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# Indirect carbon–carbon spin–spin couplings across one, two and three bonds in pyridine and diazine systems: experiment and theory

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**An excellent linear correlation is found between a large body of experimental spin–spin carbon–carbon couplings, *J*(CC), across one, two and three bonds in pyridine and diazine ring systems and the corresponding B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) computations. The correlation does not differ significantly from the simplest relationship possible, $J(\mathrm{CC})_{\mathrm{exp.}} = J(\mathrm{CC})_{\mathrm{calcd.}}$, within a small and random spread of about 1 Hz. There are 276 experimental values considered, and 124 out of these are new and come from the present work. The aromatic carbon–carbon couplings vary from −7.6 through +78.5 Hz. It is shown that the correlation provides a reliable tool for predictions of the signs of aromatic *J*(CC)'s even if the magnitudes of the latter are of the order of 1 Hz. It is demonstrated, for the first time, that the relatively weak $^2J$(CC) couplings, in the heteroaromatic systems studied, can bear either sign and span a considerable range of about 11 Hz. The character of the correlation indicates that rovibronic effects on aromatic *J*(CC)'s and those of nuclear motions on aromatic *J*(CC)'s are practically negligible. All of this is in a perfect agreement with our recent extensive studies on aromatic *J*(CC)'s in analogous benzene ring system. Substituent effects on the aromatic *J*(CC)'s turn out to be significant not only for $^1J$(CC)'s but also for most of $^3J$(CC)'s and $^2J$(CC)'s, and the computation neatly reciprocates these trends. Copyright © 2008 John Wiley & Sons, Ltd.**

**Keywords:** pyridines; diazines; one-bond; long-range; spin–spin carbon–carbon couplings; DFT calculations; substituent effects; rovibronic effects

## INTRODUCTION

Our recent studies[1,2] of indirect aromatic carbon–carbon couplings, *J*(CC)'s, in a large number of benzene derivatives revealed an excellent linear correlation between the experimental *J*(CC)'s and the corresponding B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) computations, for a total of 282 individual couplings which included 210 $^1J$(CC)'s, 15 $^2J$(CC)'s and 57 $^3J$(CC)'s. The foregoing correlation, which is practically equivalent to the simplest relationship possible, $J_{\mathrm{exp.}} = J_{\mathrm{calcd.}}$, and shows a standard deviation of about 0.6 Hz over a range of −2.9 through +82.8 Hz, amply demonstrates that quantum mechanical calculations are able to precisely reproduce a broad range of carbon–carbon couplings and that they should provide a reliable tool for predicting both the relevant magnitudes and signs. This is especially important for relatively weak aromatic $^2J$(CC) couplings which can bear either sign.

In view of these results, it is fairly obvious that such studies should be extended over aza-aromatic compounds where the presence of what is conventionally termed as lone pair electrons can bring about some complications. We decided to perform analogous density functional theory (DFT) calculations for a representative set of variously mono-, di- and tri-substituted pyridines as well as some diazine systems and compare them with the corresponding experimental *J* values. The data collected encompass 53 compounds for which 276 individual coupling constants have been measured with a special attention paid to long-range couplings. Attention is drawn to the fact that nearly a half of the experimental values are new, and come from the present work. As far as $^2J$(CC)'s and $^3J$(CC)'s are concerned, the new data contribution amounts to more than a half of the total.

It will be demonstrated that the linear correlation between experimental and computed aromatic *J*(CC)'s in pyridine and diazine systems is as good as that observed for benzene and its derivatives, and practically corresponds to the simplest relationship possible, $J(\mathrm{CC})_{\mathrm{exp}} = J(\mathrm{CC})_{\mathrm{calcd.}}$, within a small and random spread of datapoints.

It was not exactly our prime purpose to extend significantly the experimental database of *J*(CC)'s in the aza-aromatics studied, but we needed a sound experimental foundation in order to assess the potential of quantum mechanical computations from the point of view of their ability to reproduce the magnitudes of the couplings and, which is equally important, to reliably predict their signs. The latter question relates to the relatively weak $^2J$(CC) couplings which, as will be shown here, can bear either sign and span a considerable range of about 11 Hz. One should notice that all of the assignments of the experimental $^1J$(CC)'s, $^2J$(CC)'s and $^3J$(CC)'s are certain as they were derived from the relevant $^{13}$C-1D-*inadequate* measurements and $^1J$(CH) couplings (see Section 'Experimental and Computational Details').

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## RESULTS AND DISCUSSION

The experimental and quantum mechanical calculated *J*(CC) couplings have been collected in Tables 1–4. Table 1 contains $^1J$(CC)'s for pyridine and monosubstituted pyridines, while Table 2 includes those for di- and tri-substituted pyridines as well as for some diazines. Table 3 encompasses carbon–carbon couplings across three aromatic bonds, while in Table 4 those across two bonds are presented. All of the computed couplings presented in Tables 1–4 come from the present work. Among the 276 individual values of experimental aromatic carbon–carbon couplings reported in Tables 1–4, 124 are new and come from the present work. The relevant data in Tables 1–4 are referred to as 'new'. The other are quoted from the literature,[3–8] (see the tables for details); however, 27 couplings were remeasured in the present work, and are marked as such in Tables 1 and 3.

DFT calculations were carried out on the B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) level, that is, a full geometry optimization was followed by the computation of the couplings, and the two stages featured the same functional/basis combination specified above. The computational results are compared with the pertinent experimental couplings in Tables 1–4. The linear regression between the experimental aromatic *J*(CC)'s and the corresponding values computed here is as follows:

$$J(\mathrm{CC})_{\mathrm{exp.}} = [1.0040(\pm 0.0018)J(\mathrm{CC})_{\mathrm{calcd.}} - 0.13(\pm 0.08)] \pm 0.80\,\mathrm{Hz} \qquad (1)$$

where the numbers following the ± sign are the relevant standard errors of the mean for the two variables fitted, and the overall standard deviation for 276 individual *J*(CC)'s and 274 degrees of freedom. The slope (scaling) coefficient of 1.0040 does

