The NMR indirect nuclear spin–spin coupling constants for some small rigid hydrocarbons: molecular equilibrium values and vibrational corrections

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Abstract

The indirect nuclear spin–spin coupling constants of allene and of two sterically strained hydrocarbons – cyclopropane and cyclopropene – calculated at different levels of electronic-structure theory are compared with each other and with experimental equilibrium constants, obtained from experiment by subtracting calculated vibrational contributions. It is found that, even in a relatively small basis set, the coupled-cluster singles-and-doubles (CCSD) method provides very good results, outperforming the other ab initio methods considered in this work – namely, the second-order polarization propagator approximation (SOPPA) and the multiconfigurational self-consistent field (MCSCF) approach. Calculations in the same basis set are also carried out at the hybrid level of density functional theory (DFT). Compared with the experimental equilibrium values the CCSD method gives the best results for the ab initio methods, while SOPPA consistently performs better than RASSCF. Hybrid DFT performs as well as SOPPA for the one-bond coupling constants, while, for the other constants, it provides results of similar quality as CCSD. The DFT approximation is also used to evaluate the indirect nuclear spin–spin coupling constants and their vibrational corrections for the larger cyclobutene and cyclobutane molecules.

1. Introduction

The indirect nuclear spin–spin coupling constants of nuclear magnetic resonance (NMR) spectroscopy may nowadays be calculated by a variety of electronic-structure methods [1], the most popular ab initio methods being multiconfigurational self-consistent field (MCSCF) theory [2–9], the second-order polarization propagator approach (SOPPA) [10–15], and coupled-cluster theory [16–23]. Density functional theory (DFT) has also become a popular tool for the calculation of spin–spin coupling constants, after the first implementations by Malkin et al. [24] and by Dickson and Ziegler [25]. However, these early attempts had some disadvantages, in particular the omission of the spin–dipole terms. Recently, Sychrovský et al. [26], Helgaker et al. [27], and Autschbach and Ziegler [28] independently presented fully analytical spin–spin implementations at the hybrid level of DFT, including all terms in Ramsey’s theory, and demonstrating that hybrid theory represents a reliable and inexpensive method for the calculation of such constants.

The importance of the rovibrational contribution to the indirect nuclear spin–spin coupling constants has been emphasized in many studies [2,6,8,10–12,29–34]. As discussed in a recent DFT study [35], the discrepancies between the spin–spin coupling constants calculated theoretically and those observed experimentally are about as large as the rovibrational contributions to these constants. Clearly, to benchmark the performance of the different theoretical methods for the calculation of spin–spin coupling constants, we need to include in our calculations the rovibrational contributions. In addition, for a meaningful comparison with experiment, we should also include the effects of solvation on the spin–
spin coupling constants. However, for molecules subject to small intermolecular forces, these effects are relatively unimportant [36–39]. Hence, for such molecules at least, it has now become possible, by correcting the experimental coupling constants for molecular motion, to compare meaningfully experimental and calculated spin–spin coupling constants, thus enabling a systematic evaluation of the quality of the different computational methods.

Although the inclusion of rovibrational contributions has helped to clarify the picture regarding the relative performance of the different theoretical methods [35], no systematic comparison of the performance of different methods has been carried out. In the present study, we investigate the performance of the four most popular methods for the calculation of indirect spin–spin coupling constants – namely, MCSCF, SOPPA, CCSD, and DFT – in calculating the coupling constants for three rigid hydrocarbons: allene (C3H4), cyclopropane (C3H6), and cyclopropene (C3H4). In these small molecules, there are no torsional corrections to the indirect spin–spin coupling constants, only vibrational and rotational ones.

In this paper, the rovibrational contributions to indirect spin–spin coupling constants are approximated as the zero-point vibrational (ZPV) contributions [35]. Apart from the usual identification of the experimentally observed couplings with the isotropic part of the coupling tensors, the effects of molecular rotation are ignored. In addition, all contributions from excited vibrational states are ignored. However, the available investigations of temperature effects [11–13,30,32,34,40] indicate that rovibrational contributions to the indirect spin–spin coupling constants change only by about 10% when the temperature is increased from 0 to 300 K [41]. The calculated indirect spin–spin coupling constants are compared with experiment by subtracting the ZPV contributions from the experimentally measured values, providing in this manner a set of empirical equilibrium values, \( J_{\text{emp}} = J_{\text{tot}} - J_{\text{vib}} \). Finally, the indirect nuclear spin–spin coupling constants and their ZPV corrections are calculated by DFT for two larger sterically strained hydrocarbons – namely, cyclobutane (C4H8) and cyclobutene (C4H6).

