

¹H and ¹³C chemical shift calculations for 12-oxa-pentacyclo[6.2.1.1^{6,9}.0^{2,7}.0^{2,10}]dodeca-4-eno systems using GIAO method at different levels of theory

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Abstract

We present a comparison between the theoretical and experimental ¹H and ¹³C chemical shifts of molecules **1–5**. In order to compute the chemical shifts, it was necessary to calculate the geometric parameters for the cited alcohols considering in any case the level of theory used in the chemical shift treatment. Thus, RHF ab initio and DFT with at least 6-31G(d) basis sets were used. The geometry parameters of alcohol **1** compare well with X-ray data. The theoretical chemical shifts were obtained using the GIAO method in association with RHF ab initio and DFT levels of theory with at least 6-31G(d) basis sets. Associations with RHF ab initio geometry and DFT levels of theory for the GIAO calculations were also tested. This data set indicates that there are problems of geometric character in the calculation of the brominated vinylic system. On the other hand, the calculations for the nortricyclic cyclopropane ring are in good agreement with experimental findings. © 2005 Elsevier B.V. All rights reserved.

Keywords: Chemical shift calculation; GIAO method; Vinyl bromide; Cyclopropane

1. Introduction

The systematic research on the synthesis and molecular analysis of rigid polycyclic systems has provided answers to some subjects in synthetic organic chemistry such as the structure/reactivity relationship in strained compounds [1]. Also, applications of NMR spectroscopy to the conformational analysis of rigid organic molecules are well known [2]. During the past few years, our group has been working on the synthesis [3–5] and characterization of rigid polycyclic molecules by NMR [6–9] and theoretical methods [10–13]. Recently, we communicated the synthesis of 5-bromo-12-oxa-pentacyclo[6.2.1.1^{6,9}.0^{2,7}.0^{2,10}]dodeca-4-en-3-endo-ol **1** (Fig. 1) and its spectroscopic characterization [14]. In addition, the enantiomeric resolution of

alcohols **1** and **2** was well established [15]. As part of the synthetic work, we have also achieved the synthesis of 12-oxa-pentacyclo[6.2.1.1^{6,9}.0^{2,7}.0^{2,10}]dodeca-4-en-3-endo-ol **3** (Fig. 1). These compounds become interesting targets of investigation due to the possibilities of analyzing the same carbon skeleton with and without the halogen atom and the extension of the ring compression over the carbon skeleton.

The gauge-independent atomic orbital (GIAO) method was first adopted for quantum chemical NMR shift calculations by Ditchfield [16]. It has been successfully applied to the calculations of chemical shifts when performed with sufficiently large basis sets that keep electron correlation effects relatively small. A successful example of these considerations is the ab initio calculation of ¹H-NMR parameters in hydrogen-bonded systems like a (H₂O)₁₇ clusters [17] performed at the Hartree–Fock//GIAO (HF//GIAO) level of theory the 6-311G(d,p) for the central water molecule as well as the four molecules in the first

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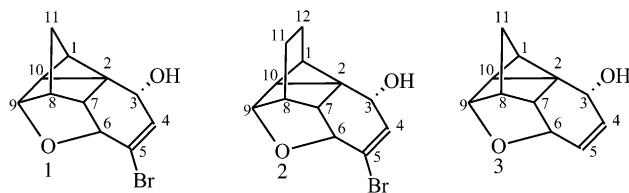


Fig. 1. Alcohols **1**, **2** and **3**.

hydration sphere, and 4-31G for the 12 molecules in the second hydration sphere.

Another factor that should be considered in the quantum calculation of the NMR properties is the employment of good quality geometries [10]. In these cases, ab initio calculations of absolute isotropic magnetic shielding tensors are believed to yield reliable results [18].

On the other hand, there are some recent reports on NMR isotropic magnetic shielding tensor calculations employing the GIAO method associated with the Density Functional Theory (DFT), producing very good results [10,18,19]. DFT calculations are less time consuming and include a significant part of the electron correlation leading to a good accuracy. Thus, they appear as a more suitable method for investigating large molecules when compared with MP2 calculations.