**Table 1.** Experimental and B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) calculated $^1J$(CC)'s in pyridine and monosubstituted pyridines; all calculations are from the present work, all calculated couplings presented in this table are positive

| | | $^1J$(C2C3) | | $^1J$(C3C4) | | $^1J$(C4C5) | | $^1J$(C5C6) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Substituents | exp. | calcd. | exp. | calcd. | exp. | calcd. | exp. | calcd. | Refs. to exp. |
| **1** | H | 54.3 | 54.0 | 53.7 | 54.8 | 53.7 | 54.8 | 54.3 | 54.0 | 5 |
| **2** | 2-F | 75.6 | 74.9 | 56.1 | 56.7 | 54.8 | 55.5 | 56.4 | 55.4 | Remeasured[a] |
| **3** | 2-$NO_2$ | 71.7 | 70.7 | 54.3 | 54.6 | 54.8 | 55.4 | 54.4 | 53.5 | 3 |
| **4**[b] | 2-OMe | 70.7 | 70.3 | 57.6 | 58.8 | 53.6 | 54.4 | 57.0 | 56.3 | 5 |
| **5** | 2-Cl | 67.4 | 67.4 | 54.1 | 55.3 | 54.3 | 55.4 | 55.3 | 54.7 | 5 |
| **6** | 2-Br | 64.9 | 64.8 | 53.3 | 54.7 | 54.4 | 55.4 | 55.4 | 54.9 | 5 |
| **7** | 2-$NMe_2$ | 63.6 | 62.8 | 58.7 | 59.5 | 54.1 | 55.0 | 56.4 | 54.9 | New |
| **8** | 2-CN | 61.3 | 59.6 | 53.5 | 55.1 | 53.3 | 54.6 | 52.9 | 52.4 | Remeasured[a] |
| **9**[b] | 2-SMe | 59.6 | 59.4 | 56.0 | 57.9 | 54.2 | 54.6 | 55.9 | 55.6 | New |
| **10** | 2-Me | 56.2 | 56.1 | 54.7 | 55.2 | 54.2 | 54.9 | 54.7 | 53.5 | 5 |
| **11** | 2-$SiMe_3$ | 45.3 | 45.7 | 52.8 | 53.3 | 54.0 | 54.6 | 54.4 | 53.2 | 4 |
| **12** | 3-F | 70.4 | 68.8 | 69.0 | 69.0 | 54.5 | 55.2 | 54.6 | 53.9 | Remeasured[a] |
| **13** | 3-$NO_2$ | 66.2 | 64.6 | 65.6 | 65.2 | 54.3 | 54.8 | 53.6 | 52.7 | 3 |
| **14**[c] | 3-OMe | 66.1 | 65.9 | 64.6 | 63.9 | 55.2 | 56.1 | 54.9 | 55.7 | 5 |
| **15** | 3-Cl | 62.4 | 61.0 | 63.0 | 63.6 | 53.5 | 54.6 | 54.3 | 54.1 | 5 |
| **16** | 3-Br | 59.9 | 58.3 | 61.4 | 62.0 | 52.9 | 54.0 | 54.3 | 54.2 | 5 |
| **17** | 3-$NMe_2$ | 61.1 | 59.3 | 60.8 | 60.7 | 57.1 | 58.2 | 55.3 | 54.8 | New |
| **18** | 3-CN | 58.3 | 56.5 | 58.0 | 58.1 | 54.2 | 55.7 | 53.0 | 53.1 | Remeasured[a] |
| **19**[c] | 3-SMe | 57.3 | 56.4 | 58.0 | 58.9 | 54.8 | 56.7 | 55.2 | 54.6 | New |
| **20** | 3-Me | 55.4 | 54.1 | 55.1 | 56.2 | 54.3 | 55.0 | 54.6 | 54.3 | 5 |
| **21** | 3-$SiMe_3$ | 46.3 | 45.3 | 46.0 | 47.0 | 53.5 | 54.1 | 55.0 | 54.0 | 4 |
| **22** | 4-$NO_2$ | 54.3 | 53.0 | 65.5 | 65.2 | 65.5 | 65.2 | 54.3 | 53.0 | 3 |
| **23**[d] | 4-OMe | 56.2 | 56.2 | 64.2 | 64.1 | 64.2 | 64.1 | 56.2 | 56.2 | 5 |
| **24** | 4-Cl | 53.6 | 53.3 | 62.5 | 62.7 | 62.5 | 62.7 | 53.6 | 53.3 | 3 |
| **25** | 4-Br | 52.7 | 52.6 | 60.8 | 61.1 | 60.8 | 61.1 | 52.7 | 52.6 | 3 |
| **26** | 4-$NMe_2$ | 58.7 | 58.0 | 60.1 | 59.4 | 60.1 | 59.4 | 58.7 | 58.0 | New |
| **27** | 4-CN | 54.1 | 54.1 | 58.2 | 58.0 | 58.2 | 58.0 | 54.1 | 54.1 | 3,5 |
| **28**[d] | 4-SMe | 55.9 | 55.7 | 57.6 | 58.2 | 57.6 | 58.2 | 55.9 | 55.7 | New |
| **29**[d] | 4-COMe | 54.6 | 54.1 | 55.9 | 56.3 | 55.9 | 56.3 | 54.6 | 54.1 | 3 |
| **30** | 4-Me | 54.9 | 54.8 | 54.7 | 55.2 | 54.7 | 55.2 | 54.9 | 54.8 | 5 |
| **31** | 4-$SiMe_3$ | 54.1 | 53.5 | 46.1 | 47.0 | 46.1 | 47.0 | 54.1 | 53.5 | 4 |

[a] For the first time reported in Reference [5]

[b] Calculated for the only stable rotamer *syn*.

[c] Calculated for zero point energies 55% *syn*, $\Delta E$ (*anti–syn*) = 0.20 kcal/mol.

[d] Averaged values.