### 2. Computational details

Unless otherwise stated, the equilibrium indirect spin–spin coupling constants were calculated at the DFT optimized geometry, using the hybrid three-parameter Becke–Lee–Yang–Parr (B3LYP) functional [42,43] in the HIII basis [44–46]. For the calculation of the equilibrium spin–spin coupling constants at these geometries, we used the HIIsu2 basis [4,35]. A description of the basis sets used in this work is given in Table 1. The adequacy of these basis sets for the calculation of equilibrium and vibrationally corrected spin–spin coupling constants within DFT has been documented elsewhere – see [27,35]. However, although the HIIsu2 basis gives acceptable results for DFT [47], it is probably too small to recover fully the correlation contribution to the indirect spin–spin coupling constants at the CCSD level of theory; its use in the CCSD calculations was dictated by practical considerations.

At the SOPPA level, we have also analysed the Fermi-contact contributions using the much larger HuzIII-su6 basis set. For the one-bond coupling constants, the largest difference with respect to the HIIsu2 numbers is 4.9 Hz for the largest coupling constant, \( J(C_1, H_1) \) in cyclopropene (see Fig. 2). For the other coupling constants the change are usually less than 0.5 Hz, only being larger for \( J(C, C) \) and \( J(H, H) \) in allene and \( J(C, H) \) in cyclopropene.

In all calculations presented here, all four Ramsey contributions to the indirect spin–spin coupling constants – that is, the dia- and paramagnetic spin–orbit contributions, the spin–dipole contribution, and the Fermi-contact contribution – were calculated. However, we shall not discuss the individual contributions here, but note that for most of the coupling constants – in particular, for the large ones – the Fermi-contact contribution dominates.

The ZPV corrections to the spin–spin coupling constants were calculated at the B3LYP level of theory, using the approach described in [35]. Following the procedure advocated in that paper, the Fermi-contact contribution to the ZPV correction was calculated using the HIIsu2 basis set, whereas the HII basis was used for the other contributions. This approach provides ZPV corrections almost identical to the B3LYP/HIIsu2 results, which in turn are very close to the B3LYP/HIVsu4 results [35].

In all DFT spin–spin calculations presented here, the B3LYP functional was employed. In the MCSCF calculations, we used restricted-active-space (RAS) SCF wavefunctions, with RAS2 comprising all the occupied orbitals and with all single and double excitations allowed into a set of 16–28 RAS3 orbitals. All MCSCF and SOPPA calculations in this paper were performed with Dalton 1.2 [48]. For the DFT calculations of equilibrium and vibrationally averaged spin–spin coupling constants, we used a development version of the Dalton program. In the CCSD calculations, the spin–spin coupling constants were calculated as second derivatives of the electronic energy without orbital relaxation, an approach developed by Gauss and Stanton.

<p>| Table 1 |</p>
<table>
<thead>
<tr>
<th>Basis sets used in the calculations</th>
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<tr>
<td></td>
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<tr>
<td>HII</td>
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<tr>
<td>HIIsu2</td>
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<tr>
<td>HIII</td>
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(for a review, see [49]). We note that, for the spin–spin coupling constants, this approach differs from the EOM-CCSD method. The CCSD calculations were carried out using a program based on ACES II [50]. Recently, this approach to the calculation of spin–spin coupling constants has been extended to include triple excitations [21].

3. Comparison of the computational models

In this section, the relative performance of the MCSCF, SOPPA, CCSD, and DFT methods is examined by comparing the calculated spin–spin coupling constants of allene, cyclopropane, and cyclopone with one another and with a set of experimentally derived equilibrium constants. We begin by considering in Section 3.1 the geometries used in the spin–spin calculations; next, we consider in Sections 3.2–3.4 the results for each molecule in turn.

