

Regular article

An ab initio study of NMR chemical shifts and spin-spin coupling constants of bicyclobutane

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Abstract. Molecular properties of bicyclobutane are calculated using ab initio methods which take into account electron correlation effects and applying relatively large basis sets. The optimized geometry, IR and NMR spectral parameters are compared with experimental values. The calculated NMR shielding constants, as well as the individual shielding tensor components – known for the carbon atoms – are in good agreement with the experimental data. For the spin-spin coupling constants, most of the computed values also agree well with experiment, the small geminal H-H constant being an exception. Our best result for the coupling constant between two bridgehead carbon atoms is -15.52 Hz.

Key words: Inverted carbon – Bicyclobutane – Ab initio calculations – NMR properties

Introduction

Significant progress has been made in the last few years in the computational studies of NMR parameters (see, e.g., the review [1]). In particular, linear response methods were developed for wavefunctions which take into account correlation effects. NMR parameters can nowadays be computed at the MCSCF level [2, 3] and within different coupled clusters approximations. The most recent approaches incorporate the effects of triple excitations within the coupled cluster linear response methods [4, 5]. For small molecules, the accuracy of the results can be very high; see for example [2, 4, 5, 6] and references therein. Following the studies of small hydrocarbons, like ethane [7], ethylene [1], and acetylene [6], we have recently [8] carried out analogous calculations for [1.1.1]propellane and bicyclopentane (Fig. 1). These molecules were of interest primarily due to the

unusual structure of [1.1.1]propellane, reflected in its NMR properties.

Hydrocarbons with unusual spatial structure having tetravalent carbon atoms strongly departing from the tetrahedral arrangement of substituents are the subject of vigorous studies [9, 10, 11] since the syntheses of molecules with inverted carbon atoms in Wiberg's group. Remarkably, the synthesis of [1.1.1]propellane has been preceded by the calculations predicting its geometry, stability and some other properties [12]. In this work we have undertaken a study of NMR chemical shifts and spin-spin coupling constants of bicyclobutane, which occupies an intermediate place between [1.1.1]propellane and bicyclopentane (Figs. 1 and 2). The first has strongly inverted carbon atoms, in bicyclobutane the bridgehead carbons are only insignificantly inverted – the C3-C2, C3-C4 and C3-H8 bonds are almost in one plane – and in bicyclopentane there is no inversion, the bridgehead carbon atoms have tetrahedral arrangement of substituents.

For propellane and bicyclopentane the chemical shifts and most of the coupling constants calculated earlier [8] reproduced experimental results. However, there was a considerable discrepancy for the values of the propellane $^1J(\text{C1-C3})$ constant involving the bridgehead carbon atoms and the reason for this discrepancy was not entirely clear. As shown by a recent review by Kuznetsova and coworkers on the application of $J(\text{C-C})$ coupling constants in structural studies of bicyclobutane heteroanalogs, prediction of these parameters is not only of theoretical importance but also has practical implications [13].

Computational aspects

In the calculations of NMR properties we used, similarly to our previous study of propellane and bicyclopentane [8], the MCSCF and CCSD approximations. In the MCSCF studies, both CASSCF (Complete) and RASSCF (Restricted Active Space Self Consistent Field) functions were applied.

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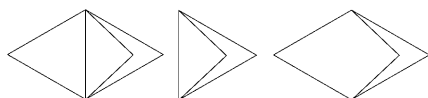


Fig. 1. [1.1.1]Propellane (left), bicyclobutane (middle), and bicyclo[1.1.1]pentane (right)

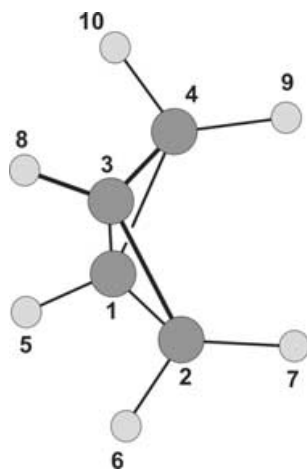


Fig. 2. Schematic view of bicyclobutane structure and the numbering of atoms

We describe the partition of the orbitals into the inactive, RAS2, and RAS3 space (RAS1 is empty) specifying the number of orbitals in A_1 , B_1 , B_2 and A_2 representations of C_{2v} symmetry. In this notation, in the SCF approximation (7 4 3 1) orbitals are occupied. The carbon 1s core orbitals are inactive in all the MCSCF functions. The choice of the active orbitals in different subspaces was based on the MP2 natural orbital occupation numbers.

