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Non-empirical calculations of NMR indirect carbon–carbon coupling constants. Part 8[†] — Monocycloalkanes

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Carbon–carbon and carbon–hydrogen spin–spin coupling constants were calculated in the series of the first six monocycloalkanes using SOPPA and SOPPA(CCSD) methods, and very good agreement with the available experimental data was achieved, with the latter method showing slightly better results in most cases, at least in those involving calculations of $J(C,C)$. Benchmark calculations of all possible 21 coupling constants $J(C,C)$, $J(C,H)$ and $J(H,H)$ in chair cyclohexane revealed the importance of using the appropriate level of theory and adequate quality of the basis sets. Many unknown couplings in this series were predicted with high confidence and several interesting structural trends (hybridization effects, multipath coupling transmission mechanisms, hyperconjugative interactions) were elucidated and are discussed based on the present calculations of spin–spin couplings. Copyright © 2004 John Wiley & Sons, Ltd.

INTRODUCTION

Seven previous publications in this series devoted to three-membered rings,[1] strained polycycloalkanes,[2] polyhedranes,[3] bicycloalkanes,[4] bridged bicycloalkanes,[5] propellanes[6] and spiroalkanes[7] of up to 14 carbon atoms manifested a real breakthrough of *ab initio* methods based on the general SOPPA (Second-Order Polarization Propagator Approach) formalism[8,9] to calculate spin–spin coupling constants into the area of organic chemistry. The unprecedented reliability of SOPPA to calculate one-bond and long-range spin–spin coupling constants $J(C,C)$, $J(C,H)$ and $J(H,H)$ in a wide range of carbocyclic compounds has been manifested, however, leaving apart the classical series of monocycloalkanes. To fill this gap, we present here a comprehensive study of spin–spin coupling constants in the first six members of this series **1–6**.

Along with the standard SOPPA, we use here the so-called SOPPA(CCSD) method,[10,11] providing a combination of classical SOPPA with the CCSD (Coupled Cluster Singles and Doubles) computational scheme to test their relative merits.
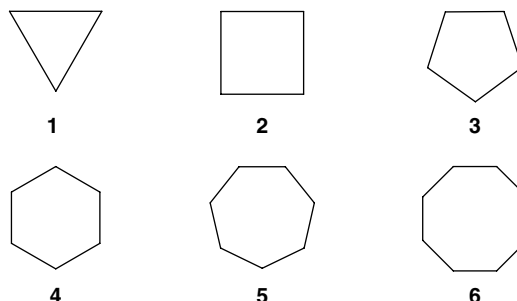
THEORETICAL METHODS

Since we use SOPPA(CCSD) for the first time in this series of publications, the general computational scheme to calculate spin–spin coupling constants within the Polarization Propagator approach and that in combination with coupled cluster single and double amplitudes are briefly outlined in this section.

Ramsey,[12] using non-relativistic quantum mechanics, originally derived the theory of the indirect nuclear spin–spin coupling constant J. The indirect nuclear spin–spin coupling constant is a second derivative of the electronic energy and the following expressions for the four contributions were derived[12] by second-order perturbation

theory:

$$J(A, B) = \frac{1}{3} \frac{\gamma_A \gamma_B}{h} \sum_{\alpha=x,y,z} \left\{ \langle \Psi_0 | \left(\hat{O}_{AB}^{OD} \right)_{\alpha\alpha} | \Psi_0 \rangle + 2 \sum_{n \neq 0} \frac{\langle \Psi_0 | \left(\hat{\hat{O}}_A^{OP} + \hat{\hat{O}}_A^{FC} + \hat{\hat{O}}_A^{SD} \right)_{\alpha} | \Psi_n \rangle \langle \Psi_n | \left(\hat{\hat{O}}_B^{OP} + \hat{\hat{O}}_B^{FC} + \hat{\hat{O}}_B^{SD} \right)_{\alpha} | \Psi_0 \rangle}{E_0 - E_n} \right\} \quad (1)$$

where the operators are defined as

$$\left(\hat{O}_{AB}^{OD} \right)_{\alpha\alpha} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^2 \hbar^2}{m_e} \sum_i \frac{\vec{r}_{iA} \cdot \vec{r}_{iB} - (\vec{r}_{iB})_{\alpha} (\vec{r}_{iA})_{\alpha}}{|r_{iA}|^3 |r_{iB}|^3} \quad (2)$$

$$\left(\hat{\hat{O}}_A^{OP} \right)_{\alpha} = \frac{\mu_0}{4\pi} \frac{e\hbar}{m_e} \sum_i \frac{(\vec{l}_{iA})_{\alpha}}{|r_{iA}|^3} \quad (3)$$

$$\left(\hat{\hat{O}}_A^{FC} \right)_{\alpha} = \frac{\mu_0 g_e e\hbar}{3 m_e} \sum_i (\vec{s}_i)_{\alpha} \delta(\vec{r}_{iA}) \quad (4)$$

and

$$\left(\hat{\hat{O}}_A^{SD} \right)_{\alpha} = \frac{\mu_0}{4\pi} \frac{g_e e\hbar}{2 m_e} \sum_i \frac{3(\vec{s}_i \cdot \vec{r}_{iA})(\vec{r}_{iA})_{\alpha} - \vec{r}_{iA}^2 (\vec{s}_i)_{\alpha}}{|r_{iA}|^5} \quad (5)$$

The magnetogyric ratio of the two nuclei A and B are γ_A and γ_B, $\vec{r}_{iA} = \vec{r}_i - \vec{R}_A$ is the difference of the position vectors of electron i and nucleus A, $\vec{s}_i$ is the electron i spin operator, $\vec{l}_{iA} = \vec{l}_i(\vec{R}_A)$ is the orbital angular momentum operator of electron i with respect to the position of nucleus A (in SI units), $\delta(x)$ is the Dirac delta function and all other symbols have their usual meanings.[13]

The coupling is transmitted by two basic mechanisms: (a) the interaction of the nuclear spins with the spins of the electrons expressed in the Fermi-contact (FC) and spin-dipolar (SD) contributions and (b) the interaction of the nuclear spins with the orbital angular momentum of the electrons which gives rise to the orbital paramagnetic (OP) and orbital diamagnetic (OD) contributions. Due to the interaction with the electron spin, the FC and SD terms arise from interaction of excited triplet states $|\Psi_n\rangle$ with the singlet ground state $|\Psi_0\rangle$, whereas the OP term involves excited states $|\Psi_n\rangle$ of the same spin symmetry as the ground state $|\Psi_0\rangle$ and the OD term is a purely ground-state property, although the latter may also be expressed in a form which involves excited states.[14] Using polarization propagator[15,16] or linear response function methods,[17] all contributions to the coupling constants can be evaluated without explicit calculation of the excited states involved.[18]

Formally, a polarization propagator can be defined by its spectral representation:[15,16]

$$\langle \langle \hat{O}_A; \hat{O}_B^{\omega} \rangle \rangle_{\omega} = \sum_{n \neq 0} \left\{ \frac{\langle \Psi_0 | \hat{O}_A | \Psi_n \rangle \langle \Psi_n | \hat{O}_B^{\omega} | \Psi_0 \rangle}{\hbar\omega + E_0 - E_n} + \frac{\langle \Psi_0 | \hat{O}_B^{\omega} | \Psi_n \rangle \langle \Psi_n | \hat{O}_A | \Psi_0 \rangle}{-\hbar\omega + E_0 - E_n} \right\} \quad (6)$$

However, for practical applications, the polarization propagator is projected[19] into a complete space of excitation and de-excitation operators $\{h_n\}$ with respect to the exact reference state $|\Psi_0\rangle$:

$$\langle \langle \hat{O}_A; \hat{O}_B^{\omega} \rangle \rangle_{\omega} = \langle \Psi_0 | \left[\hat{O}_A, \tilde{\mathbf{h}} \right] | \Psi_0 \rangle \langle \Psi_0 | \left[\mathbf{h}^{\dagger}, \hbar\omega\tilde{\mathbf{h}} - \left[\hat{H}, \tilde{\mathbf{h}} \right] \right] | \Psi_0 \rangle^{-1}$$
$$\times \langle \Psi_0 | \left[\mathbf{h}^{\dagger}, \hat{O}_B^{\omega} \right] | \Psi_0 \rangle \quad (7)$$