3.1. Geometry considerations

Two of the three molecules considered in this section are sterically strained, suggesting that the choice of geometry for the spin–spin calculations is critical. Clearly, the geometry should be chosen in the same manner for all methods; also, at the chosen geometry, the calculated spin–spin coupling constants should not differ too much from those obtained at the true equilibrium geometry. In this paper, we have calculated the coupling constants at the geometries optimized at the B3LYP level in the HIII basis. These geometries are listed in Table 2, along with a set of empirical equilibrium geometries [51–53].

In Tables 3–5, we have listed the DFT spin–spin coupling constants for allene, cyclopropane, and cyclopone, calculated at the optimized and empirical equilibrium geometries; in addition, the ZPV contributions to the coupling constants are listed. For the small couplings, the difference in the geometry may be important, affecting the coupling constants by up to 10%. Nevertheless, in nearly all cases, the ZPV contribution is much larger than the difference between the calculated coupling constants at the two geometries. In the few cases where this is not true, the ZPV contribution is negligible – except for the $J_{(H, H)}$ constants in allene and cyclopropane, which differ by more than 10% in the two geometries, while the ZPV contribution is of the same size or smaller. We conclude that, although the geometries used in this paper should not give coupling constants much different from those at the true equilibrium geometry, we should be cautious about the $J_{(H, H)}$ coupling constant in allene and cyclopropane. We also note that, if indirect nuclear spin–spin coupling constants are to be calculated to an accuracy of 1 Hz, an accuracy that current computational methods are rapidly approaching, then a good equilibrium geometry is required; even a slight change in geometry may affect some coupling constants more than 1 Hz.

3.2. Allene

In Table 6, the indirect nuclear spin–spin coupling constants calculated using MCSCF, SOPPA, CCSD,
The empirical equilibrium constants have been calculated as Table 6
larger than 1 Hz in magnitude) for all couplings except
pling constants, we find that these are substantial (i.e.,
mental values, the calculated ZPV correction, and the
and DFT are listed for allene, along with the experi-
results compare favorably with experiment, differing by
8–17 and 5–12 Hz, respectively. Moreover, from the fig-
ure, we also see that the CCSD results are consistently
better than the SOPPA results, which in turn are con-
sistently better than the RASSCF results. This clear-cut
picture of the relative performance of the three methods
emerges only since we compare with the experimentally
derived equilibrium constants – the experimentally ob-
served total \( J(C,H) \) constant, for example, is in fact
closer to the SOPPA result than to the CCSD result.

Just like the CCSD method, the RASSCF and
SOPPA methods give best results for the large coupling
constants; as the coupling constants decrease, their er-
rors do not decrease in proportion. Indeed, for the small
couplings, the SOPPA and RASSCF constants are up to
three and five times larger than the empirical constants,
respectively.

A comparison of the DFT results with the empirical
equilibrium values shows that the B3LYP functional
overestimates the magnitude of the indirect spin–spin
coupling constants. This consistent overestimation
occurs only when tight \( s \) functions (necessary for an
accurate description of the core region and the Fermi-
contact interaction) are added to the basis set. This
particular behavior of the B3LYP functional has already

and DFT are listed for allene, along with the experi-
mental values, the calculated ZPV correction, and the
empirically derived equilibrium values.

Considering first the ZPV contribution to the cou-
pling constants, we find that these are substantial (i.e.,
larger than 1 Hz in magnitude) for all couplings except
\( J(C,C) \). For \( J(C,H) \), the ZPV contribution is as large
as 5.4 Hz. This is typical of the one-bond spin–spin CH
couplings, whose ZPV correction usually falls in the
range 4–6 Hz [12,35,47]. Although the remaining signi-
ificant ZPV contributions in allene are smaller, they are
significant compared with the electronic contribution –
that is, in all cases larger than 10% of the electronic
contribution; in the case of the geminal CH coupling, it
is approximately 50% of the electronic coupling.

Analyzing the calculated equilibrium spin–spin con-
stants and the empirical equilibrium values derived from
the experimental data in Table 6, we find that the CCSD
results compare favorably with experiment, differing by
less than 4 Hz from the available empirical equilibrium
values. In view of the rather small one-electron basis in
these calculations, the high quality of the CCSD results
is somewhat surprising – in general, we would expect
that a larger basis is needed to obtain good CCSD re-
sults for spin–spin coupling constants. However, we also
note that the relative error in the CCSD coupling con-
stants increases as the coupling constants become
smaller. Indeed, as the coupling constants decrease in
magnitude, the absolute errors remain more or less con-
stant – in the worst case (the geminal CH coupling),
the calculated CCSD constant of \(-4.9 \) Hz is more than
twice as large as the empirical constant of \(-2.3 \) Hz. The
main source of error is probably the small basis set ra-
ther than the neglect of triple and higher connected ex-
citations in the CCSD model [23].