In the present work, focusing on the alcohols **1–3**, we have obtained the optimized geometries by two different ways. One is presented by the ab initio method at Restricted Hartree–Fock (RHF) level of theory and the another, using DFT-B3LYP and B3PW91 levels of theory, with different basis sets. The isotropic magnetic shielding tensors, were calculated employing the GIAO approach associated to the RHF or DFT theory with the same basis sets employed for geometries.

Once discrepancies from the experimental results were found, calculations over some model compounds such as vinyl bromide **4**, nortricyclene **5**, cyclopropane **6** and 1-bromo-cyclohexen-3-ol **7** were necessary. To these molecules, we applied the same methodologies as for compounds **1**, **2** and **3**.

Additionally, the solvent effect is considered over the geometry and shielding tensor calculation for alcohol **1**. Also, the previously reported assignment [14] of alcohol **2** was revised and reformulated based on results obtained in this work.

2. Experimental

The ^1H and ^{13}C -NMR spectra of alcohols **1–3** were recorded on a Varian VXR-200 spectrometer at a magnetic field of 4.7 T at 22 °C and/or on a Varian Inova 300 spectrometer at a magnetic field of 7.0 T at 22 °C, using the standard pulse sequences ^1H and APT. The samples were prepared with 10 mg of alcohols **1–3** in 0.5 mL of CDCl_3 containing TMS as internal standard.

The calculations were performed using the GAUSSIAN 98, Revision A.9 package of molecular orbital programs [20] on a Athlon 1.4 GHz processor, at the Computational Chemistry Laboratory of the IQ-UFRGS. Initial geometries of alcohols **1–3** were attained by the AM1 method (Austin Model 1) [21].

The AM1 structure of alcohol **1** was further optimized by the RHF ab initio calculation and also by DFT calculations at B3LYP and B3PW91 levels of theory, using 6-31G(d) and 6-31G(d,p) basis sets and compared with the X-ray analysis.

In attempt to simulate more accurately the experimental NMR conditions, geometry optimization and magnetic shielding tensors of alcohol **1** were computed considering the solvent effect promoted by CHCl_3 . In both calculations, we used a B3LYP level of theory and 6-31g(d,p) basis set. The CHCl_3 effect was considered in terms of the Integral Equation Formalism of the Polarizable Continuum (IEF-PCM) model [22], with a scaling factor of 1.7 [23] applied to Pauling radii. The set of data considering the solvent effect is provided as supplementary material.

The AM1 structures of alcohol **2**, **3** and vinyl bromide **4** were subsequently optimized using RHF ab initio calculation and DFT calculation at B3LYP and B3PW91 levels of theory with the 6-31G(d) basis set.

The AM1 structure of nortricyclene **5** was refined by the RHF ab initio calculations using 6-31G(d), 6-31+G(d), 6-31++G(d) and 6-31G(d,p) basis sets. With DFT calculation, at B3LYP and B3PW91, 6-31G(d) and 6-311G(2df,2p) basis sets were used and for MP2 refinement we used the 6-31G(d) basis set.

The AM1 structure of cyclopropane **6** was refined by RHF ab initio using 6-31G(d), 6-31G(d,p) and 6-311G(2df,2p) basis set. The MP2 refinement was performed using 6-31G(d) basis set.

Chemical shift values were obtained relative to the isotropic shielding tensors of TMS, which were calculated at the same combination of methods, levels of theory and basis sets used for geometry refinement. The isotropic magnetic shielding tensors of all TMS calculations used in this work, bond lengths, bond angles and dihedral angles of alcohol **1** are furnished as supplementary material.