Equation (7) is the starting point for several polarization propagator approximations. In the random phase approximation[20,21] (RPA), which can also be considered as a first-order polarization propagator approximation[18,22] and is equivalent[16,18] to the coupled Hartree–Fock[23] or time-dependent Hartree–Fock method,[24] the reference state $|\Psi_0\rangle$ is approximated by the Hartree–Fock self-consistent field wavefunction $|\Phi_{SCF}\rangle$ and the set of operators $\{h_n\}$ consists of single excitation and de-excitation operators with respect to $|\Phi_{SCF}\rangle$, i.e. the so-called orbital rotation operators.[25] In the second-order polarization propagator approximation[8,9] (SOPPA), a Møller–Plesset expansion for the wavefunction[26,27] is used as the reference state:

$$|\Psi_0\rangle = N \left(|\Phi_{SCF}\rangle + |\Phi^{(1)}\rangle + |\Phi^{(2)}\rangle + \cdots \right)$$
$$= N \left(|\Phi_{SCF}\rangle + \frac{1}{4} \sum_{aibj} {}^{(1)}\kappa_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{ai} {}^{(2)}\kappa_i^a |\Phi_i^a\rangle \right.$$
$$\left. + \frac{1}{4} \sum_{aibj} {}^{(2)}\kappa_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \cdots \right) \quad (8)$$

and double excitation and de-excitation operators are added to the set of operators $\{h_n\}$. The wavefunctions $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$ are obtained by replacing the occupied orbitals i and j in the Hartree–Fock self-consistent field wavefunction $|\Phi_{SCF}\rangle$ by the virtual orbitals a and b and the expansion coefficients ${}^{(1)}\kappa_{ij}^{ab}$, ${}^{(2)}\kappa_i^a$, ${}^{(2)}\kappa_{ij}^{ab}$ are the so-called Møller–Plesset correlation coefficients. All matrix elements involving single (de-)excitation operators in Eqn (7) are then evaluated to second order in the fluctuation potential, which is the difference between the instantaneous interaction of the electrons and the averaged interaction as used in the Hartree–Fock approximation. Matrix elements with single and double (de-)excitation operators are evaluated to first order and pure double (de-)excitation matrix elements only to zeroth order. With this definition of SOPPA, only the single excited terms in the second-order correction to the wavefunction $|{}^{SE}\Phi^{(2)}\rangle = \sum_{ai} {}^{(2)}\kappa_i^a |\Phi_i^a\rangle$ are needed.

In the SOPPA(CCSD) method,[10,11] SOPPA with coupled cluster single and double amplitudes, the Møller–Plesset correlation coefficients $^{(1)}\kappa_{ij}^{ab}$ and $^{(2)}\kappa_i^a$ are replaced in all SOPPA matrix elements by the corresponding coupled cluster single and double amplitudes t_i^a and t_{ij}^{ab}. A similar method had been put forward earlier by Geertsen and co-workers, but not all correlation coefficients were replaced.[28]

For a closed-shell system, the ansatz for the wavefunction in coupled cluster single and double theory[29,30] is written as

$$|\Psi_{CC}\rangle = e^T|\Phi_{SCF}\rangle \tag{9}$$

where the cluster operator T is

$$T = T_1 + T_2 \tag{10}$$

Acting on $|\Phi_{SCF}\rangle$, the single excitation cluster operator T_1 generates a linear combination of all singly excited wavefunctions $|\Phi_i^a\rangle$ with the coupled cluster single amplitudes as coefficients:

$$T_1|\Phi_{SCF}\rangle = \sum_{ai} t_i^a|\Phi_i^a\rangle \tag{11}$$

Correspondingly, the double excitation cluster operator T_2 generates a linear combination of doubly excited wavefunctions:

$$T_2|\Phi_{SCF}\rangle = \frac{1}{4}\sum_{aibj} t_{ij}^{ab}|\Phi_{ij}^{ab}\rangle \tag{12}$$

Inserting the coupled cluster wavefunction in Eqn (9) in the Schrödinger equation and pre-multiplying with e^{-T}, one obtains the coupled cluster Schrödinger equation:

$$e^{-T}H|\Psi_{CC}\rangle = E_{CC}|\Phi_{SCF}\rangle \tag{13}$$

Equations for the coupled cluster single and double amplitudes, t_i^a and t_{ij}^{ab}, are then obtained by projecting Eqn (13) on all singly and doubly excited wavefunctions, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$:

$$\langle\Phi_i^a|e^{-T}He^T|\Psi_{SCF}\rangle = 0 \tag{14}$$

$$\langle\Phi_{ij}^{ab}|e^{-T}He^T|\Psi_{SCF}\rangle = 0 \tag{15}$$

These coupled cluster equations are a coupled set of equations, which are non-linear in the amplitudes. Therefore, they have to be solved iteratively. In the first iteration, all coupling and non-linear terms are typically set to zero and the result for the double amplitudes is equal to the first-order Møller–Plesset correlation coefficients $^{(1)}\kappa_{ij}^{ab}$.

Since $^{(1)}\kappa_{ij}^{ab}$ are the results of the first iteration in the iterative solution of the coupled cluster single and double equations, one would expect that replacement with the converged amplitudes will improve the description of the reference state and hence the result of a polarization propagator calculation. Previous calculations of polarizabilities[10,31]

and in particular of indirect nuclear spin–spin coupling constants[11,32–34] showed that this is indeed the case.

The detailed scheme for calculations of indirect nuclear spin–spin coupling constants using polarization propagator methods has been described and explained previously[11,35] and will not be given here.

RESULTS AND DISCUSSION

Conformations and geometric parameters

Since the pioneering evidence of chair cyclohexane obtained by Hassel[36] via observation of its electron diffraction (ED) in the gaseous phase, a vast amount of data has appeared dealing with the stereochemistry and conformational analysis of monocycloalkanes, both theoretical[37] and experimental,[38] which have revealed a complete set of true minima and saddle structures, together with an entire network of conformational interconversions in every particular case. The most interesting results are as follows.

Cyclopropane (*1*)

Cyclopropane is the only planar and conformationally rigid monocycloalkane in this series with ideally eclipsed C—H bonds. It is noteworthy that endocyclic carbon–carbon bonds of the cyclopropane ring are substantially shortened (ca 1.51 Å) according to x-ray[39] and ED[40] results (1.508 Å from the present B3LYP/6–311G** calculations), reflecting its considerable steric strain.[41] Indeed, recent full-valence bond calculations within the active space defined by the spin-coupled orbitals revealed that the nuclear framework of cyclopropane is held together by *bent* bonds, which supports the classical model of Coulson and Moffitt rather than the idea of a two-electron, three-center bond of Walsh: due to the particular geometry of the cyclopropane nuclear framework, the participating orbitals have to bend in order to reduce strain and to be able to overlap more efficiently.[42] Steric strain and the electronic structure of cyclopropane are discussed in full elsewhere.[43]

Recently, the experimental ED geometry of cyclopropane has been revised[44] on the basis of CCSD(T) and MP4 calculations and the anharmonic force field, and this paper shows how a more accurate geometry can be obtained by combining the high-level quantum chemical calculations and experiment. The r_e structure of cyclopropane derived in the latter paper[44] from the experimental rotational constants is as follows: $r_e(CC) = 1.5030(10)$ Å, $r_e(CH) = 1.0786(10)$ Å and $r_e(HCH) = 114.97(10)°$, which seems to be the most reliable geometry of this unique carbocycle determined so far.

Cyclobutane (*2*)

Cyclobutane has long been recognized as a non-planar molecule bent across the diagonal with a puckering angle $\theta = 25–30°$, as seen from x-ray,[45] ED,[46,47] MW[48] and other spectroscopic data,[49] in line with DFT[50,51] calculations. Originally,[52] the equilibrium structure of cyclobutane was calculated by single determinant restricted Hartree–Fock theory using an extended basis set of Gaussian orbitals augmented by polarization functions; the molecule was found to be non-planar with a degree of puckering of 0.23 Å and a barrier to planarity of 0.9 kcal mol^{-1}.

Our present B3LYP/6–311G** value of $\theta = 24.3°$ is in good agreement with the corresponding B3LYP/6–311++G (3df,pd) result of 25.3° reported by Palafox *et al.*[51] It is interesting that semiempirical methods fail to establish the cyclobutane ring puckering, giving a planar form which is actually a saddle point between two degenerate bent equilibrium structures, as follows from the harmonic vibrational frequencies analysis.[50]

Cyclopentane (3)

Cyclopentane can be represented as a free pseudorotating five-membered ring; each conformation of cyclopentane in its pseudorotational movement can be described by two parameters, the pseudorotational phase angle and the puckering amplitude,[53] both of which can be calculated from the five momentary endocyclic torsion angles of the ring and related to NMR spin–spin coupling constants, which can be expressed as a function of puckering coordinates.[54] Accordingly, any momentary conformation of cyclopentane undergoing fast ring pseudorotation and fast ring inversion can be described as a superposition of envelope (C_s symmetry) and twist (C_2 symmetry) true minima energetically degenerated conformers and one saddle planar (D_{5h} symmetry) form.[54] The puckering amplitude of cyclopentane spans from 0.43 to 0.47 Å, as follows from ED,[55] IR[56] and Raman spectroscopic[57] studies, along with NMR measurements in the nematic phase[58] and most recent *ab initio* calculations on the correlated level.[54] According to our present B3LYP/6–311G** results, the averaged puckering (folding) angle of cyclopentane ring could be very roughly estimated as $\theta \approx 40°$, which is ca 15° larger than that of cyclobutane. In other words, the five-membered ring of cyclopentane is much more bent than that of cyclobutane. However, it should be kept in mind that the puckering angle of the cyclopentane envelope is rather arbitrary in nature and could not be explicitly defined owing to pseudorotation.[53] In its derivatives, cyclopentane adopts an envelope conformation, as manifested by x-ray[59] and NMR[60] measurements.

