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Ab initio study of the NMR shielding constants and spin–spin coupling constants in cyclopropene*

Andrzej Barszczewicz[1], Michał Jaszuński[1], Krystyna Kamieńska–Trela[1], Trygve Helgaker[2], Poul Jørgensen[3] and Olav Vahtras[4]

[1] Institute of Organic Chemistry, Polish Academy of Sciences, 01 224 Warsaw, Kasprzaka 44, Poland

[2] Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo 3, Norway

[3] Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

[4] Department of Physics and Measurement Technology, University of Linköping, S-581 83 Linköping, Sweden

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Summary. *Ab initio* calculations of parameters which characterize the NMR spectrum are presented for the cyclopropene molecule. The London orbitals CHF (or GIAO-CHF, Gauge-Independent Atomic Orbital Coupled Hartree–Fock) results for the shielding constants are in good agreement with the experimental data, accurately determined, and with other *ab initio* values. The calculations of the NMR spin–spin coupling constants have been performed using the Multiconfiguration Time-Dependent Hartree–Fock (MC TDHF) approach. Different basis sets and MC SCF wavefunctions were used to estimate the accuracy of the results. Good agreement is obtained with the coupling constants estimated using the available experimental data.

Key words: NMR shielding constants – Spin–spin coupling constants – Cyclopropene

1 Introduction

NMR shielding constants and spin–spin coupling constants are molecular properties characterising the response of the system to a perturbation. As such, they can be evaluated using appropriate linear response methods. Various perturbation schemes have been used in *ab initio* calculations of these molecular properties. The methods based on the Hartree–Fock (HF) approximation and its extensions have played a dominant role in the *ab initio* calculations for polyatomic systems [1–3]. When the reference state is described by the HF wavefunction and time-independent one-electron perturbing operators are considered the Random Phase

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* Dedicated to Professor Werner Kutzelnigg on the occasion of his 60th birthday

Approximation (RPA) and the Time-Dependent Hartree–Fock (TDHF) method are equivalent to the Coupled Hartree–Fock (CHF) perturbation scheme.

The second-order perturbation correction to the energy which defines the molecular properties characterising the NMR spectrum can be written as [1, 4]:

$$E^{(2)} = -\beta_p \sum_{\mathrm{A}} g^{\mathrm{A}} I_i^{\mathrm{A}} (1 - \sigma_{ij}^{\mathrm{A}}) B_j + \sum_{\mathrm{A,B}} h I_i^{\mathrm{A}} J_{ij}^{\mathrm{AB}} I_j^{\mathrm{B}}$$

where σ_{ij}^{A} is the NMR shielding constant and J_{ij}^{AB} the spin–spin coupling constant (the subscripts ij are used for the tensor components). B denotes the external magnetic field, I^{A} the nuclear spin, β_p is the nuclear magneton and g^{A} the nuclear g-factor for nucleus A. Straightforward applications of the CHF method are not as successful in the calculation of σ^{A} and J^{AB} as for some other (e.g. electric) properties.

Two problems, due to the nature of the perturbing operators, have to be dealt with in evaluating the NMR parameters. For σ, the computational problems are related to the gauge dependence of the results, due to the magnetic field. In principle the gauge dependence can be eliminated by an extension of the basis set, as the CHF method yields gauge-invariant results in the limit of a complete basis (see e.g. [5]). However, such an approach is hardly practical for molecules larger than diatomics. Numerous methods which eliminate or bypass the gauge origin problem have been developed for the CHF approximation [6–12]. It appears that only when these specially designed methods are applied reliable results can be obtained.