We considered first a CASSCF function, which has (6 3 2 0) inactive and (3 2 3 2) active orbitals, with 11,076 determinants. Next, two RASSCF wavefunctions with a subspace of (3 1 1 0) inactive orbitals, denoted RAS-I/2e and RAS-I/4e were used. In the RAS-I/2e function the RAS2 space consists of (4 3 2 1) orbitals. Since a maximum of two electrons is allowed to be excited to the RAS3 space including (4 3 3 1) orbitals, the CI expansion has only 4385 determinants. The same partition of orbitals as in RAS-I/2e is assumed in the RAS-I/4e wavefunction. However, as four (instead of two) electrons may be promoted into the RAS3 space, the CI expansion has ~ 2.8 million determinants. In the last RAS-II function, only the (2 1 1 0) carbon 1s core is inactive. The RAS2 subspace includes (5 3 2 1) orbitals and the size of RAS3 subspace is (7 5 4 2). With a maximum of two electrons in RAS3, this function has 14445 determinants. These RASSCF wavefunctions are similar to the functions we employed previously for [1.1.1]propellane and bicyclopentane molecules [8].

For the geometry optimization, we used Dunning's [14] cc-pVTZ basis set, including [10s5p2d1f/4s3p2d1f] functions for the carbon and [5s2p1d/3s2p1d] for the hydrogen atom, with a total of 204 CGTOs. The same basis set was used to compute the IR frequencies and intensities. The

calculations of the NMR shielding constants and the spin-spin coupling constants were carried out primarily in the HIII basis set [15], derived from the basis sets of Huzinaga [16, 17] and successfully used in similar previous calculations (see, e.g., [1, 18]). This basis consists of [11s7p2d/7s6p2d] functions for C and [6s2p/4s2p] for H atom and gives for C_4H_6 a total of 200 CGTOs. The HIII basis includes more tight functions (particularly of s symmetry) than standard bases and thus it is more flexible in the neighborhood of the nucleus, the region relevant for the description of NMR parameters.

To check the basis set dependence of the shielding and coupling constants, some of the calculations were repeated with the cc-pVTZ basis. In the CCSD approach, for computational reasons the spin-spin coupling constants have been calculated using the HII basis set, similar to HIII, but smaller. This basis has a [9s5p1d/5s4p1d] and [5s1p/3s1p] set for the C and H atoms, respectively, and 124 CGTOs. In all the calculations of the NMR shielding constants GIAO orbitals [19, 20, 21] were used.

The MCSCF calculations of NMR properties were carried out using the Dalton [22] program. The results at the CCSD level were obtained with a program based on Aces II [23]. The indirect spin-spin coupling constants were calculated as unrelaxed second derivatives of the CCSD energy. The relevant CCSD linear response methods (see, e.g., [24]) were introduced into the program by Gauss and coworkers, who more recently studied also the role of triple excitations for shielding and spin-spin coupling constants [4, 5].

Results and discussion

Geometry

Bicyclobutane is a small molecule with C_{2v} symmetry. This enabled Wiberg and coworkers to determine its geometry in a high precision IR study [25]. The experimental and calculated geometries are collected in Table 1. An inspection of the data in Table 1 reveals a satisfactory agreement between our RAS-I/2e results with the experimental ones. The relatively old MP2/6-31G* calculations of bicyclobutane geometry by Walters et al. [26] have already shown the importance of the inclusion of correlation effects in the optimization of geometry of such nonstandard molecules. On the other hand, the same authors observed small differences between 6-31G* and 6-31+G* results at the HF level. The recent MP2/6-31G(d,p) calculations by Sakai [27] gave much poorer reproduction of the experimental C1-C3 bond length.