Cyclohexane (4)

Cyclohexane is the most classical representative in this series owing to its remarkable conformational behavior, which laid the groundwork for the modern conformational analysis. As we have already mentioned, the first experimental evidence of chair conformation of cyclohexane was put forward by Hassel,[36] who showed that cyclohexane itself possesses D_{3d} symmetry with two geometrically different types of C—H bonds. The six bonds of the first type are parallel to the principal axis of the molecule and the six other bonds form an angle of 109°28′ with this direction and the conversion of the molecule between these two possible models of D_{3d} symmetry transforms C—H bonds of different types into each other. The complete structure of chair cyclohexane was deduced later from the rotational MW spectra of its selectively deuterated isotopic species.[61,62] Also, IR[63] and Raman[64] spectra and x-ray[65] and molecular optical rotation[66] revealed a predominantly chair conformation.

Axial carbon–hydrogen bonds are weaker and longer, as a result of hyperconjugative interaction of bonding and antibonding orbitals of the adjacent C—H bonds (see below). According to our present calculations, the axial and equatorial carbon–hydrogen bond lengths are 1.099 and 1.096 Å, respectively, in very good agreement with the corresponding DFT results (1.100 and 1.098 Å, respectively) of Juaristi *et al.*[67] Carbon–carbon bond lengths were measured also in solid cyclohexane by the EXAFS technique.[68]

In the most recent and comprehensive theoretical paper by Lee,[69] the binding energies and the geometric structures of conformational isomers of cyclohexane were determined from DFT combined with ultrasoft pseudopotentials and gradient-correlated non-local exchange-correlation functionals. It has been shown[69] that the chair conformation converts to another chair conformation via a half-chair conformation (ring inversion), whereas the twist-boat conformation converts to another twist-boat conformation via a pure boat conformation (pseudorotation), in line with molecular dynamics[70] and other earlier[71] calculations. Geometry and conformational modes of cyclohexane were recently reviewed in detail by Cremer and Szabo.[72]

Cycloheptane (5)

Several theoretical papers[73] were devoted to conformational analysis and the study of pseudorotation paths of cycloheptane. They revealed a predominant low-symmetry (C_2) twist-chair ground-state structure with a smaller contribution of the other high-energy conformations (chair, twist-boat and boat). In accordance with those results, the saturated seven-membered rings in a large number of cycloheptane derivatives adopt the same minimum-energy twist-chair conformation, as follows from the numerous x-ray,[74] NMR,[75] IR[76] and other experimental data.[77]

Cyclooctane (6)

In a pioneering paper by Hendrickson,[78] nine interconverting conformations of the cyclooctane molecule belonging to the three different families (crown, boat–chair and boat–boat) were postulated. A good deal of experimental evidence was gained in support of a boat–chair conformation dominating in the gaseous,[79] liquid,[80] nematic[81] and crystalline[82] phases, in line with early[83] and more recent[84,85] theoretical findings (see also reviews[86]). Thus, in the most recent and the most accurate MP2, MP4SDQ, CCSD and DFT studies by De Almeida and co-workers,[85] six true minimum energy structures, namely boat (B), boat–boat (BB), boat–chair (BC), crown, twist-boat–chair (TBC) and twist-chair–chair (TCC), and two transition-state structures, all characterized via harmonic frequencies analysis, were located on the potential energy surface of cyclooctane with the global minimum being the boat–chair conformation. Indeed, later results[85] showed that at low temperatures the BC conformer is completely predominant whereas above ambient temperature there is a conformational mixture of 66% of the BC, 21% of the crown, ca 5–6% of each of the TBC and TCC conformers and of less than 1% of B and BB.

In the present study, we calculated the equilibrium geometries of the six monocycloalkane **1–6** at the B3LYP level[87] of approximation using the 6–311G** basis set of

Pople and co-workers.[88] We restricted ourselves to the predominant conformations, namely planar eclipsed cyclopropane (**1**), bent cyclobutane (**2**), envelope cyclopentane (**3**), chair cyclohexane (**4**), twist-chair cycloheptane (**5**) and boat–chair cyclooctane (**6**). All conformations were verified as stationary points corresponding to global minima without imaginary frequencies, as confirmed by harmonic vibrational frequencies analysis in each particular case. Accordingly, the salient geometric parameters of **1–6** obtained in this study are given in the footnotes to Table 4 and are used in all calculations of spin–spin coupling constants presented in Tables 1–5 while optimized structures are shown in Fig. 1.

It is noteworthy that the present B3LYP/6–311G** results of geometric optimizations demonstrate very close agreement with those of the available experimental and theoretical studies published elsewhere; accordingly, we did not perform any systematic compilation of the reported theoretical and experimental geometries of the title compounds obtained by other authors. Furthermore, in one of the previous papers[4] in this series, it was unambiguously demonstrated that geometric factors play only a minor role in the calculations of J(C,C), J(C,H) and J(H,H) of carbocyclic compounds.
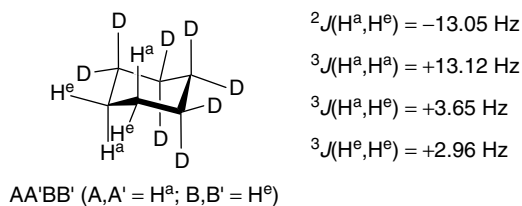
Cyclohexane: benchmark calculations

Prior to the calculation of carbon–carbon coupling constants in the series of monocycloalkanes **1–6**, we performed several benchmark calculations to adjust SOPPA for the best performance. Recently, it was demonstrated[4] that SOPPA in combination with locally dense basis sets consisting of Dunning's correlation consistent sets[89] of triple and even double zeta quality augmented with inner core s-functions,[90] cc-pVXZ-Cs (X = D, T), used for *coupled* carbons, and Sauer's spin–spin coupling sets[33] with tight s-functions, aug-cc-pVTZ-J, used for *coupled* hydrogens, performs perfectly well in reproducing experimental values of J(C,C), J(C,H) and J(H,H) for carbocyclic compounds. We use here chair cyclohexane optimized at the B3LYP/6–311G** level as a benchmark to test the performance of SOPPA and SOPPA(CCSD) when employed with the basis sets described above. We make a comparison with experimental values of J(C,C), J(C,H) and J(H,H) for the chair conformer of cyclohexane measured elsewhere with very high accuracy (see below).

All three carbon–carbon couplings of cyclohexane were measured by Roznyatovski *et al.*[91] with an ultrahigh accuracy of ±0.01 Hz from the proton decoupled ^{13}C NMR spectrum

of a monodeuterated sample providing superposition of the three ^{13}C-satellite AB subspectra induced by the ^{2}H/^{1}H isotopic effect corresponding to the three $^{13}C_2$-isotopomers shown.

^1J(C,C) = 33.10 Hz ^2J(C,C) = (−)2.12 Hz ^3J(C,C) = (+)2.05 Hz
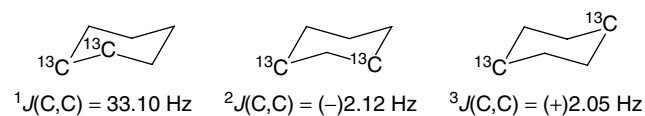
On the other hand, only average values of carbon–hydrogen and proton–proton couplings of the specifically deuterated cyclohexane could be measured at ambient temperature owing to the rapid ring inversion; however, low-temperature NMR measurements could resolve individual couplings involving axial and equatorial protons in the frozen chair conformer. This approach was first demonstrated by Garbisch and Griffith,[92] who prepared 1,1,2,2,3,3,4,4-cyclohexane-d_8 through the Diels–Alder dimerization of perdeuterobutadiene and ethylene. The deuterium broadband decoupled ^{1}H NMR spectrum of octadeuterated cyclohexane at −103 °C was resolved as an AA′BB′ spin system due to the reduced chair–chair inversion to give all 'frozen' proton–proton couplings (together with their signs) of chair cyclohexane.

^2J(H^a,H^e) = −13.05 Hz

^3J(H^a,H^a) = +13.12 Hz

^3J(H^a,H^e) = +3.65 Hz

^3J(H^e,H^e) = +2.96 Hz

AA′BB′ (A,A′ = H^a; B,B′ = H^e)

To the best of our knowledge, no longer range proton–proton couplings have been resolved so far, hence any reliable estimation of ^4J(H^a,H^a), ^4J(H^a,H^e), ^4J(H^e,H^e) and ^5J(H^a,H^a), ^5J(H^a,H^e), ^5J(H^e,H^e) seems to be lacking.