The calculation of spin–spin coupling constants presents other problems. The constant J for a pair of nuclei can be written as (see e.g. [4]):

$$J = J^{\mathrm{DSO}} + J^{\mathrm{PSO}} + J^{\mathrm{SD}} + J^{\mathrm{FC}}$$

where the acronyms denote the so-called dia- and para-magnetic spin–orbit (DSO, PSO), spin–dipole (SD) and Fermi contact (FC) terms. Usually the FC contribution, which is calculated as a response to a triplet perturbing operator, is the most important term. This means that the CHF approach cannot be used to obtain reliable results, since it is very often unstable with respect to triplet excitations or gives a very poor description of these excitations [2]. For example, in one of our calculations of J^{FC} the CHF approximation gives ca. 2000 Hz and the correlated value is ca. 70 Hz. Correlation effects thus have to be included to obtain reliable spin–spin coupling constants. An additional complication is that more tight s-type atomic orbitals than used in standard basis sets have to be included, because the $\delta(r_{i\mathrm{A}})$ operator enters the FC term.

These problems have been examined in detail in various calculations, primarily for small molecules (see for example the reviews [4, 10, 13], the recent works [14–16] and references therein). In this work, we will study both the shielding constants and the spin–spin coupling constants in cyclopropene. We thus compute at the same time all the parameters describing the NMR spectrum. We have attempted to reach uniform accuracy for all of the parameters, that is four shielding constants and ten spin–spin coupling constants. Previous applications using the MC TDHF scheme have studied molecules with only one or two spin–spin coupling constants.

Since different extensions of the CHF method are needed to compute the shielding and spin–spin coupling constants, the calculations do not have much in common. This is rather unfortunate, as it would be useful to obtain all the data at the same wave function level. In particular, for larger molecules it would be preferable to use the same reference function for the unperturbed system in all the response calculations.

2 Computational aspects

2.1 Geometry

All our results will be given for the experimental geometry of Ref. [17]. Only when we explicitly mention the geometry dependence of the computed properties, we consider a second geometry, based on the data of Ref. [18]. Experimental geometries, including these two, have also been used in other *ab initio* calculations [8, 12, 19–24].

We denote as C1 the methylenic carbon atom, and as H1 and H4 the attached hydrogen atoms; C2 and C3 are the doubly bonded atoms and H2 and H3 the hydrogen atoms bonded to C2 and C3, respectively (see Fig. 1).

We apply a simplified notation for the spin–spin coupling constants, so C2H3 stands for ^2J (C2H3), H1H4 for the geminal coupling constant in the CH_2 group etc.

2.2 Basis set

Most of the results have been obtained using a CGTO basis set including 97 functions. It is built from a (9*s*5*p*1*d*/8*s*3*p*1*d*) carbon set and an uncontracted (4*s*1*p*) hydrogen set. The carbon *s* and *p* and hydrogen *s* functions were taken from Huzinaga [25]; the polarization function exponents were 0.665 (C, *d*) and 1.0 (H, *p*). In a number of calculations we employed a second smaller basis with 64 CGTO's, obtained from the same primitive *s* and *p* set using for the carbon atom a (9*s*5*p*/6*s*2*p*) contraction with no *d* functions. Only the first *s* and *p* functions are contracted in both basis sets. Our 97 CGTO set differs from normal basis sets primarily in the method of contraction for *s* functions, since for the calculation of spin–spin coupling constants *s*-type atomic orbitals with large exponents are of utmost importance. On the other hand, it appears that a contraction of *p*-type orbitals does not affect the results significantly [16].

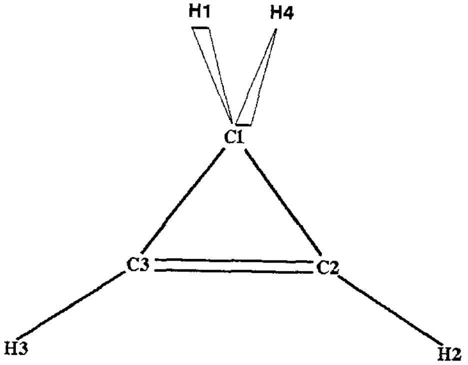

Fig. 1. The numbering of carbon and hydrogen atoms

For the shielding constants a London orbitals version of the above basis sets is used. It appears that we have reached convergence with the basis set for these constants (see below), and similar results might have been obtained with a more contracted basis. To establish convergence for the spin–spin coupling constants much larger basis sets would be required. For example, the basis B19 used for CH_4 in [16] gives for C_3H_4 228 CGTO functions. We do not aim for the same accuracy and our basis set, although much smaller, yields acceptable results.