3. Results and discussion

3.1. Experimental chemical shifts of alcohols **1**, **2** and **3**

The experimental ^1H and ^{13}C chemical shifts of alcohols **1**, **2** and **3** are given in Table 1. It is worth to mention that the first proposed assignment of alcohol **2** [14] was established in analogy with the assignment of alcohol **1**. Now, the chemical shift values for the alcohol **2** presented in Table 1 corresponds to a complete assignment and are different from those reported earlier [14].

Table 1
Experimental ^1H and ^{13}C chemical shifts of alcohols **1**, **2** and **3** (ppm)

	Alcohol 1	Alcohol 2	Alcohol 3
C ₁	18.3	13.9	18.1
C ₂	29.0	25.2	27.7
C ₃	65.8	65.7	64.5
C ₄	137.8	136.1	137.8
C ₅	127.8	125.7	129.8
C ₆	79.6	78.6	71.4
C ₇	49.1	44.8	42.9
C ₈	43.1	40.3	47.8
C ₉	83.0	79.0	82.6
C ₁₀	17.5	20.9	17.3
C ₁₁	30.1	14.5	29.5
C ₁₂	–	18.0	–
H ₁	1.82	1.36	1.77
H ₃	4.63	4.51	4.85
H ₄	6.38	6.31	6.02
H ₅	–	–	6.02
H ₆	4.43	4.14	4.33
H ₇	2.42	2.52	2.21
H ₈	2.25	1.89	2.25
H ₉	4.43	4.32	4.33
H ₁₀	1.31	1.36	1.23
H _{11a}	1.74	1.72	1.70
H _{11b}	1.74	1.72	1.70
H _{12a}	–	1.62	–
H _{12b}	–	1.62	–

The bold chemical shifts of alcohol **2** were estimated from HMQC experiments.

From a first analysis of the ^1H chemical shifts shown in Table 1, one notes the similarity among the values presented for each alcohol. On the other hand, the ^{13}C magnetic resonance as a more sensible property regarding geometric parameters, presents values that are less coherent with the structural resembling among these alcohols. Examples are the differences between carbons C₁, C₂ and C₁₀ from alcohols **1** and **3** with respect to the same carbons of alcohol **2**. In addition, a general shielding trend of the hydrogens of alcohol **2** may be detected comparing it with alcohols **1** and **3**.

A possible reason is the steric compression over the carbon skeleton manifested by alcohols **1** and **3**. The less pronounced compression in the alcohol **2** decreases the distortion of electronic clouds of the carbons and hydrogens, causing the observed shielding effects.

Concerning the presence of halogen at the carbon C₅ of alcohol **1**, it promotes a small shield effect of 2 ppm when compared with the same carbon atom of alcohol **3**. This observation is similar to the already reported for chlorinated compounds derived from ‘aldrin’ [7] for the presence or absence of chlorine atoms attached to olefinic carbon atoms.

For alcohol **1**, the X-ray analysis has already been published with CCDC deposition number 118920 that contains the supplementary crystallographic data for this paper [24]. Therefore, alcohol **1** refers as a model compound for the quantum calculations. These calculations may also

Table 2
Calculated energies for alcohol **1**

Level of theory	Energy (hartree)
RHF/6-31G(d)	–3142.4974
RHF/6-31G(d,p)	–3142.5203
B3LYP/6-31G(d)	–3147.8615
B3LYP/6-31G(d,p)	–3147.8817
B3LYP/6-31G(d,p)*	–3147.8873
B3PW91/6-31G(d)	–3147.6501
B3PW91/6-31G(d,p)	–3147.6695

1 hartree = 627.5095 kcal/mol. *Considering the solvent effect.

generate theoretical support for some of the observation mentioned above.

3.2. Geometry optimization of alcohols **1**, **2** and **3**

3.2.1. General

The energies relative to the achieved geometries for alcohol **1** are listed in Table 2.

The calculated bond lengths, bond angles and dihedral angles were compared with those measured by the X-ray analysis. Considering the bond lengths (not shown), it is observed that computed results present no significant difference from the experimental values even considering the solvent effect.