In the same manner, Chertkov and Sergeyev[93] synthesized cyclohexane-d_{11} by chlorination of cyclohexane-d_{12} followed by Grignard replacement of chlorine with hydrogen. The low-temperature proton-coupled ^{13}C NMR spectrum at −104 °C of cyclohexane-d_{11} was analyzed as arising from eight non-equivalent frozen conformers depending on whether the single proton is in an axial or equatorial position to yield the full set of the eight possible 'frozen' carbon–hydrogen couplings of cyclohexane as shown.
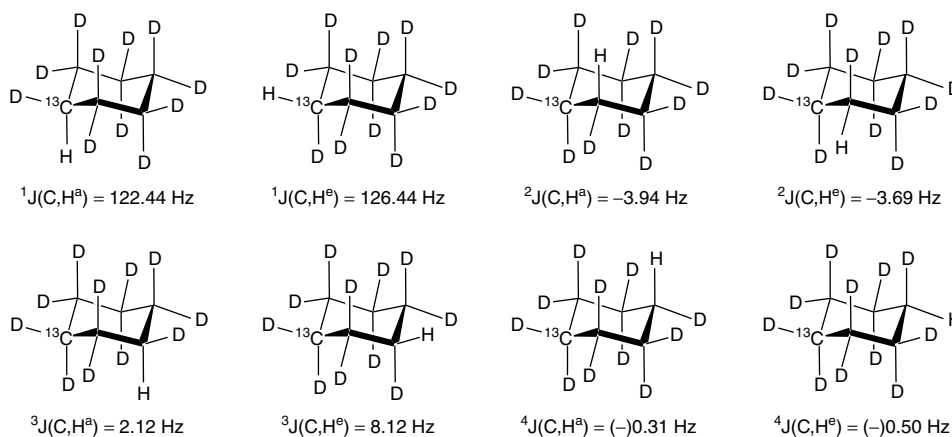

^1J(C,H^a) = 122.44 Hz

^1J(C,H^e) = 126.44 Hz

^2J(C,H^a) = −3.94 Hz

^2J(C,H^e) = −3.69 Hz

^3J(C,H^a) = 2.12 Hz

^3J(C,H^e) = 8.12 Hz

^4J(C,H^a) = (−)0.31 Hz

^4J(C,H^e) = (−)0.50 Hz

Table 1. Cyclohexane: $^{13}C-^{13}C$ spin–spin coupling constants

Coupling constant[a]	Method of calculation[b]	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J	Experiment[c]
^1J(C,C)	RPA	0.21	−0.28	1.25	58.11	59.29	
	SOPPA	0.22	−0.08	1.01	32.82	33.97	
	SOPPA(CCSD)	0.22	−0.08	0.99	31.93	33.06	33.10
^2J(C,C)	RPA	0.03	−0.13	−0.05	−5.90	−6.05	
	SOPPA	0.03	−0.14	−0.04	−2.78	−2.93	
	SOPPA(CCSD)	0.03	−0.14	−0.04	−2.44	−2.59	(−)2.12
^3J(C,C)	RPA	0.01	−0.06	−0.02	2.91	2.84	
	SOPPA	0.01	−0.07	−0.01	2.10	2.03	
	SOPPA(CCSD)	0.01	−0.07	−0.01	1.94	1.88	(+)2.05

[a] All couplings and their contributions are in hertz. Optimized B3LYP/6–311G** equilibrium geometry is used throughout; see footnotes to Table 4 for details.

[b] Coupled carbons are specified with cc-pVTZ-Cs and uncoupled carbons and all hydrogens are specified with cc-pVDZ without polarization p-functions on hydrogens. Spin–dipolar contributions of all couplings were calculated separately using cc-pVDZ-Cs for coupled carbons and cc-VDZ for the rest of the carbons and for all hydrogens. All calculations are performed within the C_1 symmetry point group (no symmetry constraints applied).

[c] Ref. 91. Measured for monodeuterated cyclohexane with reported accuracy ±0.01 Hz; given in parentheses are the *supposed* signs of the long-range J(C,C).

Table 2. Cyclohexane: $^{13}C-^1H$ spin–spin coupling constants

Coupling constant[a]	Method of calculation[b]	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J	Experiment[c]
^1J(C,H^a)	RPA	0.89	1.22	−0.32	152.83	154.62	
	SOPPA	0.90	1.26	0.26	120.16	122.57	
	SOPPA(CCSD)	0.90	1.22	0.28	115.64	118.04	122.44
^1J(C,H^e)	RPA	0.83	1.20	−0.28	158.52	160.27	
	SOPPA	0.84	1.23	0.28	125.70	128.06	
	SOPPA(CCSD)	0.84	1.20	0.29	120.88	123.22	126.44
^2J(C,H^a)	RPA	−0.07	0.06	0.08	−11.80	−11.72	
	SOPPA	−0.07	0.07	0.06	−5.31	−5.25	
	SOPPA(CCSD)	−0.06	0.07	0.06	−4.80	−4.72	−3.94
^2J(C,H^e)	RPA	−0.12	0.05	0.06	−11.57	−11.58	
	SOPPA	−0.12	0.06	0.05	−4.76	−4.77	
	SOPPA(CCSD)	−0.12	0.06	0.04	−4.30	−4.31	−3.69
^3J(C,H^a)	RPA	0.05	0.00	−0.03	2.77	2.79	
	SOPPA	0.05	0.00	−0.03	1.92	1.94	
	SOPPA(CCSD)	0.05	0.00	−0.02	1.78	1.80	2.12
^3J(C,H^e)	RPA	−0.41	0.24	0.01	10.13	9.97	
	SOPPA	−0.41	0.24	0.01	7.98	7.82	
	SOPPA(CCSD)	−0.41	0.24	0.01	7.58	7.42	8.12
^4J(C,H^a)	RPA	−0.13	0.09	−0.02	−0.65	−0.71	
	SOPPA	−0.13	0.08	−0.01	−0.31	−0.37	
	SOPPA(CCSD)	−0.13	0.08	−0.01	−0.29	−0.35	(−)0.31
^4J(C,H^e)	RPA	−0.35	0.21	−0.02	−1.32	−1.48	
	SOPPA	−0.35	0.21	−0.02	−0.69	−0.85	
	SOPPA(CCSD)	−0.34	0.21	−0.02	−0.65	−0.80	(−)0.50

[a] All couplings and their contributions are in hertz. Optimized B3LYP/6–311G** equilibrium geometry is used throughout; see footnotes to Table 4 for details.

[b] Coupled carbons and coupled hydrogens are specified with cc-pVTZ-Cs and aug-cc-pVTZ-J, respectively, and uncoupled carbons and uncoupled hydrogens are specified with cc-pVDZ without polarization p-functions on hydrogens. Spin–dipolar contributions of all couplings were calculated separately using cc-pVDZ-Cs and aug-cc-pVTZ-J for coupled carbons and coupled hydrogens, respectively, and cc-VDZ for the rest of the carbons and hydrogens. All calculations are performed within the C_1 symmetry point group (no symmetry constraints applied).

[c] Ref. 93. Measured for cyclohexane-d_{11} at −104 °C with reported accuracy ±0.02 Hz; given in parentheses are the *supposed* signs of the long-range J(C,H), as noted by the authors.

Table 3. Cyclohexane: ^{1}H–^{1}H spin−spin coupling constants

Coupling constant[a]	Method of calculation[b]	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J	Experiment[c]
$^2J(H^a,H^e)$	RPA	−1.99	1.85	0.52	−29.31	−28.93	
	SOPPA	−1.95	1.64	0.42	−17.39	−17.08	
	SOPPA(CCSD)	−1.95	1.83	0.41	−16.13	−15.84	−13.05
$^3J(H^a,H^a)$	RPA	−2.66	1.80	0.06	17.54	16.74	
	SOPPA	−2.65	1.79	0.04	13.40	12.58	
	SOPPA(CCSD)	−2.65	1.79	0.04	12.77	11.95	+13.12
$^3J(H^a,H^e)$	RPA	−0.20	0.26	0.12	5.97	6.15	
	SOPPA	−0.19	0.25	0.10	4.01	4.17	
	SOPPA(CCSD)	−0.19	0.25	0.10	3.77	3.92	+3.65
$^3J(H^e,H^e)$	RPA	−0.40	0.39	0.09	4.92	4.99	
	SOPPA	−0.39	0.37	0.08	3.08	3.14	
	SOPPA(CCSD)	−0.39	0.37	0.07	2.88	2.93	+2.96
$^4J(H^a,H^a)$	RPA	1.28	−0.84	0.03	−0.76	−0.30	
	SOPPA	1.28	−0.84	0.02	−0.44	0.02	
	SOPPA(CCSD)	1.28	−0.84	0.02	−0.40	0.05	
$^4J(H^a,H^e)$	RPA	−1.50	1.04	−0.01	−1.02	−1.48	
	SOPPA	−1.49	1.03	−0.01	−0.54	−1.01	
	SOPPA(CCSD)	−1.49	1.03	0.00	−0.50	−0.96	
$^4J(H^e,H^e)$	RPA	−1.69	1.20	0.03	0.97	0.51	
	SOPPA	−1.69	1.19	0.02	1.19	0.71	
	SOPPA(CCSD)	−1.69	1.19	0.02	1.15	0.67	
$^5J(H^a,H^a)$	RPA	−1.49	1.04	−0.02	0.04	−0.43	
	SOPPA	−1.49	1.03	−0.01	0.00	−0.47	
	SOPPA(CCSD)	−1.49	1.03	−0.01	0.00	−0.47	
$^5J(H^a,H^e)$	RPA	−1.09	0.75	−0.01	0.24	−0.11	
	SOPPA	−1.09	0.75	−0.01	0.10	−0.25	
	SOPPA(CCSD)	−1.08	0.74	−0.01	0.09	−0.26	
$^5J(H^e,H^e)$	RPA	−1.71	1.17	−0.01	0.83	0.28	
	SOPPA	−1.71	1.16	−0.01	0.65	0.09	
	SOPPA(CCSD)	−1.71	1.16	−0.01	0.60	0.05	

[a] All couplings and their contributions are in hertz. Optimized B3LYP/6−311G** equilibrium geometry is used throughout; see footnotes to Table 4 for details.