IR frequencies and intensities

The experimental measurements of vibrational frequencies and intensities by Wiberg et al. [25] were accompanied by calculations at the SCF/6-31G* level. The authors gave two sets of the calculated values: unscaled and scaled. Understandably, their scaled values repro-

Table 1. Calculated and experimental values of the bond lengths (in Å) and angles (in degrees)

Method, basis set	This work RAS-I/2e cc-pVTZ	Sakai [27] ^a MP2 6-31G(d,p)	Walters et al. [26]		Experimental [25] IR
			MP2 6-31G*	HF 6-31G*	
1. Bond lengths					
C1-C3	1.493	1.465	1.496	1.466	1.497 ± 0.003
C1-C2	1.505	1.516	1.492	1.489	1.498 ± 0.004
C1-H5	1.083		1.080	1.071	1.071 ± 0.004
C2-H6	1.092		1.092	1.082	1.093 ± 0.008
C2-H7	1.080		1.088	1.078	1.093 ± 0.008
2. Bond angles					
C1-C2-C3	59.5	58.4	60.2	59.0	60.0
C1-C3-H8	129.3		128.1	131.4	128.4 ± 0.2
H6-C2-H7	114.3		114.1	114.0	115.6
C4-C1-H5	129.8		129.6	130.5	130.4
C2-C1-C4	98.9	98.9			
C1-C3-C2	60.3				
C3-C2-H6	116.5				
C1-C2-H7	119.6				
C2-c-C4 ^b	122.1		122.4	120.6	122.7 ± 0.5
c-C4-H10 ^b	120.9		121.6	121.4	122.9 ± 0.8
c-C4-H9 ^b	124.7		124.4	124.7	121.6 ± 0.9

^aNo data on C-H bonds were given in this work^bc – the center of C1-C3 bond

duced very well the experimental results. Our frequencies, together with the corresponding unscaled values determined by the Wiberg group and with their gas-phase experimental results, are collected in Table 2. As expected, our frequencies obtained at the RAS-I/2e level better reproduced the experimental values than the unscaled results of Wiberg et al. [25]. Their scaled results are better, we recover generally 50–70% of the electron correlation effect taken into account by the scaling.

As concerns the calculated intensities, both calculations gave good agreement with the experimental data with few exceptions. Low calculated intensity of the ν_5 and ν_{22} vibrations was obtained by us and by the Wiberg group while a band of medium intensity at 1266.0 cm^{-1} was assigned to them. The strong intensities of the ν_3 band at 2935.4 cm^{-1} and the low one of ν_1 band at 3131.4 cm^{-1} were reproduced in [25] but not by our calculations. The calculated intensity of the ν_{14} band calculated by both groups is too big since only a weak band was observed at 3119.7 cm^{-1} .

Shielding

In addition to all the average values the tensor components for the carbon atoms, which have been studied theoretically and experimentally [28], are discussed. The results pertaining to the shielding are given in Tables 3 and 4.

A comparison of the computed shielding constants and experimental chemical shifts is obscured by the need for conversion to absolute shielding values. For $\sigma(\text{C})$, the values computed at the RAS-II/2e level and their difference – the relative chemical shift – are remarkably accurate. As shown in Table 3, all the computed hydrogen shielding constants are by $\sim 0.3\text{ ppm}$ too large.

On the other hand, the differences between computed and observed relative hydrogen chemical shifts are much smaller. Although the correlation effects computed in the MCSCF and CCSD approaches differ, they are small for all the wavefunctions for both carbon and hydrogen shielding constants.

We have also calculated the shielding constants using the cc-pVTZ basis set. Weak basis set dependence has been observed at the SCF level (the cc-pVTZ values are $\sim 3\text{--}5\text{ ppm}$ larger for the carbon atoms and $\sim 0.2\text{--}0.5\text{ ppm}$ larger for the hydrogen atoms), and the correlation effects are as small as in the HIII basis. Thus, we have only included, as one example, the CASSCF/cc-pVTZ results in Table 3.