A comparison with the empirical equilibrium coupling
constants indicates that, for allene, the performance of
the RASSCF and SOPPA methods is poorer than that of
the CCSD method. This is shown in Fig. 1, where the
deviations from empirical equilibrium constants are
plotted for the different methods. This figure clearly illus-
trates the superior performance of CCSD relative to SOPPA
and RASSCF. For RASSCF and SOPPA, the absolute
deviations from the empirical equilibrium constants are
8–17 and 5–12 Hz, respectively. Moreover, from the fig-
ure, we also see that the CCSD results are consistently
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Table 5

<table>
<thead>
<tr>
<th>Coupling</th>
<th>( J_{\text{eq}}^{\text{CCSD}} )</th>
<th>( J_{\text{eq}}^{\text{SOPPA}} )</th>
<th>( J_{\text{eq}}^{\text{RASSCF}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} - J_{\text{eq}}^{\text{CCSD}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} - J_{\text{eq}}^{\text{RASSCF}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} - J_{\text{eq}}^{\text{SOPPA}} )</th>
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<tr>
<td>( J(C,C) )</td>
<td>116.5</td>
<td>107.5</td>
<td>102.9</td>
<td>108.8</td>
<td>99.0</td>
<td>-0.3</td>
<td>98.7*</td>
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<td>( J(C,C) )</td>
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<td>( J(C,H) )</td>
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<td>( J(H,H) )</td>
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<td>-1.5</td>
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<td>-9.1</td>
<td>-6.0</td>
<td>-1.2</td>
<td>-7.1*</td>
</tr>
</tbody>
</table>

*Kalinowski et al. [60].

1 Koole et al. [61]. Another experimental value is 170.9 Hz from Kalinowski et al. [60].

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Table 6

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<th>( J_{\text{eq}}^{\text{SOPPA}} )</th>
<th>( J_{\text{eq}}^{\text{CCSD}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} - J_{\text{eq}}^{\text{RASSCF}} )</th>
<th>( J_{\text{eq}}^{\text{B3LYP}} - J_{\text{eq}}^{\text{SOPPA}} )</th>
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<td>-14.0</td>
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2 Koole et al. [61].
been observed with the HIIIsu6 basis for other organic molecules [47]. In allene, an increase from HIIIsu2 (used in our calculations) to HIIIsu6 increases the Fermi-contact contributions to $J(C, C)$ and $J(H, H)$ from 112.6 and 14.2 Hz to 115.0 and 14.6 Hz, respectively. This indicates that, even though at the B3LYP/HIIIsu2 level the coupling constants are overestimated, there is, in this particular basis, some cancellation of the basis-set error and the intrinsic error of the B3LYP functional.

From Table 6, we note that the performance of DFT is comparable to that of CCSD for the small coupling constants and to that of SOPPA for the large ones. Moreover, although the DFT maximum absolute error is about the same as for SOPPA, the mean absolute and mean absolute relative errors are much smaller. In fact, the DFT maximum relative error of about 50% is even smaller than that of CCSD theory. Similar to what has been found in [47], B3LYP provides a balanced description of the large and small coupling constants in allene.

### 3.3. Cyclopropane

For cyclopropane, the ZPV contributions to the spin-spin coupling constants are less important than for allene – in fact, from Table 7, we see that molecular vibrations are important only for $J(C, C)$, $J(C, H)$, and $J(H, H)$. Again, the ZPV contribution to $J(C, H)$ is large (4.9 Hz); for $J(C, C)$ and $J(H, H)_{\text{trans}}$, the contributions are smaller but large relative to the total couplings (18% and 11%, respectively).

Comparing the calculated indirect spin-spin coupling constants of cyclopropane in Table 7 and in Fig. 1 with one another and with the empirical equilibrium values, we note the same performance as for allene. The CCSD method gives results close to the empirical equilibrium values, deviating by only about 2 Hz or less. As for allene, the relative errors increase as the size of the coupling constants decreases, although this effect is not as pronounced as in allene with a maximum relative deviation of about 50%.