[b] Coupled hydrogens are specified with aug-cc-pVTZ-J and the rest of the hydrogens and all carbons with cc-pVDZ without polarization p-functions on hydrogens. Spin−dipolar contributions of all couplings were calculated separately using aug-cc-pVTZ-J for coupled hydrogens and cc-VDZ for the rest of the hydrogens and for all carbons. All calculations are performed within the C_1 symmetry point group (no symmetry constraints applied).

[c] Ref. 92. Measured for specifically deuterated 1,1,2,2,3,3,4,4-cyclohexane-d_8 at −103 °C with reported accuracy ±0.05 Hz; indicated are the *determined* signs of J(H,H), as follows from the AA′BB′ spectral analysis.

Following the known structural trends of carbon−hydrogen couplings,[94,95] both geminal and vicinal couplings were *assigned* as negative and positive, respectively, whereas both four-bond couplings were *assumed* to be negative.[93]
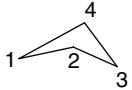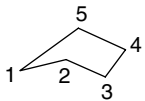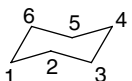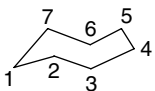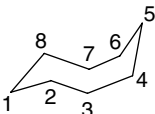
All 21 spin−spin couplings of chair cyclohexane, namely three J(C,C), eight J(C,H) and 10 J(H,H), calculated at the SOPPA and SOPPA(CCSD) levels and compared with available experiment, are presented in Tables 1–3 together with the corresponding RPA results. The latter were included only for the purpose of estimating the effects of electronic correlation (see next section).

First it should be noted that all 15 experimentally known couplings of different types in cyclohexane were reproduced fairly well within both approximations, with SOPPA(CCSD) results (standard deviation 0.9 Hz) slightly better than those

of SOPPA (standard deviation 1.1 Hz); see Figs 2 and 3. It is noteworthy that our present SOPPA and SOPPA(CCSD) calculations unambiguously confirmed the signs of ^2J(C,C), ^4J(C,H^a) and ^4J(C,H^e), which were *assumed* to be negative in the original experimental studies.[91,93]

Recently, Bagno *et al.*[96] performed DFT calculations of the eight possible J(C,H) in the frozen cyclohexane taking into account only three terms (Fermi contact, diamagnetic and paramagnetic spin−orbit contributions). Geminal, vicinal and four-bond couplings were well reproduced by those calculations whereas one-bond J(C,H) were considerably underestimated (by ca 9–13 Hz) owing to the too small Fermi contact contributions. It seems that even taking into account the missing spin−dipolar contribution (which is ca 0.3 Hz, Table 2) would not improve this disagreement. In contrast, the present SOPPA results give almost ideal agreement with

Table 4. Monocycloalkanes: $^{13}C-^{13}C^a$ spin–spin coupling constants

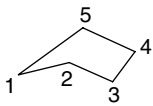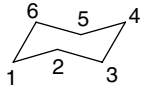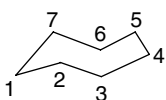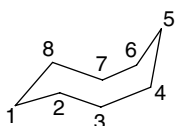| Compound	Formula[b]	Coupled nuclei	Method of calculation	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J	Experiment[c]
1		1,2	SOPPA	0.15	−0.46	−0.09	14.61	14.21	
			SOPPA(CCSD)	0.15	−0.48	−0.08	14.23	13.81	12.4
2		1,2	SOPPA	0.19	1.11	1.15	27.13	29.57	
			SOPPA(CCSD)	0.18	1.03	1.12	25.90	28.23	28.4
		1,3	SOPPA	0.02	−0.21	−0.21	−11.09	−11.36	
			SOPPA(CCSD)	0.02	−0.19	−0.08	−10.19	−10.44	(−)8.1
3		1,2	SOPPA	0.21	−0.19	1.00	32.38	33.50	
			SOPPA(CCSD)	0.21	−0.09	0.98	31.46	32.56	32.6
		1,3	SOPPA	0.02	−0.18	−0.04	0.62	0.42	
			SOPPA(CCSD)	0.02	−0.17	−0.04	0.77	0.58	(+)2.8
4		1,2	SOPPA	0.22	−0.08	1.01	32.82	33.97	
			SOPPA(CCSD)	0.22	−0.08	0.99	31.93	33.06	33.10[d]
		1,3	SOPPA	0.03	−0.14	−0.04	−2.78	−2.93	
			SOPPA(CCSD)	0.03	−0.14	−0.04	−2.44	−2.59	(−)2.12[d]
		1,4	SOPPA	0.01	−0.07	−0.01	2.10	2.03	
			SOPPA(CCSD)	0.01	−0.07	−0.01	1.94	1.88	(+)2.05[d]
5		1,2	SOPPA	0.22	−0.07	0.99	33.51	34.65	
			SOPPA(CCSD)	0.22	−0.08	0.97	32.62	33.73	34.0
		1,3	SOPPA	0.03	−0.23	−0.04	−2.13	−2.37	
			SOPPA(CCSD)	0.03	−0.22	−0.04	−1.78	−2.01	
		1,4	SOPPA	−0.01	0.00	−0.01	0.00	−0.02	
			SOPPA(CCSD)	−0.01	0.00	−0.01	−0.02	−0.03	
6		1,2	SOPPA	0.22	−0.06	0.97	34.35	35.48	
			SOPPA(CCSD)	0.22	−0.07	0.95	33.43	34.54	
		1,3	SOPPA	0.03	−0.18	−0.03	−2.34	−2.52	
			SOPPA(CCSD)	0.03	−0.17	−0.03	−1.99	−2.16	
		1,4	SOPPA	−0.01	0.00	−0.01	0.21	0.19	
			SOPPA(CCSD)	−0.01	0.00	−0.01	0.18	0.16	
		1,5	SOPPA	0.02	−0.01	−0.01	−0.14	−0.14	
			SOPPA(CCSD)	0.02	−0.01	−0.01	−0.12	−0.13	
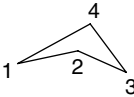
[a] All couplings and their contributions are in hertz. Coupled carbons are specified with cc-pVTZ-Cs and uncoupled carbons and all hydrogens with cc-pVDZ without polarization p-functions on hydrogens. Spin–dipolar contributions of all couplings were calculated separately using cc-pVDZ-Cs for coupled carbons and cc-VDZ for the rest of the carbons and for all hydrogens. All calculations are performed within the C_1 symmetry point group (no symmetry constraints applied).

[b] B3LYP/6–311G** equilibrium geometries were used throughout; the salient bond lengths r (Å), bond angles a (°) and dihedrals d (°) of the title compounds are as follows. Cyclopropane (**1**): $r(C^1C^2) = 1.508$, $r(C^1H) = 1.084$, $a(C^1C^2C^3) = 60.0$, $a(C^2C^1H) = 118.1$, $a(HC^1H) = 114.1$, $d(cis\text{-}HC^1C^2H) = 0.0$, $d(trans\text{-}HC^1C^2H) = 144.1$. Cyclobutane (**2**): $r(C^1C^2) = 1.555$, $r(C^1H^a) = 1.093$, $r(C^1H^e) = 1.092$, $a(C^1C^2C^3) = 88.6$, $a(HC^1H) = 108.4$, $d(C^1C^2C^3C^4) = 17.1$, $d(H^aC^1C^2H^a) = 150.8$, $d(H^aC^1C^2H^e) = 24.5$, $d(H^eC^1C^2H^e) = 101.5$. Cyclopentane (**3**): $r(C^1C^2) = 1.542$, $r(C^1H^a) = 1.097$, $r(C^1H^e) = 1.093$, $a(C^1C^2C^3) = 105.3$, $a(HC^1H) = 107.4$, $d(C^1C^2C^3C^4) = 12.5$, $d(H^aC^1C^2H^a) = 158.5$, $d(H^aC^1C^2H^e) = 39.9$, $d(H^eC^1C^2H^e) = 80.3$. Cyclohexane (**4**): $r(C^1C^2) = 1.537$, $r(C^1H^a) = 1.099$, $r(C^1H^e) = 1.096$, $a(C^1C^2C^3) = 111.6$, $a(HC^1H) = 106.4$, $d(C^1C^2C^3C^4) = 54.5$, $d(H^aC^1C^2H^a) = 173.5$, $d(H^aC^1C^2H^e) = 56.7$, $d(H^eC^1C^2H^e) = 59.7$. Cycloheptane (**5**): $r(C^1C^2) = 1.539$, $r(C^1H^a) = 1.098$, $r(C^1H^e) = 1.097$, $a(C^1C^2C^3) = 113.4$, $a(HC^1H) = 106.0$, $d(C^1C^2C^3C^4) = 85.7$, $d(H^aC^1C^2H^a) = 177.3$, $d(H^aC^1C^2H^e) = 67.3$, $d(H^eC^1C^2H^e) = 47.4$. Cyclooctane (**6**): $r(C^1C^2) = 1.540$, $r(C^1H^a) = 1.099$, $r(C^1H^e) = 1.097$, $a(C^1C^2C^3) = 115.9$, $a(HC^1H) = 105.7$, $d(C^1C^2C^3C^4) = 100.2$, $d(H^aC^1C^2H^a) = 177.4$, $d(H^aC^1C^2H^e) = 63.8$, $d(H^eC^1C^2H^e) = 50.0$.