In Table 4 we have collected the data for the tensor components of the carbon shielding. We define the orientation of the principal axes following Orendt et al., see Fig. 3 of [28] for details (only one axis is determined for each tensor by symmetry). For both tensors, we confirm the assignment of the axes which Orendt et al. obtained in their largest basis set SCF calculation (the values quoted in Table 4). Although some of the differences between tensor components are small, the correlation corrections are even smaller and do not affect the assignment of the components.

Spin-spin coupling

We do not analyze the individual components of the spin-spin coupling tensors, as there are no experimental data for comparison. The total coupling constants, calculated including all the contributions to the coupling (dia- and paramagnetic spin-orbit, spin-dipole and Fermi contact terms), are given in Table 5 together with the experimental data. We do not include the unreliable SCF results, and to illustrate

Table 2. Calculated and experimental values of frequencies (cm^{-1}) and intensities (km/mol)

Mode	This work RAS-I/2e cc-pVTZ		Wiberg et al. ^a SCF/6-31G*		Experimental ^b Frequencies, relative intensities
	Frequencies	Intensities	Frequencies	Intensities	
A ₁ (ν_9)	433.6	0.8	473	1.0	422.5 w (ν_9)
A ₁ (ν_8)	717.2	5.5	802	9.0	656.9 m (ν_8)
B ₁ (ν_{18})	763.8	67.4	825	78.3	736.7 s (ν_{18})
A ₂ (ν_{13})	874.5	0.0	935	0.0	
A ₁ (ν_7)	885.8	0.0	958	0.5	838.8 w (ν_7)
A ₂ (ν_{12})	942.9	0.0	1010	0.0	
B ₂ (ν_{24})	976.1	1.0	1034	0.9	935.2 w (ν_{24})
B ₁ (ν_{17})	1050.2	4.4	1133	4.6	979.9 m (ν_{17})
B ₂ (ν_{23})	1122.3	0.1	1192	0.8	1080.7 ^c
A ₁ (ν_6)	1137.7	0.4	1210	0.0	
A ₂ (ν_{11})	1150.3	0.0	1205	0.0	
B ₁ (ν_{16})	1199.9	0.0	1248	2.4	
B ₁ (ν_{15})	1207.6	15.5	1305	14.4	1110.0 s (ν_{15})
					1145 m ($\nu_9 + \nu_{18}$)
A ₂ (ν_{10})	1229.5	0.0	1306	0.0	1245 w ($\nu_7 + \nu_9$)
A ₁ (ν_5)	1326.9	1.6	1417	1.3	1266.0 m (ν_5, ν_{22})
B ₂ (ν_{22})	1352.2	0.6	1445	1.5	1295 w ($2\nu_8$)
					1394 w ($\nu_8 + \nu_{18}$)
					1453 w ($2\nu_{18}$)
B ₂ (ν_{21})	1568.4	0.9	1644	1.1	1484.6 w (ν_{21})
A ₁ (ν_4)	1595.2	0.3	1684	0.0	1501.3 ^c
					1630 w ($\nu_8 + \nu_{17}$)
					2888 s ($\nu_4 + \nu_5^2$)
					2902 s ($2\nu_{21}^?$)
A ₁ (ν_3)	3099.0	3.1	3251	51.2	2935.4 s (ν_3)
B ₂ (ν_{20})	3101.0	61.6	3251	62.9	2968.7 s (ν_{20})
B ₁ (ν_{14})	3208.4	6.4	3423	8.2	3119.7 w (ν_{14})
A ₁ (ν_2)	3210.4	82.4	3343	33.7	3043.7 s (ν_2, ν_{19})
B ₂ (ν_{19})	3221.7	9.8	3345	23.0	
A ₁ (ν_1)	3224.0	32.8	3437	3.9	3131.2 w (ν_1)

^aUnscaled, for a discussion of the scaled values, see text^bData taken from [25] unless stated otherwise^cAdditional data taken from [26]**Table 3.** Calculated and experimental values of shielding constants (absolute values in ppm)