**Table 2.** Experimental and B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) calculated $^1J$(CC)'s in di- and tri-substituted pyridines and in diazines; all calculations are from the present work, all calculated couplings presented in this table are positive (n.o. = not observed)

| | | $^1J$(C2C3) | | $^1J$(C3C4) | | $^1J$(C4C5) | | $^1J$(C5C6) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| No. | Position of substituents | exp. | calcd. | exp. | calcd. | exp. | calcd. | exp. | calcd. | Refs. to exp. |
| | | | | di- and tri-substituted pyridines | | | | | | |
| **32**[a] | 2-Br, 3-OMe | 78.0 | 78.0 | 64.6 | 65.4 | 55.3 | 57.2 | 55.4 | 55.8 | 3 |
| **33** | 2-Cl, 3-$NO_2$ | n.o. | 77.7 | 65.7 | 66.9 | 55.8 | 55.9 | 53.9 | 51.8 | New |
| **34** | 2-Cl, 3-Cl | 75.9 | 75.2 | 64.2 | 64.6 | 54.7 | 55.5 | 54.9 | 54.1 | New |
| **35** | 2-Br, 4-$NO_2$ | 65.5 | 64.7 | n.o. | 66.0 | 66.3 | 66.0 | 54.1 | 54.1 | 3 |
| **36** | 2-$NH_2$, 4-Me | 61.1 | 62.1 | 59.3 | 61.0 | 54.1 | 54.9 | 56.8 | 56.8 | New |
| **37**[b] | 2-OMe, 5-$NO_2$ | 69.9 | 68.9 | 59.1 | 59.8 | 65.9 | 65.0 | 69.3 | 67.6 | New |
| **38** | 2-F, 6-F | 77.1 | 76.2 | 57.0 | 57.8 | 57.0 | 57.8 | 77.1 | 76.2 | New |
| **39** | 2-Cl, 6-Cl | 68.3 | 67.8 | 55.1 | 56.0 | 55.1 | 56.0 | 68.3 | 67.8 | New |
| **40** | 2-Br, 6-Br | 65.9 | 65.2 | 54.4 | 55.3 | 54.4 | 55.3 | 65.9 | 65.2 | New |
| **41** | 2-Me, 6-$NH_2$ | 58.9 | 57.6 | 54.7 | 55.5 | 58.6 | 59.8 | 61.9 | 61.4 | New |
| **42** | 2-Me, 6-Me | 56.6 | 55.4 | 54.7 | 55.3 | 54.7 | 55.3 | 56.6 | 55.4 | 3, 7 |
| **43** | 3-Br, 5-Br | 60.2 | 58.1 | 60.8 | 61.2 | 60.8 | 61.2 | 60.2 | 58.1 | 3 |
| **44** | 2-Me, 6-Me, 4-$NH_2$ | 59.1 | 59.9 | 60.8 | 60.1 | 60.8 | 60.1 | 59.1 | 59.9 | New |
| **45** | 2-Cl, 3-$NO_2$, 5-$NO_2$ | 78.5 | 77.2 | 68.5 | 67.6 | 69.1 | 68.5 | 66.4 | 64.7 | New |
| **46** | 2-Cl, 3-Cl, 5-Cl | 76.0 | 75.4 | 64.9 | 65.3 | 64.7 | 65.0 | 63.2 | 61.5 | New |
| | | | | 1,2-diazines | | | | | | |
| **47** | H | | | 50.4 | 51.2 | n.o. | 53.4 | 50.4 | 51.2 | 8 |
| **48** | 3-Me | | | 52.2 | 52.1 | n.o. | 54.4 | 50.7 | 52.1 | 6 |
| **49** | 4-Me | | | 51.0 | 50.4 | 53.9 | 54.7 | 51.2 | 51.4 | 6 |
| | | | | 1,3- diazines | | | | | | |
| **50** | H | | | | | 52.8 | 52.8 | 52.8 | 52.8 | 8 |
| **51** | 2-Me | | | | | 53.1 | 52.6 | 53.1 | 52.6 | 6 |
| **52** | 4-Me | | | | | 54.3 | 53.5 | 53.7 | 54.1 | 6 |
| | | | | 1,4- diazine | | | | | | |
| **53** | 2-Me | 54.6 | 54.1 | | | | | 53.6 | 52.6 | 6 |

[a] Calculated for the only stable rotamer *anti*.

[b] Calculated for the only stable rotamer *syn*.

not significantly depart from the ideal value of unity nor does the free term, −0.13 Hz, with respect to the ideal value of zero.

The standard deviations shown in Eqn (1), for the number of datapoints involved, provide a confidence level of only two-thirds, that is, 66.67%. On the 95% confidence level, Eqn (1) is transformed into the Eqn (2):

$$J(\mathrm{CC})_{\mathrm{exp.}} = [1.0040(\pm 0.0036)\,J(\mathrm{CC})_{\mathrm{calcd.}} - 0.13(\pm 0.16)] \pm 1.57\,\mathrm{Hz} \qquad (2)$$

where only the relevant limits (the numbers following the ± sign) are modified. Now, the ±1.57 Hz range, referred to the regression line, should embrace 95% datapoints as the number of the latter tends to infinity. In the present case, there are only 13 out of 276 $J$(CC)'s which slightly exceed the limit, and this corresponds to 95.3% datapoints within the limits: the latter percentage, in turn, is just within the expectation limits for the confidence level involved, and the number of datapoints. Eqns (1) and (2) presents uniform ranges of 66.7 and 95% confidence limits, respectively, but this not exactly true in general, as the limits are a function of ($J_{\mathrm{calcd.}} - J_{\mathrm{calcd.,mean}}$) squared; however, in the present case of 276 datapoints which are distributed quite evenly throughout the correlation range, the corrections are negligible as they do not exceed 0.1 Hz, and the relevant confidence limit may be considered as uniform throughout the whole of the datapoints concerned.

The sign test for the deviations from the regression line shows that the latter are random, that is, there is no statistically significant preponderance of either sign and there is no significant clustering of like signs of deviations along the regression line. The correlation expressed by Eqn (1) matches, within a statistically insignificant margin, the analogous relationship reported by us for the aromatic carbon–carbon couplings in substituted benzenes.[1,2] Practically, all these correlations represent the simplest correspondence between experiment and theory, that is, $J(\mathrm{CC})_{\mathrm{exp.}} = J(\mathrm{CC})_{\mathrm{calcd.}}$, within a narrow and random spread of about 1 Hz.