As for allene, the cyclopropane plots in Fig. 1 demonstrate that the CCSD model performs consistently better than the SOPPA model, which in turn performs better than the RASSCF model. Again, this clear-cut picture of their relative performances emerges only upon the inclusion of contributions from vibrational motion – without these corrections included, it would appear that the best results are obtained using SOPPA and RASSCF theory for $J(C, H)$, $J(H, H)_{\text{cis}}$, and $J(H, H)_{\text{trans}}$.

Just like the CCSD method, the SOPPA and RASSCF methods perform better for cyclopropane than for allene – the calculated SOPPA and RASSCF coupling constants are all within 10 and 7 Hz, respectively, of the empirical equilibrium values (compared with 17 and 12 Hz for allene); also the absolute relative errors are smaller. As for allene, the relative error increases for the smaller coupling constants, some of the smaller calculated constants being twice as large as the empirical ones. In passing, we note that our SOPPA value for $J(C, C)$ is very close to that of Krivdin et al. [15]. Using SOPPA with a modified correlation-consistent basis,
Indirect spin–spin coupling constants of cyclopropene (Hz). The empirical equilibrium constants have been calculated as $J_{eq}^{emp} = J_{eq}^{tot} - J_{vib}^{DFT}$

<table>
<thead>
<tr>
<th>$J_{(C, C)}$</th>
<th>$J_{(C, H)}$</th>
<th>$J_{(C, H)}$</th>
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<td>5.0</td>
<td>3.1</td>
<td>1.9</td>
<td>1.8</td>
</tr>
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</table>

$a$ See Barszczewicz et al. [3].
$b$ Günther and Seel [63].
$c$ Kamienieńska-Trela et al. [54].
$\pm$ Reported as $\pm(1.3-1.4)$; Baldwin and Reddy [64].
$\pm$ Sign according to our calculations.

For DFT, the performance for cyclopropane in Table 7 is again much like that for allene – all coupling constants are overestimated except $2J_{(C, H)}$, which is underestimated by only 0.2 Hz. For the smaller coupling constants, DFT seem to give results of similar quality as the CCSD method; however, for $1J_{(C, H)}$ – the only large coupling constant in cyclopropane – the CCSD result is much better than the DFT result, which in turn is similar to the RASSCF and SOPPA results – see Fig. 1. Again the DFT relative errors are all small, being less than 20% for all coupling constants in cyclopropane, giving a mean absolute relative error that is smaller than all other methods.

We finally note that the calculated DFT spin–spin coupling constants do not change much when the basis is increased to HIIIsu6 [47], and that our $1J_{(C, C)}$ value agrees well with the B3LYP value in [15].

3.4. Cyclopropene

With respect to the ZPV corrections to the coupling constants of cyclopropene in Table 8, we find that these are substantial for five of the 10 coupling constants: $1J_{(C_1, H_3)}$, $1J_{(C_1, H_1)}$, $2J_{(C_1, H_2)}$, $2J_{(H_3, H'_1)}$, and $3J_{(H_1, H_2)}$. As for allene and cyclopropane, the ZPV corrections to the one-bond CH coupling constants are large (4–5 Hz); for the other three coupling constants, it is their relative size (15–30%) that makes them important.

For the ab initio methods, we see from Fig. 1 the same pattern as for the two previous molecules. Thus, having corrected for vibrations, we find that the CCSD method performs consistently better than the SOPPA method, which in turn outperforms the RASSCF method. Moreover, the maximum absolute errors are similar to (albeit slightly larger than) those in allene and cyclopropane: 18.0, 9.7, and 6.4 Hz for RASSCF, SOPPA, and CCSD, respectively. Also, as previously observed, the relative errors increase as the couplings decrease – for cyclopropane, the RASSCF, SOPPA, and CCSD values for the smallest constant are, respectively, five times, four times, and two times larger than the empirical equilibrium value.

As for allene and cyclopropane, DFT overestimates the size of the equilibrium spin–spin coupling constants of cyclopropane – in particular, in the large HIIIsu6 basis [47]. For the small spin–spin couplings, DFT...
performs as well as the CCSD method; for the large couplings, its performance is similar to that of RASSCF and SOPPA methods, with a maximum absolute error of 16.5 Hz.