Method, basis set	SCF HIII	CCSD HIII	CASSCF HIII	CASSCF cc-pVTZ	RAS-II/2e HIII	Experimental ^{a,b}
Atom						
C1	198.61	197.18	202.25	203.53	202.54	203.3 ± 2, 204.7 ^c
C2	164.39	164.76	166.91	169.11	167.71	167.3 ± 2, 167 ^c
H5	30.54	30.26	30.59	30.51	30.50	30.232 ± 0.002
H6	30.59	30.32	30.56	30.53	30.43	30.090 ± 0.002
H7	31.69	31.44	31.61	31.56	31.55	31.101 ± 0.002

^aConverted to absolute shielding using $\sigma(\text{C}) = 199.0$ ppm for TMS [28] and, if needed, 192.7 ppm as the chemical shift of CS_2 with respect to TMS [29], and $\sigma(\text{H}) = 31.59$ ppm for TMS [30]^b[31] unless stated otherwise^c[28]

the basis set dependence CASSCF and RAS-I/2e cc-pVTZ values are presented. To test the accuracy of our results, the most important Fermi contact (FC) contributions were recomputed using some other approximations, and these results are shown in Table 6. In the following discussion of the coupling constants and their comparison with experiment, the differences between various tabulated RASSCF and CCSD results for the FC terms are considered as an additional source of information.

For the carbon-carbon coupling constants, the RASSCF and CCSD results are similar, and the RAS-II/2e results agree fairly well with the experimental

data. For $^1\text{J}(\text{C1}-\text{C2})$, the CCSD value of FC contribution is smaller than all the RASSCF values, and the experimental value is also smaller. These constants have been calculated previously. Galasso, within his EOM approach, obtained $^1\text{J}(\text{C1}-\text{C3}) = -7.77$, $^1\text{J}(\text{C1}-\text{C2}) = 27.83$, and $^2\text{J}(\text{C2}-\text{C4}) = -7.87$ Hz [36] and, more recently in [37], $^1\text{J}(\text{C1}-\text{C3}) = -9.43$ Hz. The results of Carmichael [38], who included the FC terms only ($^1\text{J}(\text{C1}-\text{C3}) = -13.6$ and $^1\text{J}(\text{C1}-\text{C2}) = 24.3$ Hz) as well as the results of [39] are much closer to our values. The set of coupling constants given in [39] is not consistent with C_{2v} symmetry of the molecule, so these constants are not discussed here in detail. We note that the basis

sets used in our work are much larger than any previously applied.

All the RAS-II/2e results for $^1J(\text{C-H})$ couplings are in excellent agreement with experiment. Similarly to our previous work [8], for these constants the CCSD approach appears to give (at least for the HIII basis set) too small values. The RAS-II/2e values of the other C-H and H-H coupling constants are also in fairly good agreement with experimental data. For all the $^2J(\text{C-H})$ constants, further improvement would be obtained using the CCSD results for the FC contribution. The largest discrepancy is found for

Table 4. Individual components of the ^{13}C shielding tensors (absolute values in ppm)

	SCF HIII	CASSCF HIII	SCF [28]	Experimental ^a [28]
CH ₂				
$\sigma_{\text{A}'}$	184.90	187.26	189	(179)
σ_{B}	158.06	158.24	161	(164)
$\sigma_{\text{C}'}$	150.22	155.23	156	(158)
δ	60°23'	59°17'	56°	
σ_{iso}	164.39	166.91	168.7	167
CH				
σ_{\parallel}	159.16	163.05	167	(176)
σ_{\perp}	216.51	220.74	223	(218)
σ_{\perp}'	220.16	222.97	225	(220)
δ'	-7°47'	-10°22'	-6°	
σ_{iso}	198.61	202.25	205	204.7

^a Converted to absolute shielding using $\sigma(\text{C}) = 199.0$ ppm for TMS [28]. For a detailed description of the principal axis systems, see [28]

$^2J(\text{H6-H7})$. For this constant there are also relatively large differences between various CASSCF, RASSCF, and CCSD results. Using the CCSD value of the FC term would bring the total value closer to experiment, but the difference nevertheless remains more significant than for other coupling constants. We have observed similar problems in the calculation of geminal H-H coupling constant in ethylene (Table 8 in [1]). It ap-

Table 6. Fermi contact components of spin-spin coupling constants (in Hz)