The linear correlation is presented in Fig. 1; attention is drawn to the fact that among 276 individual experimental values of $J$(CC)'s there are:

| | | | | |
|---|---|---|---|---|
| 160 | $^1J$(CC)'s | +45.3 | through | +78.5 Hz; |
| 74 | $^3J$(CC)'s | +6.8 | through | +18.5 Hz; |
| 42 | $^2J$(CC)'s | −7.6 | through | +3.6 Hz. |

It should be accentuated that the range of variation of $^2J$(CC)'s is about the same, within 11 Hz, as that of $^3J$(CC)'s, but the

**Table 3.** Experimental and B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) calculated $^3J$(CC)'s in pyridine and substituted pyridines and diazines; all calculations are from the present work, all calculated couplings presented in this table are positive (n.o. = not observed)

| | $^3J$(C2C5) | | $^3J$(C3C6) | | |
|---|---|---|---|---|---|
| No. | exp. | calcd. | exp. | calcd. | Refs. to exp. |
| | | Monosubstituted pyridines | | | |
| **1** | 13.9 | 13.8 | 13.9 | 13.8 | 5 |
| **2** | 12.4 | 11.9 | 8.9 | 8.5 | Remeasured[a] |
| **3** | 12.2 | 11.3 | 9.8 | 9.5 | New |
| **4**[b] | 11.7 | 11.2 | 9.7 | 9.3 | 5 |
| **5** | 12.8 | 12.4 | 10.5 | 10.1 | Remeasured[a] |
| **6** | 13.1 | 12.3 | 10.9 | 10.6 | 5 |
| **7** | 11.0 | 10.7 | 10.6 | 10.3 | New |
| **8** | 14.7 | 14.3 | 12.1 | 12.3 | Remeasured[a] |
| **9**[b] | 12.6 | 12.1 | 12.3 | 12.0 | New |
| **10** | 13.2 | 13.0 | 12.4 | 12.2 | 5 |
| **11** | 13.3 | 13.2 | 15.8 | 15.3 | New |
| **12** | 9.9 | 9.7 | 15.4 | 15.1 | Remeasured[a] |
| **13** | 11.0 | 10.7 | 14.4 | 13.4 | New |
| **14**[c] | 10.5 | 10.4 | 13.6 | 13.6 | 5 |
| **15** | 11.2 | 11.1 | 16.1 | 15.8 | 5 |
| **16** | 11.8 | 11.5 | 16.2 | 16.1 | 5 |
| **17** | 11.3 | 11.6 | 12.0 | 11.9 | New |
| **18** | 13.1 | 13.0 | 15.6 | 15.1 | Remeasured[a] |
| **19**[c] | 12.7 | 12.8 | 13.9 | 13.6 | New |
| **20** | 12.6 | 12.5 | 13.3 | 13.1 | 5 |
| **21** | 15.2 | 15.1 | 12.1 | 12.2 | New |
| **23**[d] | 10.5 | 10.5 | 10.5 | 10.5 | 5 |
| **24** | 11.3 | 11.2 | 11.3 | 11.2 | 5 |
| **25** | 11.8 | 11.6 | 11.8 | 11.6 | 5 |
| **26** | 11.3 | 11.6 | 11.3 | 11.6 | New |
| **27** | 13.3 | 13.1 | 13.3 | 13.1 | Remeasured[a] |
| **28**[d] | 12.7 | 12.8 | 12.7 | 12.8 | New |
| **29**[d] | 12.7 | 12.6 | 12.7 | 12.6 | New |
| **30** | 12.6 | 12.6 | 12.6 | 12.6 | 5 |
| **31** | 15.3 | 15.1 | 15.3 | 15.1 | New |
| | | di- and tri-substituted pyridines | | | |
| **32**[e] | 9.6 | 9.2 | 11.3 | 10.7 | New |
| **33** | 10.9 | 9.5 | 12.0 | 10.3 | New |
| **34** | 10.5 | 9.8 | 12.3 | 12.1 | New |
| **35** | 10.0 | 9.4 | 8.3 | 8.0 | New |
| **36** | n.o. | 10.9 | 8.5 | 9.3 | New |
| **37**[b] | n.o. | 10.6 | 6.8 | 6.3 | New |
| **39** | 9.8 | 9.0 | 9.8 | 9.0 | New |
| **40** | 10.1 | 9.5 | 10.1 | 9.5 | New |
| **41** | 10.1 | 10.6 | 9.3 | 9.8 | New |
| **42** | 11.8 | 11.5 | 11.8 | 11.5 | 7 |
| **43** | 13.4 | 13.2 | 13.4 | 13.2 | New |
| **45** | 10.9 | 9.4 | 9.0 | 8.2 | New |
| **46** | 11.3 | 10.3 | 9.5 | 9.2 | New |
| | | 1,2-diazines | | | |
| **48** | | | 18.5 | 19.5 | 6 |
| **49** | | | 17.8 | 18.8 | 6 |
| | | 1,4-diazine | | | |
| **53** | 17.3 | 16.9 | 16.4 | 16.0 | 6 |

[a] For the first time reported in Reference[5]

[b] Calculated for the only stable rotamer *syn*.

[c] Calculated for zero point energies 55% *syn*, Δ (*anti*–*syn*) = 0.20 kcal/mol.

[d] Averaged values.

[e] Calculated for the only stable rotamer *anti*.

magnitudes of the former are smaller. This originates from the range of $^2J$(CC)'s which encompasses zero coupling so that a good deal of $^2J$(CC)'s are likely to escape detection. For those which can be observed, the theory on the present level of sophistication provides a convenient tool for reliable predictions of their signs. This is shown for the first time for pyridine ring systems that their $^2J$(CC)'s can bear either sign and vary within quite a considerable range, while so far such couplings have been considered as weak and negative. A convincing example of the foregoing is provided by 3-fluoropyridine **12** where the experimental magnitude of $^2J$(C2C4) is 3.6 Hz while the computation yields $^2J$(C2C4) = +3.3 Hz (Table 4). There is no doubt that the experimental value amounts to +3.6 Hz. Should the opposite be true, that is, $^2J$(C2C4) = −3.6 Hz, the discrepancy between experiment and computation would be as large as 7.8 Hz, far beyond any reasonable confidence limits with respect to the overall regression. The same applies to $^2J$(C2C4) in 2-chloro-3,5-dinitropyridine **45** where the experimental magnitude is (+)1.6 Hz and the computation yields $^2J$(C2C4) = +1.4 Hz. Now, if we append the plus sign to the experimental magnitude, chances that we are wrong do not exceed 0.1%. All of this clearly shows the predictive power of the regression expressed by Eqn (1) (Fig. 1), from the point of view of the computation based sign appending to experimental magnitudes of *J*(CC)'s, even if the latter are of the order of 1 Hz. For this reason we present, in Table 4, the computational results for weak couplings where no experimental data are available.

