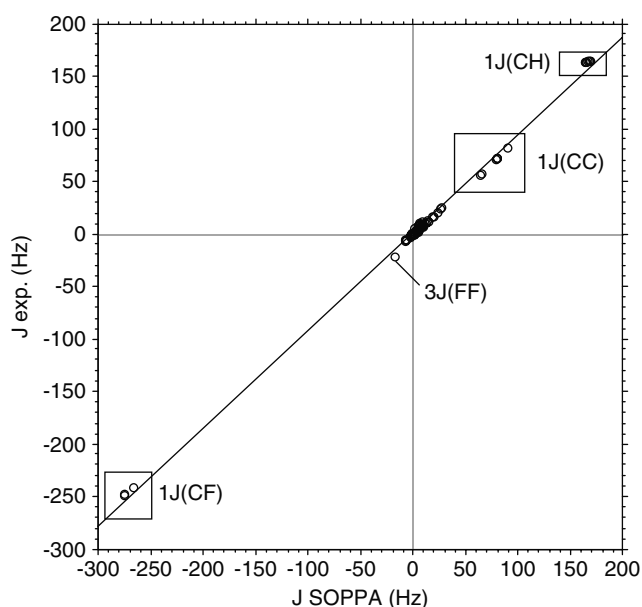

Figure 2. Experimental *versus* computed SOPPA coupling constants.

Table 2. Intercepts and slopes of trendlines, and values of correlation coefficients for graphs relating computed and experimental coupling constants for various pairs of atoms. The best values are shown in bold

J		Intercept	Slope	R^2	Comments
J_{CC}	SOPPA	−6.3	0.99	1.00	
	EOM-CCSD	−5.2	1.02	1.00	Similar
J_{CF}	SOPPA	−40.4	0.75	**0.99**	
	EOM-CCSD	**−11.2**	**0.93**	0.96	Better[a]
J_{FF}	SOPPA	**0.3**	**1.10**	0.96	Similar[b]
	EOM-CCSD	0.9	1.21	**1.00**	
J_{HH}	SOPPA	**0.3**	**1.01**	0.97	Better
	EOM-CCSD	0.5	1.11	**0.98**	
J_{CH}	SOPPA	0.7	**0.99**	1.00	Better[c]
	EOM-CCSD	**0.3**	1.06	1.00	
J_{FH}	SOPPA	−2.4	7.1	–	Only two points are
	EOM-CCSD	−1.9	**1.8**	–	Available[d]

[a] Only three points.
[b] J_{FF} SOPPA and EOM-CCSD values are similar, but previous studies have shown that EOM-CCSD better describes F–F coupling.[29]
[c] These data are for two-, three-, and four-bond C–H couplings. Only $^1J_{CH}$ for **3** has been computed at EOM-CCSD, and its value is 10 Hz too low, in agreement with our previous observations.[29]
[d] SOPPA couplings involving F usually deviate significantly from experimental values.[29]

The model is given by Eqn (9).

$$J(\text{Exp}) = (0.991 \pm 0.004) \times J(\text{SOPPA}) - (6.6 \pm 0.7) \times \delta_{1JC-C}$$
$$+ (25.0 \pm 1.5) \times \delta_{1JC-F}; \, n = 80, \, R^2 = 0.9994 \qquad (9)$$

where δ_{1JC-C} is the Kronecker delta equal to 1 if J is $^1J(C-C)$, and δ_{1JC-F} is the Kronecker delta equal to 1 if J is $^1J(C-F)$.

With the coefficient of the first-order term so close to 1, this equation indicates that there are no systematic corrections for the 80 SOPPA coupling constants in Table 1, except for $^1J(C-C)$ in which case 6.8 Hz is subtracted from the computed SOPPA value, and for $^1J(C-F)$ in which case 25.0 Hz is added to the SOPPA value. The largest deviations [$J(\text{Exp}) - J(\text{Fitted})$] are found for $^3J(F1F2)$ of **1**

(−3.58 Hz) and $^4J(F1F3)$ of **2** (+4.93 Hz), which are the uncorrected couplings.

To illustrate the utility of Eqn (9), we report in Table 3 values of $^1J(C-F)$ and $^1J(C-C)$ for the three difluorobenzenes as computed by SOPPA and SOPPA adjusted by Eqn (9); EOM-CCSD and EOM-CCSD adjusted by Eqns (6) and (8); and experimental values. The consistency among adjusted SOPPA, EOM-CCSD, and experimental values is evident. However, it can be seen that even the unadjusted EOM-CCSD coupling constants are close enough to the experimental values that they do not require empirical corrections.

Table 3. SOPPA, adjusted SOPPA, EOM-CCSD, adjusted EOM-CCSD, and experimental values of $^1J(C-F)$ and $^1J(C-C)$ (Hz)

$^1J(C-F)$/Isomer	SOPPA	EOM	SOPPA Eqn (9)	EOM Eqn (6)	Experimental
1	−275.3	−253.5	−247.7	−246.8	−246.6
2	−275.5	−252.9	−247.8	−246.2	−247.6
3	−267.1	−246.6	−239.6	−240.3	−240.9

$^1J(C-C)$/Isomer	SOPPA	EOM	SOPPA Eqn (9)	EOM Eqn (8)	Experimental
$^1J(C1C2)$ **1**	90.4	86.3	82.9	82.7	82.3
$^1J(C2C3)$ **1**	79.7	76.2	72.4	72.4	72.3
$^1J(C3C4)$ **1**	64.7	61.5	57.5	57.4	57.2
$^1J(C1C2)$ **2**	80.0	76.7	72.6	72.8	73.1
$^1J(C3C4)$ **2**	78.5	75.1	71.2	71.3	71.7
$^1J(C4C5)$ **2**	65.0	61.9	57.8	57.8	57.7
$^1J(C1C2)$ **3**	79.8	76.3	72.4	72.5	72.5

The agreement between the adjusted SOPPA and EOM-CCSD coupling constants, and the agreement of these computed values with the corresponding experimental coupling constants, imply that Eqn (9) can be used to predict the values of coupling constants $^1J(C-C)$ missing from Table 1. Moreover, this agreement also suggests that SOPPA can be used as a tool to investigate coupling constants in larger aromatic rings. These rings may serve as models for predicting coupling constants in even larger aromatic systems for which direct calculations are not feasible. This approach will be further investigated in future studies.

Acknowledgements

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