3 Results

3.1 *The NMR shielding tensors*

The shielding constants in cyclopropene have been studied using a variety of methods based on the CHF approximation [8, 12, 19–22]. All the tensor components have been examined for the carbon atoms. In particular, the shielding of the ethylenic carbon atom is interesting because there is a large antisymmetric component of the σ tensor which cannot be observed in standard NMR experiment. This theoretical prediction has recently been supported by an analysis of relaxation rates in a cyclopropene derivative [26].

In our calculation of the chemical shifts we apply the London orbitals CHF method. We use the GIAO-CHF program of Wolinski, Hinton and Pulay [8] (we shall use the name London orbitals rather than GIAO). They have included C_3H_4 in their studies, but they did not discuss the components of the σ tensor in detail. For the isotropic values of the shielding, our smaller basis set values agree with the small basis set results reported by Wolinski et al. [8]. The 97 CGTO results, shown in Table 1, are in good agreement with previous *ab initio* calculations and with

Table 1. The NMR shielding constants in cyclopropene (in ppm)[a]

	Isotropic σ_{av}			Anisotropy $\Delta\sigma$		
	This work	Other *ab initio*	Exp.	This work	Other *ab initio*	Exp.
Nucleus						
C1	195.8	198[b], 189.1[c] 193.99[f]	190.4[d]	108.0	107[b], 89[e] 108[f]	94[h]
C2	73.6	77[b], 72.7[c] 73.08[f]	84.0[d]	190.9	191[b], 182[g]	154[h]
H1	31.0	29.3[c]	30.1[i]	14.3		
H2	24.4	23.2[c]	24.0[i]	6.2		

[a] Absolute values of the shielding
[b] LORG results [12]
[c] IGLO II values taken from Ref. [10]
[d] Based on experimental liquid phase data, see Ref. [27] and Ref. [10]
[e] Computed in Ref. [12] from the IGLO data [20]
[f] GIAO results [8]
[g] Computed in Ref. [12] from the IGLO data [21]
[h] Computed in Ref. [12] from the experimental data [22]
[i] Based on experimental liquid phase data, see Ref. [28] and Ref. [10]

experiment. Thus, it appears that we have obtained results close to the Hartree–Fock limit and that the correlation corrections to the shielding constants are small.

The agreement between the calculated anisotropies $\Delta\sigma$ is not so good as for the trace of the tensor; our results agree well with the LORG values [12]. For both carbons we find the asymmetry η to be slightly smaller than deduced [12] from experiment: 0.14 (0.18) for C1, and 1.35 (1.55) for C2, whereas in the other calculations it is slightly larger. We use here the definitions $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$, $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\mathrm{av}})$ and $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$ given in Ref. [12], they are different in Ref. [19]. On the other hand, for the antisymmetric part of the tensor we find almost exactly the same values as the other authors – 101.0 ppm, compared with 100 [12] and 99 ppm [21], respectively.

We find the dependence of the anisotropies on the basis set and geometry (different geometries have been used in [8] and [12]) to be of the order of ± 20 ppm, to be compared with ± 10 ppm for the variations of the isotropic shielding for the ^{13}C atoms. The antisymmetric component changes by less than 10 ppm.