Constant	RAS-II/2e HIII	CCSD HIII	RAS-I/4e HIII	RAS-II/2e HIII
$^1J(\text{C1-C3})$	-15.06	-14.50	-12.33	-13.79
$^1J(\text{C1-C2})$	31.41	24.63	30.73	29.86
$^2J(\text{C2-C4})$	0.36	1.80	4.06	0.30
$^1J(\text{C1-H5})$	206.96	189.82	196.29	205.08
$^1J(\text{C2-H6})$	154.94	138.73	149.51	153.35
$^1J(\text{C2-H7})$	172.37	156.75	188.19	171.16
$^2J(\text{C1-H6})$	-6.16	-3.82	-4.94	-5.36
$^2J(\text{C1-H7})$	-2.81	-1.45	-3.34	-2.14
$^2J(\text{C1-H8})$	-5.65	-4.09	-5.24	-5.43
$^2J(\text{C2-H5})$	3.04	3.45	3.29	3.17
$^3J(\text{C2-H9})$	5.23	5.22	2.98	4.86
$^3J(\text{C2-H10})$	15.44	14.72	15.75	15.28
$^2J(\text{H6-H7})$	-6.55	-3.55	-6.19	-5.46
$^3J(\text{H5-H6})$	2.61	2.25	2.51	2.64
$^3J(\text{H5-H7})$	0.11	0.31	-0.21	-0.06
$^3J(\text{H5-H8})$	10.90	8.98	11.04	11.47
$^4J(\text{H6-H10})$	4.21	3.66	4.81	4.99
$^4J(\text{H7-H9})$	0.96	0.88	3.56	1.37
$^4J(\text{H7-H10})$	-0.39	-0.36	-0.92	-0.36

Table 5. Total spin-spin coupling constants (in Hz)

Constant	CASSCF cc-pVTZ	RAS-I/2e cc-pVTZ	CASSCF HIII	RAS-I/2e HIII	RAS-II/2e HIII	Experimental ^a
$^1J(\text{C1-C3})$	-13.45	-14.46	-12.10	-13.65	-15.52	-17.49 ^b , -16.0 ± 0.5 ^c , -5.4 ^d
$^1J(\text{C1-C2})$	29.30	24.83	36.83	31.60	28.37	21.0 ± 0.2 ^e
$^2J(\text{C2-C4})$	-0.24	2.65	-0.53	2.47	-0.09	
$^1J(\text{C1-H5})$	213.09	196.10	221.60	203.24	206.09	205 ± 2 ^f
$^1J(\text{C2-H6})$	163.38	146.59	173.18	154.86	154.44	153 ± 1 ^f
$^1J(\text{C2-H7})$	184.15	182.97	191.17	189.87	172.15	169 ± 1 ^f
$^2J(\text{C1-H6})$	-7.78	-5.62	-8.35	-5.97	-5.59	(-)3.3 or 0 ± 0.2 ^{f,g}
$^2J(\text{C1-H7})$	-4.41	-3.90	-3.93	-3.36	-1.89	0 or 3.3 ± 0.2 ^{f,g}
$^2J(\text{C1-H8})$	-6.31	-4.71	-7.34	-5.46	-4.90	(-)3.3 ± 0.2 ^f
$^2J(\text{C2-H5})$	2.01	2.45	2.63	3.19	3.16	5.3 ± 0.2 ^f
$^3J(\text{C2-H9})$	4.28	2.86	4.80	3.36	4.76	5.3 ± 0.2 ^f
$^3J(\text{C2-H10})$	15.31	15.10	15.92	15.69	15.21	16.0 ± 0.5 ^f
$^2J(\text{H6-H7})$	-7.22	-5.86	-7.77	-6.29	-5.00	(-) 0.6 or 0.4 ± 0.2 ^f
$^3J(\text{H5-H6})$	2.54	2.21	2.85	2.50	2.59	2.9 ± 0.2 ^f
$^3J(\text{H5-H7})$	-0.42	-0.70	-0.07	-0.21	-0.08	1.2 ± 0.2 ^f
$^3J(\text{H5-H8})$	12.84	10.88	13.71	11.63	11.59	10.4 ± 0.2 ^f
$^4J(\text{H6-H10})$	4.62	4.07	5.48	4.92	5.04	5.9 ± 0.2 ^f
$^4J(\text{H7-H9})$	1.84	3.03	1.80	3.06	1.40	1.1 ± 0.5 ^f
$^4J(\text{H7-H10})$	-0.81	-1.16	-0.55	-0.91	-0.46	0.6 or 0.4 ± 0.2 ^f