DFT calculations of the indirect spin–spin coupling constants of cyclopropene have already been presented by Kamieśka-Trela et al. [54]. Using the BP91 functional and the HIII (IGLO-III) basis, these authors obtained 53.9, 162.2, and 224.9 Hz, respectively, for the equilibrium values of $^1J(C_1,C_2)$, $^1J(C_3,H_3)$, and $^1J(C_1,H_1)$. Clearly, the BP91/HIII results agree much better with the corresponding empirical equilibrium values in Table 8 (57.3, 162, and 223.7 Hz) than do the B3LYP/HIII su2 results obtained by us (66.7, 174.9, and 239.7 Hz). In fact, the BP91/HIII results are also better than the CCSD results. We note, however, that B3LYP results of the same high accuracy have previously been obtained for several other organic molecules, using the HIII basis or similar, small basis sets [47]. As pointed out in [47], this good agreement with experiment is largely fortuitous, arising from a cancellation of errors in the exchange-correlation functional and in the basis set (i.e., the lack of tight $s$ functions).

For a better comparison with the BP91/HIII calculations on cyclopropene, we have carried out additional B3LYP calculations in the HIII basis, obtaining 66.2, 164.6, and 226.0 Hz for $^1J(C_1,C_2)$, $^1J(C_3,H_3)$, and $^1J(C_1,H_1)$, respectively. Clearly, for the CH couplings, there is essentially no difference between BP91 and B3LYP, confirming that the agreement between experiment and BP91/HIII for these couplings is fortuitous. By contrast, for $^1J(C_1,C_2)$, there is a significant difference between BP91/HIII (53.9 Hz) and B3LYP/HIII (66.2 Hz), the BP91 result being closer to experiment (57.3 Hz). Since the necessary augmentation of the HIII basis with steep $s$ functions will further increase the coupling constants by 2–3 Hz, it appears that, for the CC coupling at least, the BP91 functional performs better than the hybrid B3LYP functionals. Still, for a meaningful comparison of the BP91 and B3LYP functionals, it would be necessary to carry out a large number of spin–spin calculations in the same large basis, carefully comparing with empirical equilibrium coupling constants.

The indirect nuclear spin–spin coupling constants of cyclopropene have previously also been studied at the MCSCF level of theory [3]. However, the experimental estimates used in that work were mostly derived from data for other molecules such as propene. Having here carried out additional DFT calculations on propene itself, we can reproduce most of these values – for example, for $^2J(C_3,H_2)$ and $^2J(H_1,H_1)$, we obtain 6.8 and 1.4 Hz, respectively, compared with the experimental values of 5.0 Hz [55] and 2.2 Hz [56]. These DFT propene calculations suggest that our DFT results for cyclopropene are reliable and that there are significant differences between the two-bond coupling constants in propene and cyclopropene, thus explaining why there are some significant differences between the estimated experimental coupling constants of [3] and the cyclopropene results in this study – in particular, for the CCSD and DFT methods.

Comparing the RASSCF results in Table 8 with the MCSCF values in [3], we find that most constants differ by 10–15%. Significant discrepancies are found mainly for the hydrogen–hydrogen coupling constants. We believe that these discrepancies are due to the larger number of $s$ functions on the hydrogen atoms in the present work (7$s$ rather than 4$s$ as in [3]).

4. Four-carbon rings: cyclobutene and cyclobutane

Having discussed the indirect nuclear spin–spin coupling constants of three-carbon molecules, we now go on to consider two strained molecules containing four carbon atoms – namely, cyclobutene and cyclobutane. We shall treat these systems in the same manner as the smaller ones – that is, by comparing the calculated equilibrium coupling constants with a set of empirical equilibrium constants, obtained by subtracting calculated ZPV corrections from the experimentally observed total coupling constants. However, because of their larger size, these systems cannot be properly treated by the more expensive ab initio methods such as the MCSCF and CCSD methods. For cyclobutene and cyclobutane, therefore, we have restricted ourselves to DFT calculations of the indirect nuclear spin–spin coupling constants – see Table 9.