[c] Experimental values of $J(C,C)$ measured in the title compounds or those estimated from their derivatives; taken from compilations,[111] if not indicated otherwise; given in parentheses are the *supposed* signs of the long-range $J(C,C)$.

[d] Ref. 91. Measured for monodeuterated cyclohexane with reported accuracy ±0.01 Hz.

Table 5. Monocycloalkanes: $^{13}C-^{1}H$ one-bond spin–spin coupling constants[a]

Compound	Formula[b]	Coupled nuclei	r(CH) (Å)	Method of calculation	J_{OD}	J_{OP}	J_{SD}	J_{FC}	J	Experiment[c]
1		1,H	1.084	SOPPA	0.69	1.19	0.43	156.96	158.85	
				SOPPA(CCSD)	0.70	1.16	0.44	151.46	153.75	160.3
2		1,H^a	1.093	SOPPA	0.76	1.17	0.32	128.42	130.68	
				SOPPA(CCSD)	0.77	1.14	0.34	123.60	125.84	
		1,H^e	1.092	SOPPA	0.73	1.07	0.35	134.46	136.61	
				SOPPA(CCSD)	0.74	1.05	0.35	129.51	131.65	
										(133.8)
3		1,H^a	1.097	SOPPA	0.85	1.27	0.28	122.29	124.69	
				SOPPA(CCSD)	0.86	1.23	0.30	117.71	120.09	
		1,H^e	1.093	SOPPA	0.80	1.20	0.31	129.32	131.63	
				SOPPA(CCSD)	0.81	1.17	0.32	124.43	126.73	
										(128.5)
4		1,H^a	1.099	SOPPA	0.90	1.26	0.26	120.16	122.57	
				SOPPA(CCSD)	0.90	1.22	0.28	115.64	118.04	122.44[d]
		1,H^e	1.096	SOPPA	0.84	1.23	0.28	125.70	128.06	
				SOPPA(CCSD)	0.84	1.20	0.29	120.88	123.22	126.44[d]
										(124.56)[d]
5		1,H^a	1.098	SOPPA	0.91	1.22	0.26	121.27	123.66	
				SOPPA(CCSD)	0.91	1.18	0.28	116.71	119.07	
		1,H^e	1.097	SOPPA	0.85	1.25	0.26	122.78	125.14	
				SOPPA(CCSD)	0.86	1.21	0.28	118.02	120.36	
										(123.6)
6		1,H^a		SOPPA	0.91	1.21	0.26	121.20	123.58	
				SOPPA(CCSD)	0.92	1.17	0.27	116.62	118.97	
		1,H^e		SOPPA	0.86	1.23	0.26	122.18	124.54	
				SOPPA(CCSD)	0.86	1.20	0.28	117.43	119.77	
										(124.5)

[a] All couplings and their contributions are in hertz. Coupled carbons and coupled hydrogens are specified with cc-pVTZ-Cs and aug-cc-pVTZ-J, respectively, and uncoupled carbons and uncoupled hydrogens are specified with cc-pVDZ without polarization p-functions on hydrogens. Spin–dipolar contributions of all couplings were calculated separately using cc-pVDZ-Cs and aug-cc-pVTZ-J for coupled carbons and coupled hydrogens, respectively, and cc-VDZ for the rest of the carbons and hydrogens. All calculations are performed within the C_1 symmetry point group (no symmetry operators applied).

[b] B3LYP/6–311G** equilibrium geometries were used throughout; see footnotes to Table 4 for details.

[c] Taken from compillations,[94,95] if not indicated otherwise; conformationally averaged values are given in parentheses.

[d] Ref. 93. Measured for cyclohexane-d_{11} at $-104\,°C$ with reported accuracy ± 0.02 Hz. Conformationally averaged value (in parentheses) measured at ambient temperature with the same accuracy.

experiment (ca 1–2 Hz) whereas the SOPPA(CCSD) results are slightly worse (ca 3–4 Hz) (see Table 2).

Also, all six unknown longer range proton–proton couplings are predicted with high confidence. It is interesting that previously unknown four-bond couplings markedly alternate in sign with $^4J(H^a,H^e)$ of ca -1 Hz and $^4J(H^e,H^e)$ of ca $+0.7$ Hz. On the other hand, $^4J(H^a,H^a)$ appears to be vanishingly small, less than 0.1 Hz. Five-bond couplings, $^5J(H^a,H^a)$ and $^5J(H^a,H^e)$, are negative (-0.3 to -0.5 Hz) whereas $^5J(H^e,H^e)$ is almost zero (<0.1 Hz). This is the first

information about long-range proton–proton couplings in cyclohexane.

All one-bond, geminal and vicinal couplings $^nJ(C,C)$, $^nJ(C,H)$ and $^nJ(H,H)$, $n = 1$, 2 and 3, are by far dominated by the Fermi contact contribution whereas longer range couplings ($n = 4$ and 5) possess a substantial and in some cases even dominating contribution of the non-contact interactions (Tables 1–3). However, also in these cases the orbital paramagnetic and orbital diamagnetic contributions have similar values but opposite signs. This implies that the
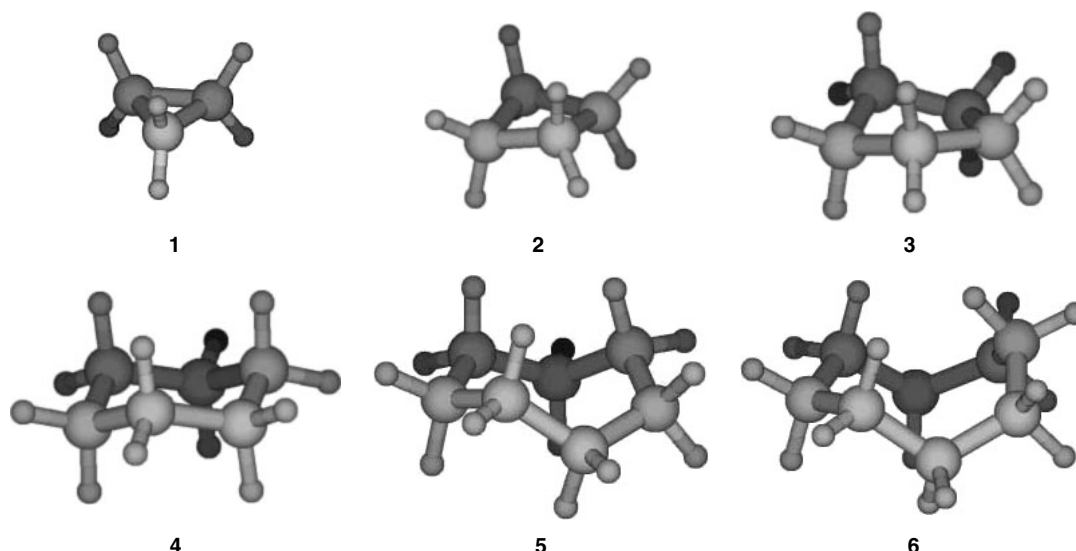
Figure 1. B3LYP/6–311G** optimized true global minimum conformations of monocycloalkanes.
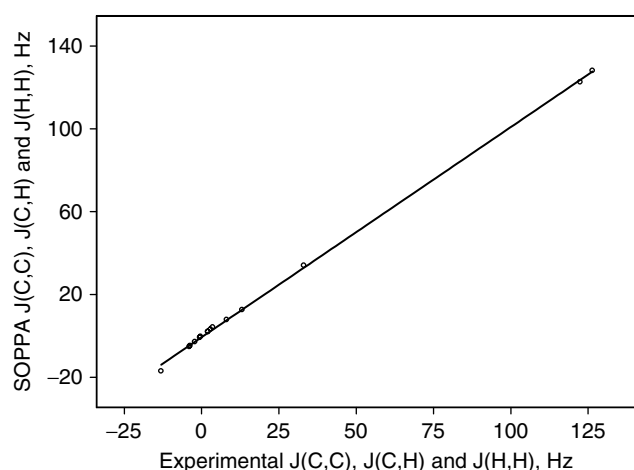

Figure 2. Plot of calculated at SOPPA level vs experimental J(C,C), J(C,H) and J(H,H) of cyclohexane ($r = 0.9997$; $s = 1.1$ Hz; $n = 15$).

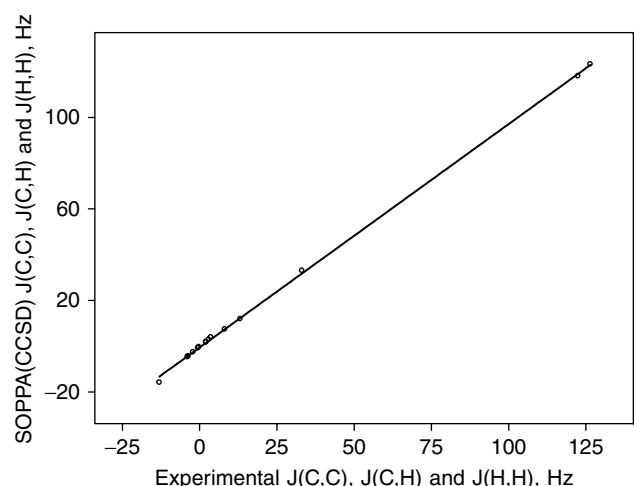**Figure 3.** Plot of calculated at SOPPA(CCSD) level vs experimental J(C,C), J(C,H) and J(H,H) of cyclohexane ($r = 0.9998$; $s = 0.9$ Hz; $n = 15$).

total couplings are still of the same order of magnitude as the Fermi contact contribution and that all changes in the Fermi contact contribution due to electron correlation are directly reflected in the total couplings.