^a The (-) signs are attributed to some of the constants on the basis of our calculations

^b For 2,2,4,4-tetra(trideuteriomethyl)bicyclo[1.1.0]butane-1,3- $^{13}\text{C}_2$ [32]

^c For 1-cyanobicyclo[1.1.0]butane [33]

^d For 1-methyl- ^{13}C -3-phenylbicyclo[1.1.0]butane-1,3- $^{13}\text{C}_2$ -*exo,exo*-2,4-dicarboxylate [34]

^e [35]

^f [31]

^g On the basis of our calculations we attribute the first of the two values to this constant

pears that for such small constants strong dependence on the basis set and description of correlation effects makes it difficult to achieve very accurate results. Nevertheless, on the basis of our calculations and comparison with the geminal H-H coupling in cyclopropane [40] we attribute a minus sign to the ${}^2J(\text{H6-H7})$ constant.

Conclusions

As a first step towards a systematic analysis of the NMR parameters of bicyclobutane, we optimized the molecular structure using a RASSCF function. The computed bond lengths and angles compare well with experimental values; the accuracy is practically the same as at MP2 level. A following study of IR frequencies and intensities shows that the applied wavefunction recovers a significant part of correlation corrections, the RASSCF values being significantly better than SCF results.

In the calculation of shielding and spin-spin coupling constants we used a series of MCSCF functions and a CCSD wavefunction. Basis sets suitable for the description of these properties were chosen, and the dependence of the results on the wavefunction and basis set was analyzed. The calculated shielding constants agree with the experimental data, and we confirm the assignment of individual components obtained at the SCF level for the carbon shielding tensors. The spin-spin coupling constants are also close to the experimental values, except for the geminal H-H coupling. This discrepancy appears to be due to stronger than expected dependence of our result on the approximations used in the theory. However, we did not analyze the rovibrational and solvent effects, which may also contribute to the differences between the computed values and the experimental spectrum.

An important result of this study is that for most NMR parameters we have obtained similar results in the MCSCF and CCSD approaches, since these two approximations are of a very different nature. In the first, it is relatively easy to account for the static correlation effects (like the dominant excitation from the bonding to the antibonding C-C orbital) relevant for electronic states that require a multiconfiguration description, but it is fairly difficult to describe within MCSCF the dynamic correlation effects. In the CCSD, in contrast, the dynamic electron correlation is taken into account but the method starts with a single-determinant Hartree-Fock description of the reference state. The similarity of our final MCSCF and CCSD results, in particular the values of the bridgehead C-C coupling constant, indicates that we have a reasonably accurate description of both types of electron correlation effects. Finally, as expected from the structure of bicyclobutane, the value of the bridgehead C-C coupling constant indeed lies between the corresponding values for [1.1.1]propellane and bicyclopentane.