4.1. Cyclobutene

From Table 9, we see that the ZPV corrections in cyclobutene are significant for nine of 18 indirect spin–spin coupling constants. As for the smaller hydrocarbons in this paper, the vibrational contributions to the $^1J(C,H)$ couplings are quite large (4–5 Hz); the remaining significant ZPV corrections are smaller but large compared with the electronic contributions (10–70%).

Comparing the calculated and empirical equilibrium values, we find as before that the B3LYP functional tends to overestimate the equilibrium indirect spin–spin coupling constants; the largest absolute error of 12 Hz occurs for $^1J(C_1,H_1)$. The mean absolute relative error is 10%, which is similar to those of the smaller molecules.

More interestingly, the indirect nuclear spin–spin coupling across the CC double bond in cyclobutene has not been measured experimentally. In view of the systematic overestimation of spin–spin coupling constants by the B3LYP functional, it is possible to suggest a value
for this double-bond coupling constant. Thus, in allene and cyclopropene, the double-bond coupling constant is overestimated by 9.8 and 9.4 Hz, respectively. Assuming a similar overestimation in cyclobutene, we arrive at a $J_{\text{C1,C2}}$ equilibrium value of about 51 Hz and a total, vibrationally corrected value of about 52 Hz.

For the remaining unobserved coupling constants in cyclobutene, the magnitude of the overestimation is more uncertain. The B3LYP functional probably overestimates these coupling constants by up to 30%, perhaps more for the smallest coupling constants.

4.2. Cyclobutane

In cyclobutane, the treatment of the vibrational corrections to the indirect nuclear spin–spin coupling constants is complicated by a low-frequency puckering motion, arising from a double-well potential with a $D_{4d}$ inversion barrier of about 500 cm$^{-1}$ [57,58], well above the lowest vibrational levels [59]. Because of the tunneling between the two equivalent $D_{2d}$ minima [57], there is only one experimentally observed value for the one-bond pair $J_{\text{C1,H1}}$ and $J_{\text{C1,H2}}$ and similarly for the two-bond pair $J_{\text{C1,H1}}$ and $J_{\text{C1,H2}}$ – see Fig. 2. To make a comparison with the calculated equilibrium values for these constants, we have generated the empirical equilibrium constants listed in Table 9 in the following manner. Let us assume that, for the two couplings A and B, there is only one experimentally observed vibrationally averaged value $J_{\text{exp}}$. The empirical equilibrium values are then calculated from $J_{\text{eq}}$, the sum of the DFT vibrational contributions, and the difference of the DFT equilibrium values:

$$J_{\text{eq}} = J_{\text{exp}} + J_{\text{DFT}}$$

Table 9

<table>
<thead>
<tr>
<th>Coupling</th>
<th>$J_{\text{DFT}}$</th>
<th>$J_{\text{exp}}$</th>
<th>$J_{\text{DFT}}$</th>
<th>$J_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{\text{C1,C2}}$</td>
<td>60.4</td>
<td>57.2</td>
<td>1.3</td>
<td>(58.5)$^a$</td>
</tr>
<tr>
<td>$J_{\text{C1,C3}}$</td>
<td>31.6</td>
<td>31.1</td>
<td>1.0</td>
<td>32.1$^b$</td>
</tr>
<tr>
<td>$J_{\text{C1,C4}}$</td>
<td>25.1</td>
<td>25.0</td>
<td>1.3</td>
<td>26.3$^b$</td>
</tr>
<tr>
<td>$J_{\text{C1,H1}}$</td>
<td>-7.7</td>
<td>-9.4</td>
<td>0.5</td>
<td>-8.9$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H1}}$</td>
<td>176.8</td>
<td>164.7</td>
<td>3.9</td>
<td>181.6$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H2}}$</td>
<td>142.5</td>
<td>133.1</td>
<td>4.1</td>
<td>137.3$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H2}}$</td>
<td>1.2</td>
<td>2.0</td>
<td>-0.8</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H3}}$</td>
<td>-6.3</td>
<td>-0.1</td>
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<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H3}}$</td>
<td>5.7</td>
<td>-0.9</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H4}}$</td>
<td>-3.6</td>
<td>-1.3</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C1,H4}}$</td>
<td>7.5</td>
<td>1.6</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C2,H1}}$</td>
<td>14.1</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C2,H1}}$</td>
<td>-15.3</td>
<td>-0.9</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C2,H2}}$</td>
<td>5.2</td>
<td>0.3</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C2,H2}}$</td>
<td>2.0</td>
<td>0.5</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C2,H3}}$</td>
<td>3.3</td>
<td>0.4</td>
<td>1.2</td>
<td>1.2$^d$</td>
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<tr>
<td>$J_{\text{C2,H4}}$</td>
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<td>0.3</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
<tr>
<td>$J_{\text{C2,H4}}$</td>
<td>-1.3</td>
<td>0.0</td>
<td>1.2</td>
<td>1.2$^d$</td>
</tr>
</tbody>
</table>