3.2 The spin–spin coupling constants

The disadvantages of the CHF method for triplet perturbation operators have been overcome using perturbation schemes that include correlation effects [29–31]. The approximation we use is the MC TDHF, a multiconfiguration extension of TDHF [32–36]. It has been demonstrated that a Complete Active Space SCF (CAS SCF) wavefunction which incorporates the essential correlation effects yields very good results for spin–spin coupling in HD and CH_4 molecules [36]. The method has also recently been applied to analyse the spin–spin coupling of N_2 and CO [37]. In this work we calculate all spin–spin coupling constants for cyclopropene. The only previous *ab initio* calculation of these constants has been carried out by Fronzoni and Galasso [23]. Their EOM method takes into account a significant part of the correlation effects, however they have used a basis set too small to describe adequately the coupling to hydrogen atoms.

In all the calculations we use C_{2v} symmetry. We shall describe the number of occupied orbitals for various wavefunctions as $[\mathrm{n}_1, \mathrm{n}_2, \mathrm{n}_3, \mathrm{n}_4]$, where n_i for $i = 1$ to 4 is the number of orbitals in symmetry A_1, B_1, B_2 and A_2, respectively (B_2 includes the orbitals antisymmetric with respect to the plane of C atoms).The Hartree–Fock function has [6,3,2,0] occupation, the full valence CAS SCF wavefunction would have a [2,1,0,0/7,5,3,1] inactive/active space partitioning. The corresponding CI expansion would include over 40×10^6 determinants. We have used much shorter CI expansions for the MC TDHF reference functions, obtained either by reducing the CAS SCF active space or by partitioning a large active space according to the RAS SCF scheme [38]. In the selection of the active orbitals we used the occupation numbers of natural orbitals derived from second-order perturbation theory calculations. We recall that all the inactive orbitals (including also the core) are reoptimized in each MC SCF calculation, not frozen at the SCF level.

The CAS SCF function MC1 has 4 active electrons in 5 active orbitals, it can be described as [5,3,1,0/2,1,1,1]. The CI expansion includes 28 determinants of proper space and spin symmetry. The function MC2 is a [4,2,1,0/4,3,2,1] function with 8 electrons in the active space (and 11100 determinants). In the RAS SCF calculation we have included in 18 active orbitals 8 electrons, maximum 2 in RAS3. This wavefunction can be described using the notation [inactive/RAS1/RAS2/RAS3] as

[4,2,1,0/0,0,0,0/2,1,1,1/6,4,3,0] and has 6553 determinants. All the MC SCF calculations have been performed using the SIRIUS program [35]; in the calculations of spin–spin coupling constants we used a set of response programs accompanying SIRIUS.

We have analysed these wavefunctions comparing the FC contribution to the coupling constants. This is usually the most important contribution. Once the accuracy of J^{FC} is satisfactory, the same approximation can be used for the other terms. The results for four different constants are given in Table 2. The other coupling constants are too small to draw any conclusions from their variations with the wavefunction, $|J^{FC}| < 5$ Hz.

The TDHF results in Table 2 are meaningless. In fact for some of the basis sets we found a triplet instability for the SCF wavefunction. As can be seen from Table 2 the results become reasonable only when correlation effects are accounted for. The rate of convergence for solving the matrix perturbation equations in the RAS SCF calculation was not as good as in the CAS SCF based response, so the RAS SCF calculations are much more time consuming.

We have also used for a test basis set [4,1,1,0/4,4,2,1] and [3,2,1,0/5,3,2,1] CAS SCF functions, each with 10 active electrons and more than 50 000 determinants. The resulting changes in J^{FC} were rather small, for most of the constants a fraction of 1 Hz. The largest differences from MC2 were observed for the C2C3 constant, −4.85 and +7.06 Hz, respectively. However, as these were of different sign, it appears that the active space of the MC2 function is sufficiently accurate.