Effects of electronic correlation, vibrational averaging and medium effects

The comparison of the RPA, SOPPA and SOPPA(CCSD) results for J(C,C), J(C,H) and J(H,H) in cyclohexane, as presented in Tables 1–3, reveals some very interesting trends. All changes in the total couplings are due solely to changes in the Fermi contact contribution. As a consequence, all these couplings are only incorrectly reproduced at the RPA level since the excited triplet states contributing to the Fermi contact term are not properly described by this method. Correlation changes the RPA results by 20–60% and in the case of some longer range proton–proton couplings by more than 100%.

In comparison with the SOPPA results, the SOPPA(CCSD) results are numerically smaller for all couplings in cyclohexane apart from two longer range proton–proton couplings. The changes are <1.5 Hz or in the range 3–10% of the SOPPA values, with the exception of the one-bond carbon–proton coupling, where the change amounts to almost 5 Hz or 4%.

SOPPA(CCSD) slightly underestimates all but one of the experimental couplings. The deviation is <1.2 Hz (with a standard deviation $\sigma = 0.4$ Hz) when we ignore the extreme cases [1]J(C,H), where the maximum error is 4.4 Hz or 4%, and [2]J(H^a,H^e), where the error is 2.8 Hz. For SOPPA the error is slightly larger, 1.3 Hz and $\sigma = 0.6$ Hz, for the same set of couplings, but more important, no systematic trend with respect to the sign of the error was found.

Similar conclusions can be drawn from the results for the carbon–carbon and carbon–proton couplings in the other monocycloalkanes (in Tables 4 and 5). SOPPA(CCSD) gives in general numerically smaller results for the carbon–carbon and carbon–proton couplings in monocycloalkanes than SOPPA, with the exception of [2]J(C,C) in cyclopentane. Furthermore, SOPPA(CCSD) underestimates all couplings apart

from the unusual carbon–carbon coupling in cyclopropane, whereas nothing systematic can be inferred about the sign of the error in SOPPA.

With modern *ab initio* and DFT methods, the accuracy of coupling constant calculations is so good that it becomes important to discuss the effects of vibrational averaging.[32,97,98] In principle, one should calculate zero-point vibrational averaging (ZPVA) corrections for all coupling constants and compare only ZPVA corrected couplings with experimental values. Alternatively, one can compare the calculated coupling constants with 'empirical' equilibrium geometry values, which are obtained by subtracting calculated ZPVA corrections from the experimental couplings. Following the latter approach, Ruden *et al.*[98] recently generated empirical equilibrium values for the coupling constants in cyclopropane (**1**) and cyclobutane (**2**) using their ZPVA corrections obtained by DFT calculations with the B3LYP functional. The main conclusions from their study are that (a) the empirical equilibrium values for the couplings considered in our study are numerically smaller than the raw experimental values and (b) the ZPVA corrections amount to ~1 Hz for the carbon–carbon couplings and 3–4 Hz for the carbon–proton couplings studied here. The general conclusions from our comparison with the raw experimental values are therefore not altered. However, a more detailed analysis shows that compared with the raw experimental values, the agreement between the SOPPA(CCSD) results and the empirical equilibrium values is improved for the carbon–proton couplings, $^1J_{eq}^{emp}$ (C^1,H) = 155.4 Hz in **1**, $^1J_{eq}^{emp}$ (C^1,H^a) = 126.8 Hz and $^1J_{eq}^{emp}$ (C^1,H^b) = 132.7 Hz in **2**,[98] and is slightly worse for the carbon–carbon couplings, $^1J_{eq}^{emp}$ (C^1,C^2) = 11.9 Hz in **1**, $^1J_{eq}^{emp}$ (C^1,C^2) = 27.0 Hz and $^2J_{eq}^{emp}$ (C^1,C^3) = −7.8 Hz in **2**.[98] The comparison of the SOPPA and SOPPA(CCSD) results shows that, whereas for carbon–carbon couplings the SOPPA(CCSD) results are in better agreement with both types of experimental values, the SOPPA(CCSD) results are now also superior for the carbon–hydrogen couplings.

The medium effects, which are also to be taken into account when comparing calculated and measured spin–spin coupling constants, in the case of cycloalkanes are negligible, at least if *J*(C,C) are considered.[111] The only well-defined example of the pronounced medium effects in the values of *J*(C,C) was found in acetylene. The latter constant was measured recently with ultrahigh experimental accuracy by Chertkov in acetone-d_6 liquid phase (166.010 ± 0.004 Hz), cited as a personal communication by Wigglesworth *et al.*,[32d] and also by Jackowski *et al.*[99] in dilute xenon gaseous solution (174.78 ± 0.02 Hz). The former (166.01 Hz) seems to be surprisingly small and the latter (174.78 Hz) seems to be surprisingly large compared with the originally reported value of 171.5 Hz measured in CCl$_4$ liquid phase.[100] The only explanation of this fact implies that ^1J(C,C) across a triple bond is extremely sensitive to medium effects, which is, however, not the case with the cycloalkanes studied here.

Carbon–carbon couplings in monocycloalkanes

The present results of SOPPA and SOPPA(CCSD) calculations of *J*(C,C) in the series of monocycloalkanes **1**–**6** together with the available experimental data are given in Table 4. We note that the Fermi contact contribution dominates for both one-bond and longer-range *J*(C,C) and hence it is responsible for the all structural trends discussed later.

One-bond couplings rapidly increase with the ring size, being ca 14 Hz in **1**, ca 28 Hz in **2** and ca 33–35 Hz in **3**–**6**, the latter typical for the ordinary carbon–carbon bonds in strain-free aliphatics. Apparently, the unusually small *J*(C,C) in cyclopropane (**1**) and, to a lesser extent, in cyclobutane (**2**) are due to the ring strain and, as a result, decreased s-character of their endocyclic bonds. It is noteworthy that the SOPPA(CCSD) results are especially good for the one-bond *J*(C,C), showing extraordinarily good agreement with experiment, which we believe is not a fortuitous result of the possible cancellation of errors which may arise when an obviously small portion of electronic correlation is taken into account and an inadequate basis set is applied.

However, a serious caveat is associated with the manifestation of the two different aspects of the *J*(C,C) behavior in cycloalkanes, i.e. a multipath coupling mechanism and, on the other hand, pseudorotational averaging.

In the recent and the most comprehensive publication by Wu and Cremer,[101] it was shown that the multipath spin–spin coupling mechanism in cyclic compounds leads to spin–spin coupling constants that deviate strongly from their normal values. This was shown for carbon–carbon coupling constants of several cyclic compounds using the recently developed decomposition of the total coupling into orbital contributions using originally proposed orbital currents and partial spin polarization (J-OC-PSP) method at the coupled perturbed density functional theory (CP-DFT) level.[102] As follows from these results,[101] a typical multipath coupling constant depends on a through-space part, two or more through-bond parts and the path–path interaction part where the latter results from steric exchange repulsion between the bond paths.

For example, in cyclopropane, the simplest carbocycle with the dual-pathway coupling ^{1+2}J(C,C), the situation is not as obvious as one can assume based on the simple additive dual-pathway model of Stöcker,[103] Klessinger and co-workers[104] and Krivdin and co-workers.[105] In spite of its obvious vividness, this interpretation was found by Wu and Cremer[101] to be highly misleading; according to their own results, for cyclopropane, the one-bond contribution of *J*(CC) is 54.4 Hz as it should be for a carbon–carbon bond with substantial p character. Accordingly, through-space (−27.1 Hz) and two-bond (10.1 Hz) contributions lead in sum to a typical geminal ^2J(C,C) of a strongly strained carbon ring (−17.1 Hz). The path interaction term is −24.5 Hz, reflecting the strong interaction between the carbon–carbon bond orbitals in the three-membered ring. The resulting total *J*(C,C) of cyclopropane is reduced by the two-bond and the path interaction contributions to 12.9 Hz, which is in excellent agreement with the experimental value of 12.4 Hz.[106]

Also, it was shown by Wu and Cremer[101] that measured and calculated *J*(C,C) coupling constants of pseudorotating cyclopentane are the averages over its pseudorotational motion, where each individual coupling of a conformation passed in the pseudorotation is the sum of the different

path contributions. This has a much larger impact on the spin–spin coupling constants than normal vibrational effects and, generally, should be considered for all types of couplings if rigorously compared with their experimental values.