One should notice that we compare experimental results taken on solutions at room temperature with the relevant computations for isolated molecules whose geometries relate to zero-point energy. In other words we neglect solvent effects on the solute, rovibronic effects on the *J*(CC)'s at room temperature, and vibrational ground state effects at zero K; the latter two have been considered in detail in a recent account.[9] The fact that the statistical correlation between the experiment and theory has the form $J_{\text{exp.}} = J_{\text{calcd.}}$, and the relevant deviations are random and small, amply suggests that such effects are practically negligible for aromatic *J*(CC)'s. There are no reasons to believe that rovibronic and ground vibrational state effects on the constants in the pyridine ring system should vary significantly within the large body of pyridine derivatives examined. Thus, if the effects were considerable, the regression (Eqn (1) and (2)) should reveal a bias, that is, the value of the free term should deviate significantly from zero; actually its value of −0.13 ± 0.16 Hz on the 95% confidence level (Eqn (2)) is not significantly different from zero and suggests that such effects, if any, may eventually be of the order of 0.1 Hz, and as such are unimportant for any practical purposes. Similar conclusions have already been drawn from our recent studies on benzene ring systems.[1,2]

The extensive experimental material collected, combined with the reliable quantum mechanical computations of aromatic *J*(CC)'s, allow one to arrive at some interesting conclusions. First of all, pyridine and diazine ring systems, those studied in the present work, as well as the large number of benzene derivatives examined in our previous studies,[1,2] show quite clearly that substituent effects on $^1J$(CC)'s are fairly short ranged. In most cases, significant effects appear on $^1J$(CC)'s which relate to the nearest carbon—carbon bonds, that is, one bond in each direction from $C_{\text{ipso}}$. Thus, significant effects are revealed on $^1J$(C2C3) for 2-substituted pyridines, on $^1J$(C2C3) and $^1J$(C3C4) for 3-substituted pyridines, on $^1J$(C3C4)/$^1J$(C4C5) for 4-substituted

**Table 4.** Experimental and B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) calculated ${}^2J$(CC)'s in pyridine and substituted pyridines; all calculations are from the present work and all values are in Hz (n.o. = not observed)

| | ${}^2J$(C2C4) | | ${}^2J$(C2C6) | | ${}^2J$(C3C5) | | ${}^2J$(C4C6) | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | exp. | calcd. | exp. | calcd. | exp. | calcd. | exp. | calcd. | Refs. to exp. |
| **1** | (−)2.9 | −2.4 | n.o. | −5.6 | n.o. | −2.9 | (−)2.9 | −2.4 | 5 |
| **2** | n.o. | +0.5 | n.o. | −0.6 | n.o. | −2.9 | n.o. | −1.4 | |
| **3** | n.o. | −0.5 | n.o. | −2.7 | n.o. | −2.6 | n.o. | −1.8 | |
| **4**[a] | n.o. | +0.4 | n.o. | −1.9 | (−)3.5 | −2.9 | n.o. | −1.4 | 5 |
| **5** | n.o. | −0.8 | (−)3.3 | −3.3 | n.o. | −2.9 | n.o. | −1.8 | 5 |
| **6** | n.o. | −1.4 | (−)5.6 | −4.4 | n.o. | −2.9 | n.o. | −2.0 | 5 |
| **7** | n.o. | −0.1 | n.o. | −2.0 | (−)3.0 | −2.9 | n.o. | −1.3 | New |
| **8** | (−)2.0 | −1.6 | (−)5.0 | −4.0 | (−)3.0 | −2.8 | (−)2.5 | −2.1 | New |
| **9**[a] | n.o. | −1.5 | (−)5.8 | −5.0 | (−)3.2 | −2.9 | (−)2.5 | −2.0 | New |
| **10** | n.o. | −1.8 | (−)5.8 | −4.9 | n.o. | −2.8 | n.o. | −1.9 | 5 |
| **11** | n.o. | −2.8 | (−)7.6 | −7.2 | n.o. | −2.7 | n.o. | −2.5 | New |
| **12** | (+)3.6 | +3.3 | (−)6.9 | −5.9 | n.o. | −1.2 | n.o. | −3.0 | New[c] |
| **13** | n.o. | +0.2 | (−)6.9 | −5.8 | n.o. | −1.6 | n.o. | −2.3 | New |
| **14**[b] | n.o. | +2.4 | (−)6.8 | −5.9 | n.o. | −1.0 | n.o. | −3.0 | 5 |
| **15** | n.o. | +0.8 | (−)6.8 | −5.9 | n.o. | −2.8 | n.o. | −2.8 | 5 |
| **16** | n.o. | +0.2 | (−)6.7 | −5.8 | n.o. | −3.5 | n.o. | −2.7 | 5 |
| **17** | n.o. | +0.9 | (−)6.6 | −5.7 | n.o. | −1.0 | (−)2.9 | −2.9 | New |
| **18** | (−)2.6 | −2.0 | (−)6.9 | −5.9 | (−)2.4 | −2.2 | (−)2.7 | −2.4 | New[c] |
| **19**[b] | (−)1.0 | −1.0 | (−)6.6 | −5.8 | (−)2.8 | −2.8 | (−)3.1 | −2.8 | New |
| **20** | n.o. | −0.6 | (−)6.5 | −5.6 | n.o. | −2.5 | n.o. | −2.6 | 5 |
| **21** | n.o. | −3.2 | (−)6.4 | −5.4 | n.o. | −3.4 | n.o. | −2.3 | New |
| **22** | n.o. | −1.2 | n.o. | −5.7 | n.o. | −1.0 | n.o. | −1.2 | |
| **23**[d] | n.o. | −0.3 | n.o. | −5.0 | n.o. | +1.3 | n.o. | −0.3 | |
| **24** | n.o. | −1.7 | n.o. | −5.6 | n.o. | −0.3 | n.o. | −1.7 | |
| **28**[d] | (−)2.4 | −1.9 | n.o. | −5.3 | n.o. | −1.5 | (−)2.4 | −1.9 | New |
| **31** | n.o. | −2.9 | n.o. | −5.5 | n.o. | −3.4 | n.o. | −2.9 | |
| **33** | n.o. | +2.0 | (−)5.2 | −4.2 | n.o. | −1.8 | n.o. | −2.1 | New |
| **34** | n.o. | +2.8 | (−)4.6 | −3.6 | (−)2.8 | −2.7 | (−)3.1 | −2.5 | New |
| **42** | (−)1.9 | −1.4 | n.o. | −4.4 | n.o. | −2.8 | (−)1.9 | −1.4 | 7 |
| **45** | (+)1.6 | +1.4 | (−)5.6 | −4.6 | n.o. | −0.3 | n.o. | +1.0 | New |
| **46** | (+)2.3 | +2.6 | (−)4.8 | −3.7 | n.o. | −1.8 | n.o. | +1.1 | New |

[a] Calculated for the only stable rotamer *syn*.