To estimate the role of the various approximations applied we have carried out test calculations for acetylene (experimental values are known for C_2H_2). Our results are shown in Table 3. The first basis set b1 corresponds to the 97 CGTO

Table 2. The FC contribution to the coupling constants in cyclopropene (in Hz)[a]

Wave function	SCF	MC1	MC2	RAS
Constant				
C1C2	30.0	30.9	18.7	19.6
C2C3	2093.2	75.1	72.8	73.0
C1H1	168.7	167.8	163.6	164.6
C2H2	1299.7	219.8	212.7	216.4

[a] Basis set 97 CGTO

Table 3. The FC contribution to the coupling constants in C_2H_2 (in Hz)[a]

Wave function/ basis set	MCA/b1	MCA/b2	MCA/b3	RAS/b1	Exp.[b]
Constant					
CC	160.8	170.0	170.1	150.1	160.6
^{1}CH	235.8	242.6	269.6	229.1	248.8
^{2}CH	35.6	36.6	40.7	37.4	45.3
HH	14.4	14.4	17.8	13.2	9.2

[a] For a description of the wavefunctions and basis sets, see text

[b] Estimated from Ref. [39], subtracting from the quoted experimental data the SOPPA values of all the other contributions (DSO, PSO and SD)

basis set for cyclopropene. Basis set b2 has extra carbon *s*-type functions with large exponents (the innermost CGTO was decontracted and a function with $\alpha = 25\,000.$ added), basis set b3 contained an additional hydrogen *s*-type function ($\alpha = 100.$). The MCA wavefunction is a CAS SCF function including in 8 active orbitals 8 electrons, the RAS calculation includes 8 electrons in the active space, 8 orbitals in RAS 2 and 4 in RAS 3 (at most doubly occupied) subspace.

For CC and ^{1}CH (one-bond CH constant) the effects due to enlargement of the basis set and extension of the correlation treatment are somewhat large, but are of opposite sign. For HH the effects are smaller and of different sign, and for ^{2}CH both corrections are small and positive.

These results, as well as test calculations with other basis sets (including the 64 CGTO basis described above) for cyclopropene, suggest that there are two effects of opposite nature. Roughly speaking, increase of the *s*-type atomic basis set brings the electrons closer to the nuclei (and the coupling constants become larger), while increase of the active space pulls them away from the nuclei. On the basis of the analysis of FC contributions for both C_2H_2 and C_3H_4 we may assume that the MC2/b1 results for cyclopropene provide a reasonably balanced description of these two effects.

All contributions to the spin–spin coupling constants of cyclopropene are given in Table 4. The SD, PSO and DSO terms have been computed with the 64 CGTO basis set and MC1 active space. They are so small that their variation with the basis set and active space can be expected to change very little the total values of J. The DSO contributions are for all the constants in good agreement with the calculation of Scuseria [24]. The calculation of the PSO and SD contributions is time consuming in comparison with the FC term, because of the large number of tensor components. This is the major reason why we decided not to compute the SD, PSO and DSO terms with the same wavefunction as used for J^{FC}. We have also used the MC1 wavefunction with the 64 CGTO basis in order to compare the FC contributions for the two molecular geometries mentioned above. For the C2C3 constant the difference was 7 Hz, for the other constants the geometry dependence of J^{FC} is much weaker.

Table 4. Individual contributions to the total spin–spin coupling constants (in Hz)[a]

Constant	FC	SD	PSO	DSO
C1C2	18.7	− 0.4	− 0.6	0.1
C2C3	72.8	3.8	− 5.5	0.2
C1H1	163.6	0.2	0.3	0.6
C2H2	212.7	0.5	− 0.7	0.6
C1H2	1.5	0.6	0.3	− 0.7
C2H3	− 3.8	0.1	0.3	− 0.9
C2H1	− 4.5	− 0.2	0.1	− 0.4
H1H2	− 0.7	− 0.1	0.9	− 2.2
H1H4	3.3	0.4	2.0	− 3.3
H2H3	4.0	− 0.4	1.1	− 2.7

[a] The FC contribution is calculated in a different approximation than the SD, PSO and DSO contributions – see text

The results in Table 4 indicate that the one-bond coupling constants are dominated by the Fermi contact contribution. The same pattern has been observed for other molecules, and appears to be typical for carbon–carbon and carbon–hydrogen coupling constants in organic compounds [40]. For the coupling through two or three bonds all four contributions must be taken into account.