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References

1. Helgaker T, Jaszunski M, Ruud K (1999) *Chem Rev* 99: 293
2. Ruud K, Helgaker T, Kobayashi R, Jorgensen P, Bak KL, Jensen HJA (1994) *J Chem Phys* 100: 8178
3. Vahtras O, Ågren H, Jorgensen P, Jensen HJA, Padkjaer SB, Helgaker T (1992) *J Chem Phys* 96: 6120
4. Gauss J, Stanton JF (2000) *Phys Chem Chem Phys* 2: 2047
5. Auer AA, Gauss J (2001) *J Chem Phys* 115: 1619
6. Jaszunski M, Ruud K (2001) *Chem Phys Lett* 336: 473
7. Pecul M, Jaszunski M, Sadlej J (1999) *Chem Phys Lett* 305: 139
8. Pecul M, Dodziuk H, Jaszunski M, Lukin O, Leszczynski J (2001) *Phys Chem Chem Phys* 3: 1986
9. Dodziuk H (1994) *Top Stereochem* 21: 351
10. Dodziuk H (1995) *Modern conformational analysis. Elucidating novel exciting molecular structures*. VCH Publishers, New York
11. Komarov IV (2001) *Russ Chem Rev* 70: 991
12. Wiberg KB (1989) *Chem Rev* 89: 997
13. Kuznetsova TA, Istomina NV, Krivdin LB (2000) *Russ J Org Chem* 36: 638
14. Kendall RA, Dunning TH Jr, Harrison RJ (1992) *J Chem Phys* 96: 6796
15. Schindler M, Kutzelnigg W (1982) *J Chem Phys* 76: 1919
16. Huzinaga S (1971) *Approximate atomic functions*. Technical report. University of Alberta, Edmonton
17. Huzinaga S (1965) *J Chem Phys* 42: 1293
18. Helgaker T, Jaszunski M, Ruud K, Górska A (1998) *Theor Chem Acc* 99: 175
19. London F (1937) *J Phys Radium* 8: 397
20. Ditchfield R (1972) *J Chem Phys* 56: 5688
21. Wolinski K, Hinton JF, Pulay P (1990) *J Am Chem Soc* 112: 8251
22. Helgaker T, Jensen HJA, Jørgensen P, Olsen J, Ruud K, Ågren H, Auer AA, Bak KL, Bakken V, Christiansen O, Coriani S, Dahle P, Dalskov EK, Enevoldsen T, Fernandez B, Hättig C, Hald K, Halkier A, Heiberg H, Hettema H, Jonsson D, Kirpekar S, Kobayashi R, Koch H, Mikkelsen KV, Norman P, Packer MJ, Pedersen TB, Ruden TA, Sanchez A, Saue T, Sauer SPA, Schimmelpfennig B, Sylvester-Hvid KO, Taylor PR, Vahtras O (2001) *Dalton, a molecular electronic structure program*. Release 1.2. See <http://www.kjemi.uio.no/software/dalton/dalton.html>
23. Stanton JF, Gauss J, Watts JD, Lauderdale WJ, Bartlett RJ (1994) *ACES II Program System*. Release 2.0. QTP, University of Florida, Gainesville
24. Szalay PG, Gauss J, Stanton JF (1998) *Theor Chem Acc* 100: 5
25. Wiberg KB, Waddell ST, Rosenberg RE (1990) *J Am Chem Soc* 112: 2184
26. Walters VA, Hadad CM, Thiel Y, Colson SD, Wiberg KB, Johnson PM, Foresman JB (1991) *J Am Chem Soc* 113: 4782
27. Sakai S (2000) *Chem Phys Lett* 319: 687
28. Orendt AM, Facelli JC, Grant DM, Michl J, Walker FH, Dailey WP, Waddell ST, Wiberg KB, Schindler M, Kutzelnigg W (1985) *Theor Chim Acta* 68: 421
29. Kalinowski HO, Berger S, Braun S (1994) *Carbon-13 NMR spectroscopy*. Wiley, Chichester
30. Ochsenfeld C (2000) *Phys Chem Chem Phys* 2: 2153
31. Wüthrich K, Meiboom S, Snyder LC (1970) *J Chem Phys* 52: 230
32. Finkelmeier H, Lüttke W (1978) *J Am Chem Soc* 100: 6261
33. Pomerantz M, Hillenbrand DF (1973) *J Am Chem Soc* 95: 5809
34. Pomerantz M, Fink R, Gray GA (1976) *J Am Chem Soc* 98: 291
35. Bertrand RD, Grant DM, Allred EL, Hinshaw JC, Strong AB (1972) *J Am Chem Soc* 94: 997
36. Galasso V (1987) *Chem Phys* 117: 415
37. Galasso V (1994) *Chem Phys Lett* 230: 387
38. Carmichael I (1993) *J Phys Chem* 97: 1789
39. Sekino H, Bartlett RJ (1994) *Chem Phys Lett* 225: 486
40. Günther H (1980) *NMR spectroscopy. An introduction*. Wiley, Chichester