$^a$ From a methyl-substituted compound [54].
$^b$ Efimov et al. [65].
$^c$ From a methyl-substituted compound [65].
$^d$ Kalinowski et al. [60].

Fig. 2. Numbering of atoms in cyclopropene, cyclobutene, and cyclobutane.
We have calculated the vibrational contributions for all modes in cyclobutane in the standard manner. For the puckering motion, such a local treatment is perhaps not fully satisfactory, making the vibrational corrections and hence the empirical coupling constants of cyclobutane more uncertain than those for the other molecules in this study. However, since a more advanced treatment would be much more expensive and since only the vibrational corrections would be affected, we have chosen to describe cyclobutane in this simple manner.

From Table 9, we see that the ZPV corrections in cyclobutane are significant for seven out of the 15 coupling constants. The ZPV correction to the \( J_{\text{eq}}(\mathbf{A}) \) coupling constants are of the expected size, while the remaining significant ZPV corrections are smaller but large compared with the calculated electronic contributions (10–50%). As for cyclobutene, DFT probably overestimates the unknown coupling constants by less than 30%, perhaps more for the smallest coupling constants.

5. Conclusions

In this paper, we compare the calculated indirect nuclear spin–spin coupling constants for allene, cyclopropene, cyclopropane, cyclobutene, and cyclobutane with experiment. For a valid comparison, we have generated a set of empirical equilibrium coupling constants by subtracting the vibrational corrections calculated by hybrid DFT from the experimentally observed total coupling constants. We emphasize that, since the spin–spin vibrational corrections are typically of the same order of magnitude as the differences between theory and experiment, such corrections should always be applied for a meaningful benchmarking of computational methods. On the other hand, these corrections may be calculated with sufficient accuracy at the hybrid DFT level.

For allene, cyclopropene, and cyclopropane, calculations were carried out at the MCSCF, SOPPA, CCSD, and DFT (B3LYP) levels of theory. In general, the effects of electron correlation are underestimated by MCSCF theory, somewhat better described by SOPPA, and well described by CCSD theory. Moreover, even though the molecules studied here are rather small (allowing us to use a fairly large RASSCF space), the description of dynamical correlation is incomplete in RASSCF theory, leading to an uneven quality of the calculated coupling constants. By contrast, this problem does not arise in SOPPA and CCSD theories, where correlation is carried out in the full orbital space. The quality of the B3LYP results is comparable to that of the best ab initio methods SOPPA and CCSD. For small molecular systems, it appears that the currently most accurate approach to the a priori calculation of indirect nuclear spin–spin coupling constants is to combine CCSD equilibrium constants with B3LYP vibrational contributions.

For larger molecules, it is more difficult to perform reliable ab initio studies, making hybrid DFT the method of choice for such systems. We here applied the hybrid B3LYP functional to the calculation of vibrationally averaged spin–spin coupling constants in cyclobutene and cyclobutane, comparing the results with the available measured coupling constants and predicting the remaining ones.

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References


\[ J_{\text{eq}}(\mathbf{A}) = J_{\text{ave}} - \frac{1}{2}[J_{\text{vib}}(\mathbf{A}) + J_{\text{vib}}(\mathbf{B})] + \frac{1}{2}[J_{\text{ave}}(\mathbf{A}) - J_{\text{ave}}(\mathbf{B})] \]

\[ J_{\text{eq}}(\mathbf{B}) = J_{\text{ave}} - \frac{1}{2}[J_{\text{vib}}(\mathbf{A}) + J_{\text{vib}}(\mathbf{B})] - \frac{1}{2}[J_{\text{ave}}(\mathbf{A}) - J_{\text{ave}}(\mathbf{B})] \]