3.3 Comparison with experimental spin–spin coupling constants

We compare our results with the experimental data deduced from cyclopropene, substituted cyclopropene and propene NMR spectra, since not all the coupling constants have been measured for C_3H_4. Only four of the results quoted in Table 5 are taken directly from cyclopropene measurement – the C1H1, C1H2, H1H2 and H2H3 constants [27, 41]. The constants given in brackets are estimates based on the results for other molecules.

The one-bond CC values have recently been reported for substituted cyclopropene [42]. The coupling was found to be 48.8 Hz for the double bond and 32.0 and 33.5 Hz across the single bonds, respectively. An analysis of the substituent effects in aliphatic compounds suggests appropriate corrections, which have been added to give the tabulated values.

For the carbon–carbon constants the agreement of our results with the EOM values of Fronzoni and Galasso [23] is very good. This is another indication that our MC2 function adequately describes the important correlation effects. For C1H1 and C2H2 our results agree better with experiment, as Fronzoni and Galasso have used a basis set that is too small to properly describe hydrogen.

The computed C1H2, C2H3 and C2H1 constants are compared to the corresponding experimental values for propene [43]. The agreement is satisfactory, considering the small magnitude of the calculated constants.

As the experimental result for the H1H4 constant we quote the value of the geminal coupling in the $=CH_2$ group in propene. The value of the C1H1 constant indicates this is a more appropriate comparison than with the geminal coupling constant in aliphatic compounds. Anyhow, our results for the HH

Table 5. The total spin–spin coupling constants (in Hz)

Constant	This work	*Ab initio* Ref. [23]	Experiment	
C1C2	17.8	18	(25)	[42]
C2C3	71.2	70	(60)	[42]
C1H1	164.7	151	167	[27]
C2H2	213.1	181	226	[41]
C1H2	1.7		(4.95)	[43]
C2H3	− 4.3		(− 1.15, − 2.60)	[43]
C2H1	− 5.0		(− 6.75)	[43]
H1H2	− 2.1		|1.75|	[41]
H1H4	2.4		(2.17)	[44]
H2H3	2.0		|1.3|	[41]

constants may be less reliable. As shown in Table 4, for these constants the FC contribution is not the dominant one. The approximations we have made (computing the other terms from a different function and with a different basis set) are therefore less reliable than for the other constants.

4 Conclusions

We have computed the shielding constants and spin–spin coupling constants for cyclopropene using rather simple wavefunctions and moderate size basis sets (similar approximations could be used in calculations for larger molecules). Comparison of the calculated shielding constants with experimental data suggests that correlation corrections may improve the results; however, correlation effects are in general not very significant. On the other hand, for spin–spin coupling one has to incorporate the main correlation effects in the calculation to obtain accurate and reliable results.

Our final results, shown in Tables 1 and 5, agree in most cases with the experimental data within ± 15%. For the shielding constants, this is similar to what has been obtained in other calculations for molecules of this size; for the spin–spin coupling our results appear to be better than the previous *ab initio* values. The MC TDHF method has previously been applied to compute spin–spin coupling in small molecules (CH_4 with two constants was the largest system studied). Our results indicate that the method is also a viable approach for calculations of spin–spin coupling constants in polyatomic molecules.

We have chosen MC SCF functions to describe the correlated reference state. A recent formulation of the London orbitals method [45] indicates that this approach may be applied to compute magnetic susceptibilities and shielding constants using correlated wavefunctions. Thus, it appears that within the MC TDHF scheme it is possible to calculate accurately all the theoretical parameters for NMR spectroscopy from a single reference function.

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