[b] Calculated for zero point energies 55% *syn*, $\Delta$ (*anti–syn*) = 0.20 kcal/mol.

[c] Only the relevant ${}^2J$(C2C6) coupling has already been reported in Reference[5]

[d] Averaged values.

pyridines. A notable exception is provided by the $NMe_2$ substituent whose range of influence on ${}^1J$(CC)'s extends over two bonds in each direction (Table 1, compounds **7**, **17** and **26**). An interesting feature of the pyridine system is that the influence of substituent on ${}^1J$(CC) depends on its position. Thus, the strongest influence is exerted by the substituents in position 2 while those of the substituents in position 3 or 4 are smaller and comparable to each other. In other words, for a given substituent X, the ${}^1J$(C3C4) coupling is practically the same for 4-X- and 3-X-pyridines. However, this does not hold for ${}^1J$(C2C3) and the corresponding 2- and 3-substituted derivatives. All these trends are valid for all of the substituents considered and are duly reproduced by the present computations.

The magnitudes of ${}^1J$(CC)'s in the heteroaromatics involved are roughly governed by the electronegativity of the first atom of the substituent. However, nitrogenous substituents like $NMe_2$ or $NO_2$ deviate from this simple rule as was shown by us for amino and nitro substituted nitrosobenzenes.[1]

The long-range carbon–carbon couplings collected in Tables 3 and 4 deserve a special comment. Those across three bonds are fairly strong as they span a range of 8.9 (${}^3J$(C3C6) in **2**) through 16.2 Hz (${}^3J$(C3C6) in **16**) and are invariably positive as is shown by the computation; they can be divided in two groups. One of them comprises ${}^3J$(CC)'s where one of the carbon atoms involved is $C_{ipso}$, that is, that bound directly to the substituent. This group includes ${}^3J$(C2C5)'s in 2-substituted pyridines as well as ${}^3J$(C3C6)'s in 3-substituted pyridines. Substituent effects on the latter are fairly weak and irregular. The other group contains ${}^3J$(CC)'s which involve a carbon atom located next to $C_{ipso}$; ${}^3J$(C3C6)'s in 2-substituted pyridines, ${}^3J$(C2C5)'s in 3-substituted pyridines and ${}^3J$(C2C5)/${}^3J$(C3C6)'s in 4-substituted pyridines belong to this group. All of the latter reveal a trend which is shown in Fig. 2.

There seems to be a nonlinear relationship between the coupling constants and the Pauling's electronegativity, $E_P$ of the first atom in the substituent concerned. The direction of the trend which shows that the coupling is enhanced by the decreasing

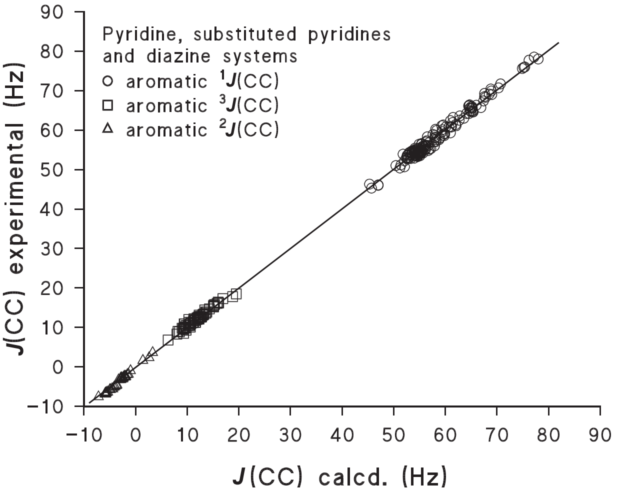


**Figure 1.** Experimental aromatic carbon–carbon coupling constants in pyridine, mono-, di- and tri-substituted pyridines, and some diazines, plotted against B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) calculated values. There are 276 individual coupling constants involved, and the relevant linear regression is shown according to Eqn (1)

electronegativity of substituent X, is just opposite to that observed in $^1J$(CC)'s which relate to $C_{ipso}$ (Table 1). The strongest $^3J$(CC)'s couplings, of *ca.* +15 Hz, are found for compounds **11**, **21** and **31** where the least electronegative trimethylsilyl substituent is involved whereas the smallest ones, of +8.9 and +9.9 Hz (compounds **2** and **12**, respectively), are found when the strongly electronegative fluorine substituent is involved. It is noteworthy that the effects on $^3J$(C2C5)'s of the substituents in positions 3 and 4 are almost the same, as was already observed for $^1J$(C3C4)'s which do not significantly depend on whether the substituent is in position 3 or 4.

In view of this, Fig. 2 presents a parabolic regression which involves a combined set of $^3J$(C2C5)'s in both 3- and 4-substituted pyridines, and the corresponding $E_P$ values for the first atoms in the substituents concerned: $SiMe_3$ (1.9); H, that is, pyridine, (2.2); $CH_3/CN$ (2.55); SMe (2.58); Br (2.96); Cl (3.16); $NMe_2/NO_2$ (3.04); OMe (3.41); F (3.98).[10] The parabolic regression yields the following equation for $^3J$(C2C5) as a function of $E_P$

$$^3J(\mathrm{CC})_{\mathrm{exp.}} = [0.82752(\pm 0.13654)E_P^2 - 7.4929(\pm 0.8069)E_P + 26.51(\pm 1.17)] \pm 0.25\,\mathrm{Hz} \qquad (3)$$

over a set of 21 datapoints and 18 degrees of freedom; the numbers following the ±sign are the corresponding standard errors of the mean for the three variables fitted, and the last one is the overall standard deviation for the least squares fit, $^3J$(CC) vs. $E_P$. For 4-F-pyridine **54** which is too unstable to withstand the *inadequate* NMR measurements, the value of $^3J$(C2C5) is obtained from the computation (Scheme 1) and the regression according to Eqn (1); the latter yields $^3J$(C2C5) = +9.7 Hz for **54**. An analogous correlation exists for $^3J$(C3C6)'s in 2-substituted pyridines, but we did not combine the latter data into the set of couplings considered in the correlation according to Eqn (3) (Fig. 2) as the relevant values for a given substituent are fairly close to each other for 3- and 4-substituted pyridines while those for 2-substituted pyridines deviate from the latter.