Geminal couplings span from ca −2 Hz in **6** to ca −10 Hz in **2**. The typical range of $^2J(C,C)$ is −2 to −3 Hz for the larger monocycloalkanes **4–6**, where the geminal route is the principal coupling path, whereas the large and negative 'double-geminal' coupling constant $J(C^1,C^3) \approx -10$ to −11 Hz calculated in bent cyclobutane (**2**) is due to the dual-geminal-path coupling mechanism with the possible negative contribution of the through-space interaction involving diagonal coupled carbons (separated by ca 2.2 Å). The latter may arise from the non-bonded interactions of those carbons such as that involving bridgehead carbons in bicyclo[1.1.1]pentane (separated by ca 1.9 Å), as manifested in the series of papers by Barfield and co-workers[107] and later by Contreras and co-workers[108] and well reproduced in our previous SOPPA calculations.[4] Unfortunately, both methods, SOPPA and SOPPA(CCSD), slightly overestimate this interesting coupling, giving ca −10 to −11 Hz compared with the experimental value of ca −8 Hz.[109]

Vicinal couplings are ca +2 Hz in cyclohexane (**4**) and near zero (<0.2 Hz) in larger monocycloalkanes **5** and **6**, which is due to the Karplus dependence of $^3J(C,C)$: the dihedral angles of the coupling paths are $\varphi = 54.4°$ in **4**, 85.7° in **5** and 100.2° in **6**, corresponding to a *gauche* arrangement of the coupled carbons in **4** and a near *orthogonal* arrangement in **5** and **6**.

The longer range spin–spin coupling $J(C^1,C^5)$ in cyclooctane (**6**) involving two four-bond coupling paths is very small, which follows from both SOPPA and SOPPA(CCSD) calculations (ca −0.14 Hz), leaving only ca −0.07 Hz per each four-bond contribution, in reasonably good agreement with the available theoretical[4] and experimental[110] estimations and in line with the known structural trends of $J(C,C)$.[111]

Carbon–hydrogen couplings in monocycloalkanes

Historically, a good deal of interest has been focused on the nature and manifestation of stereoelectronic effects depending on the mutual orientation of chemical bonds and lone pairs of heteroatoms.[112] The carbon–hydrogen bond which is antiperiplanar to the lone pair is longer and weaker than those in *syn* and *gauche* orientations owing to the hyperconjugative electron density transfer $n_\sigma - \sigma^*_{C-H}$ of the former (the so-called 'Perlin effect' or a particular case of the anomeric effect).[113] The same effect was manifested later for carbon–carbon bonds ($n_\sigma - \sigma^*_{C-C}$ hyperconjugation) based on the observation of orientational lone pair effect upon the corresponding values of $^1J(C,C)$ couplings.[114,115]

In the pioneering paper by Perlin and Casu,[116] it was found that the axial one-bond carbon–hydrogen couplings in the six-membered saturated heterocycles are dramatically smaller (by ca 10 Hz) than those of the equatorial C—H bonds adjacent to either oxygen or nitrogen of the ring, and this was attributed[117] to the hyperconjugative $n_\sigma - \sigma^*_{C-H}$ interaction involving the antibonding orbital of the axial C—H bond and the heteroatom lone pair (see

also reviews[118] and references cited therein). In the same manner, the smaller value of $^1J(C, H^a) = 122.44$ Hz than $^1J(C, H^e) = 126.44$ Hz measured from the low-temperature NMR experiment in cyclohexane[93] can be interpreted as arising from the electron density hyperconjugative transfer from the bonding C—H^a orbital to the adjacent antibonding C—H^a orbital ($\sigma_{C-H} - \sigma^*_{C-H}$ hyperconjugation),[119] which makes axial bonds longer and weaker and, as a result, possessing smaller $^1J(C,H)$.
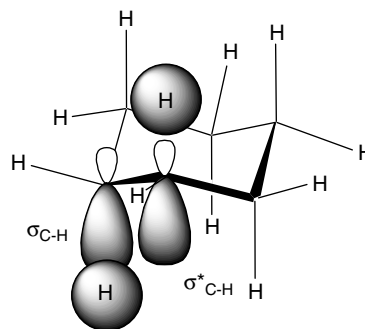
Indeed, in the whole series of monocycloalkanes (Table 5), axial carbon–hydrogen bonds are markedly longer and are characterized by smaller magnitudes of $^1J(C,H)$, which safely can be attributed to the discussed $\sigma_{C-H} - \sigma^*_{C-H}$ hyperconjugation. Also, it is noteworthy that a reasonably good agreement is observed between calculated 'frozen' and experimental 'average' carbon–hydrogen couplings (which, of course, cannot be compared directly), with SOPPA results being better than SOPPA(CCSD) results. In spite of the fact that SOPPA(CCSD) results essentially underestimate the experimental values of $^1J(C,H)$, the numerical magnitude of the Perlin effect experimentally measured for cyclohexane of ca 4 Hz[93] is well reproduced in the present study by both SOPPA and SOPPA(CCSD) calculations, being ca 5–7 Hz in cyclobutane (**2**), cyclopentane (**3**) and cyclohexane (**4**) and much less (ca 1–2 Hz) in cycloheptane (**5**) and cyclooctane (**6**).

CONCLUSION

The relative merits of the general SOPPA and SOPPA(CCSD) methods to calculate spin–spin coupling constants in a series of six monocycloalkanes were investigated. Benchmark calculations of all possible 21 coupling constants $J(C,C)$, $J(C,H)$ and $J(H,H)$ in chair cyclohexane revealed the appropriate level of theory and adequate quality of the basis sets being used. Very good agreement with the available experimental data was achieved, with the second method showing slightly better results in most cases, at least in those involving calculations of $J(C,C)$. SOPPA(CCSD) appeared to be especially good at reproducing experimental one-bond carbon–carbon couplings whereas SOPPA performed better in calculations of $^1J(C,H)$.

A more detailed comparison of the two SOPPA methods showed that for almost all couplings the SOPPA(CCSD) results are numerically smaller than the corresponding SOPPA values. Furthermore, the SOPPA(CCSD) results are

Table 6. Specification of the basis sets used in SOPPA calculations of J(C,C), J(C,H) and J(H,H)

Basis set	Atom	No. of basic AO per atom	Contraction[a]	Core and/or tight s-functions Exponent	Core and/or tight s-functions Contraction coefficient
cc-VDZ	H	2	$(4s) \rightarrow [2s]$		
	C	9	$(9s, 4p) \rightarrow [3s, 2p]$		
cc-VDZ-Cs	C	10	$(10s, 4p) \rightarrow [4s, 2p]$	4.530	1.00000000000
cc-pVDZ	H	5	$(4s, 1p) \rightarrow [2s, 1p]$		
	C	14	$(9s, 4p, 1d) \rightarrow [3s, 2p, 1d]$		
cc-pVDZ-Cs	C	15	$(10s, 4p, 1d) \rightarrow [4s, 2p, 1d]$	4.530	1.00000000000
cc-VTZ	H	9	$(5s, 2p) \rightarrow [3s, 2p]$		
	C	23	$(10s, 5p, 2d) \rightarrow [4s, 3p, 2d]$		
cc-VTZ-Cs	C	25	$(12s, 5p, 2d) \rightarrow [6s, 3p, 2d]$	4.292	1.00000000000
				11.876	1.00000000000
cc-pVTZ	H	14	$(5s, 2p, 1d) \rightarrow [3s, 2p, 1d]$		
	C	30	$(10s, 5p, 2d, 1f) \rightarrow [4s, 3p, 2d, 1f]$		
cc-pVTZ-Cs	C	32	$(12s, 5p, 2d, 1f) \rightarrow [6s, 3p, 2d, 1f]$	4.292	1.00000000000
				11.876	1.00000000000
aug-cc-pVTZ-J	H	20	$(10s, 3p, 1d) \rightarrow [6s, 3p, 1d]$	225.000	0.00036650000
				1496.000	0.00004256000
				9950.000	0.00000309700
				66145.000	0.00000041370
	C	46	$(15s, 6p, 3d, 1f) \rightarrow [9s, 5p, 3d, 1f]$	54924.000	0.00003761000
				366281.000	0.00000434900
				2442668.000	0.00000031470
				16289729.000	0.00000004196

[a] Spherical harmonic Gaussian functions (1s, 3p, 5d and 7f) are used in all contraction schemes. The full set of the contraction coefficients of the individual s-, p-, d- and f-functions may be found in the original publications by Dunning and co-workers[89,90] and by Sauer and co-workers.[34]

smaller than the available experimental values with only two exceptions, whereas no general trend was observed for the SOPPA results.

Many unknown couplings were predicted with high reliability, and many interesting structural trends including hybridization effects, multipath coupling transmission mechanisms and hyperconjugative interactions have been discussed. As an example, it was found that in the whole series of monocycloalkanes axial carbon–hydrogen bonds are markedly longer and are characterized by smaller magnitudes of ^1J(C,H) which was explained by the $\sigma_{C-H}-\sigma^*_{C-H}$ hyperconjugation involving hyperconjugative transfer from the bonding C—H^a orbital to the adjacent antibonding C—H^a orbital.

EXPERIMENTAL

Geometric optimizations at DFT level were performed with GAMESS code[120] and all calculations of spin–spin coupling constants at RPA and SOPPA were carried out using the DALTON package,[9,11,121,122] whereas the SOPPA(CCSD) results were obtained with a modified version of the Dalton package.[10,11,30] Both codes, GAMESS and DALTON, were compiled as LFS (Large Files System) versions for Linux. All basis sets used in this study with DALTON either were taken from the Dalton Basis Sets Library as they are or were slightly modified by adding or removing polarization, core, tight or diffuse functions or decontracting their s-parts as specified

in previous papers.[5,6] These basis sets together with some other closely related ones are specified in Table 6.

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