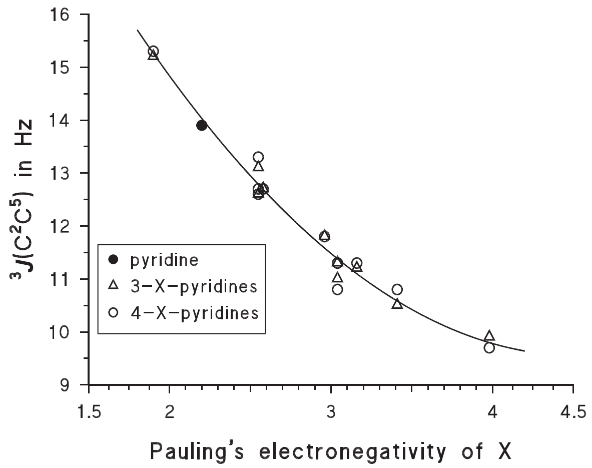


**Figure 2.** Experimental $^3J$(C2C5) coupling constants in 3- and 4-substituted pyridines plotted against the Pauling's electronegativity of the first atom of substituent X. The parabolic regression shown is according to Eqn (3)

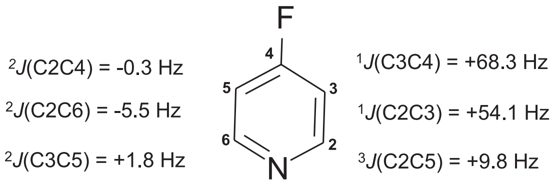
The couplings across two bonds can be divided into three distinct groups:

(i) The couplings where none of the carbons involved bear any substituent and the shortest formal pathway does not include $C_{ipso}$; all of them are negative and their values are fairly constant within the groups specified below:
$^2J$(C2C6) in 3- and 4-substituted compounds, *ca.* −7 and −5 Hz, respectively;
$^2J$(C3C5) in 2-substituted compounds, *ca.* −3 Hz;
$^2J$(C4C6) in 2- and 3-substituted compounds, *ca.* −2 and −3 Hz, respectively.

(ii) The couplings in which $C_{ipso}$ is directly involved; the $^2J$(CC)'s concerned algebraically increase with the increasing electronegativity of the substituent involved:
$^2J$(C2C4) in 2- and 4-substituted pyridines which span a range from *ca.* 0 to −3 Hz;
$^2J$(C2C6) in 2-substituted pyridines which attain values from *ca.* 0 to −8 Hz.

(iii) The third group involves couplings whose shortest formal pathway goes across $C_{ipso}$; they can be of either sign and their values algebraically increase with the increasing electronegativity of the substituent involved. These are:
$^2J$(C2C4) in 3-substituted compounds: *ca.* +3 to −3 Hz,
$^2J$(C3C5) in 4-substituted compounds: *ca.* +2 to −3 Hz.

Thus, it can be concluded that the couplings across two bonds, −7.6 through +3.6 Hz, are generally weaker than those across three bonds, +8.9 through +16.2 Hz. However, their range of variation is nearly twice as large as that indicated by their magnitudes, in view of the fact that they can bear either sign; thus the algebraical range of variation of aromatic $^2J$(CC)'s, about 11 Hz, exceeds that observed for $^3J$(CC)'s, about 7 Hz. This conclusion is new, and is based on the extensive set of experimental magnitudes of aromatic J(CC)'s employed here and combined with the present calculations, and on the excellent relationship found between experiment and theory which allows one to append signs to the experimental couplings even if their magnitudes are as low as 1 Hz. Needless to say, the range of aromatic $^2J$(CC)'s includes zero coupling so that ones which are close to the latter are likely to escape detection.



Computed $J$(CC)'s in 4-fluoropyridine **54**

**Scheme 1.** Carbon–carbon coupling constants in 4-fluoropyridine predicted by B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p) calculations

The computations can be employed in order to predict $J$(CC)'s in 4-fluoropyridine **54** (Scheme 1) which is obviously missing from the set of halogeno-substituted pyridines examined (Table 1).

The compound is unstable and readily undergoes polymerization; it can be kept only in the form of its hydrochloride. The predictions of carbon–carbon couplings in **54** are presented in Scheme 1, and they show that the estimates actually follow the trends in $^1J$(CC)'s which were discussed in the foregoing. For example, $^1J$(C3C4/C4C5) = 68.3 Hz predicted for **54** is fairly close to $^1J$(C3C4) = 69.0 Hz in 3-fluoropyridine **12** (Table 1) while the predicted $^1J$(C2C3) = 54.1 Hz for **54** does not significantly depart from the analogous value for pyridine **1** (Table 1).

## CONCLUSIONS

The large set of 276 experimental aromatic $J$(CC)'s considered in the present study, where about a half of these are new, shows that the couplings span a range of $-7.6$ through $+78.5$ Hz. This provided a sound experimental basis for exploring the potential of DFT quantum mechanical calculations from the point of view of aromatic carbon–carbon indirect couplings. The DFT computations employed, B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p), where the geometry optimization and the subsequent calculation of $J$(CC)'s are on the same level of sophistication, when confronted with the experiment, yield an excellent linear relationship which is sufficiently close to $J(\mathrm{CC})_{\mathrm{exp.}} = J(\mathrm{CC})_{\mathrm{calcd.}}$. It is demonstrated that the foregoing correlation can reliably predict or reproduce not only the magnitudes of the couplings but also the signs if the experimental magnitudes exceed about 1 Hz. The latter question is important for relatively weak aromatic $^2J$(CC)'s which have so far been assumed negative, by analogy with benzene, where the sign of $^2J$(CC) = $-2.5$ Hz was experimentally established.[11] In the present work, it is shown for the first time as far as pyridine and analogous heteroaromatics are concerned, that aromatic $^2J$(CC)'s can bear either sign and span a range of $-7.6$ through $+3.6$ Hz. If we combine these results with those obtained by us for benzene derivatives,[1,2] the overall range of aromatic $^2J$(CC)' turns out to be quite significant, $-7.6$ through $+7.8$ Hz.

Substituent effects on $^1J$(CC)'s in pyridines are significant but largely localized, that is, the couplings affected are those which include $C_{\mathrm{ipso}}$ and the neighbouring carbon(s); the coupling is augmented along the following sequence of substituents for a given position thereof (2-, 3- or 4-): $SiMe_3$, H, Me, SMe, CN, $NMe_2$ and Br, Cl, OMe, $NO_2$, F. Intuitively, this is a sequence of the increasing electron-withdrawing power, but not exactly in terms of Pauling's electronegativity of the first atom in a given substituent; the $NO_2$ group is a notable exception from the latter. The present calculations duly reproduce these trends in $^1J$(CC)'s.

The couplings across two bonds, $^2J$(CC)'s show analogous, albeit weaker effects of substituents, but solely in the cases where either $C_{\mathrm{ipso}}$ is directly involved or the coupling relates to the two closest neighbours of $C_{\mathrm{ipso}}$; thus the substituent effects here are fairly localized. The trend concerned is analogous to that observed for $^1J$(CC)'s, the coupling constant algebraically increase with the electron withdrawing power of the substituent involved. Again, all of this is reciprocated by our computations.

Three-bond couplings, $^3J$(CC), where $C_{\mathrm{ipso}}$ is directly involved do not show any regularity in their response to the presence of substituents, while the other couplings show clearly a trend whose direction is opposite to those for $^1J$(CC)'s and some of $^2J$(CC)'s. This is presented in Fig. 2. Needless to say, all of these regular trends as well as irregular variations are finely reproduced by our calculations.

The relationship between experiment and theory obtained in the present work as well as the fact that the computations even reproduce the less pronounced variations in the long-range $J$(CC)'s indicate that the role of any rovibronic effects and that of nuclear motions at 0 K are practically negligible for aromatic carbon–carbon couplings. This corroborates analogous conclusions drawn from our earlier studies on benzene and its substituted derivatives.[1,2]

Needless to say, all of the foregoing conclusions rely heavily on the extensive set of experimental data presented here, one which nearly doubles what has so far been available in the literature on aromatic $J$(CC)'s in pyridine and related systems.

## EXPERIMENTAL AND COMPUTATIONAL DETAILS

Most of the compounds subject to NMR measurements in the present work were available commercially (Aldrich), except for **9**,[12,13] **17**,[14] **19**,[13,15] and **28**[16] and which were synthesized according to published procedures. The purity of the samples was monitored by means of proton and carbon NMR. Generally the spectra were taken on 2 M solutions in $CDCl_3$ in standard 5 mm tubes. The carbon–carbon couplings were obtained from one-dimensional proton-decoupled $^{13}$C *inadequate* NMR spectra taken at 125 MHz ($^{13}$C) on a Bruker Avance DRX-500 system (11.7 T) with the Bruker standard microprogram, 32-phase Freeman cycle with automatic data storage. Typical conditions included acquisition time 2.4 s, digital resolution 0.16 Hz per point, and 215 cycles within 12 h.

The map of the molecular framework of carbon–carbon bonds which is obtained by the $^{13}$C *inadequate* sequence adjusted to typical magnitudes of $^1J$(CC)'s requires a point of anchorage in at least one of the carbon atoms concerned. In the present case of pyridine and azine systems, there is really no problem in obtaining unequivocal assignments of the $^1J$(CC)'s by the proton decoupled *inadequate* procedure as such, if the latter is supplemented by the relevant data on $^1J$(CH) couplings; one does not have to resort to any analogies in the carbon chemical shifts or the values of coupling constants with respect to simple model molecules, nor is there any need to employ quantum mechanical calculations for carbon resonance signal assignments. From this point of view, the characteristic *inadequate* $^{13}$C signals of pyridine are those for C2 and C6 as they show $^1J$(CC) coupling to only one $^{13}$C nucleus, that of C3 or C5, respectively. If a substituent is present at any of the pyridine ring carbon atoms, the $^{13}$C resonance of the latter does not show any $^1J$(CH) coupling; in some cases, where the substituent contains a carbon atom bonded directly to the ring (e.g. Me, CN, COMe) then $^1J$(CC) across the single bond concerned appears in the *inadequate* resonance signals of these two atoms. For fluorine substituent $^1J$(CF) is found in the *inadequate* resonance signal of the carbon atom which bears the substituent. All of this was more than enough to produce unequivocal assignments for the $^{13}$C resonance signals and, in consequence, for the relevant $^1J$(CC), $^2J$(CC) and $^3J$(CC) indirect spin–spin couplings. As we were interested not only in $^1J$(CC)'s, but also in the significantly weaker couplings across more than one aromatic bond, the latter were measured in separate experiments where the $^{13}$C *inadequate* pulse sequence was tailored to fit their average magnitudes.

As far as *J*(CC) measurements quoted from the literature are concerned (Tables 1–4) chloroform-$d_1$ was employed as a solvent for compounds **3**, **11**, **13**, **21**, **31** and **43**; acetone-$d_6$ for compounds **1**, **4–6**, **10**, **14–16**, **20**, **23–25**, **30**, **42**, **47–53**; DMSO-$d_6$ for compounds **22**, **27**, **32** and **35**; compound **29** was a neat liquid.

The *J*(CC) computations and geometry optimizations employed the Gaussian 03 (revision B.05) software package[17] where the Fermi contact term (FC) is calculated together with contributions of paramagnetic (PSO) and diamagnetic (DSO) spin–orbital interactions, as well as the spin-dipole term (SD). DFT was employed in order to account for electron–electron interactions, using the hybrid B3PW91 functionals together with the 6-311++G(d,p) set of basis functions; this selection was based on our previous experience with nitrogen nuclear magnetic shielding computations[18,19] as well as on our results for *J*(CC)'s in substituted benzenes.[1,2] Attention is drawn to the fact that B3PW91/6-311++G(d,p) geometry optimizations were run prior to the computations of the respective *J*(CC)'s where the same combination of functional/(basis set) was engaged; in this way, the whole of the computation procedure is internally consistent and can be described, in a shorthand notation, as B3PW91/6-311++G(d,p)//B3PW91/6-311++G(d,p). Vibrational frequency computations were routinely employed as a test for reaching an energy minimum.

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