3.2.2. Gas phase geometry

Some of the calculated bond angles are given in Table 3. The agreement with the X-ray results is satisfactory (max. diff. 3.4° for H₉–C₉–C₁₀). Especial attention has been drawn to the internal angles composing the cyclopropane ring (C₁–C₂–C₁₀, C₁–C₁₀–C₂ and C₂–C₁–C₁₀). Although compressed, they agree very well with the experimental values.

Table 4 shows the dihedral angles presenting differences that are more significant. The differences between the calculated and the experimental values of C₁–C₂–C₃–OH, C₁–C₂–C₃–C₄, C₄–C₃–C₂–C₁₀, C₂–C₇–C₆–C₅ dihedrals are 5.2, 4.6, 5.4 and 4.6°, respectively (calculated greater than experimental as may be seen from the Table 4). On the other hand, larger differences of dihedrals HO–C₃–C₂–C₁₀ and C₂–C₇–C₆–O were 6.1 and 3.8°, respectively, but smaller than the experimental value.

In view of the minor differences observed among the experimental and the calculated data for alcohol **1**, the calculations were considered consistent. Thus, the geometries of alcohols **2** and **3** were attained at the same three levels of theory already employed, but using only the 6-31G(d) basis set.

Considering the experimental chemical shifts given in Table 1, one expects different charge distribution at each atom of the molecule when comparing alcohols **1** and **3** with alcohol **2**. Instead, a very similar charge distribution was found. Table 5 denotes this effect at carbon C₁₀ on the basis of Mulliken charges.

Table 3

Experimental and calculated bond angles of alcohol **1** (°)

	X-ray	RHF		B3LYP		B3PW91	
		6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)
H ₉ –C ₉ –C ₁₀	113.7	117.2	117.1	117.3	117.2	117.1	117.8
C ₁ –C ₂ –C ₁₀	60.2(3)	60.2	60.2	60.1	60.1	60.1	60.1
C ₁ –C ₁₀ –C ₂	59.4(3)	59.5	59.5	59.4	59.4	59.4	59.4
C ₂ –C ₁ –C ₁₀	61.4(3)	60.3	60.3	60.5	60.5	60.5	60.5

Table 4

Selected experimental and calculated dihedral angles of alcohol **1** (°)

	X-ray	RHF		B3LYP		B3PW91	
		6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)	6-31G(d)	6-31G(d,p)
C ₁ –C ₂ –C ₃ –OH	–29.7(6)	–34.8	–34.8	–34.9	–34.9	–34.9	–34.7
C ₁ –C ₂ –C ₃ –C ₄	–151.3(4)	–155.7	–155.7	–155.9	–155.9	–155.7	–155.7
HO–C ₃ –C ₂ –C ₁₀	47.0(5)	41.6	41.6	40.9	40.9	41.1	41.1
C ₄ –C ₃ –C ₂ –C ₁₀	–74.6(5)	–79.2	–79.2	–80.0	–80.0	–79.9	–79.9
C ₂ –C ₇ –C ₆ –O	–77.3(4)	–73.5	–73.5	–74.0	–74.0	–74.1	–74.1
C ₂ –C ₇ –C ₆ –C ₅	42.2(4)	46.8	46.8	46.5	46.5	46.5	46.5

3.2.3. Geometry with solvent effect¹

In a general way, computations considering the solvent effect do not increase accuracy for the calculated bond angles. The angle H₉–C₉–C₁₀ persist being the major variation with a difference of 3.6° from the experimental value obtained by X-ray analysis. Concerning the cyclopropanic bond angles, the results obtained considering the solvent effect agree very well with those achieved without consideration of the solvent effect.

With respect to the torsion angles, the major differences (larger and smaller) from the experimental values were observed at the same angles already compared in Section 3.2.2. The differences between the calculated and the experimental values of C₁–C₂–C₃–OH, C₁–C₂–C₃–C₄, C₄–C₃–C₂–C₁₀, C₂–C₇–C₆–C₅ dihedrals are 5.5, 4.5, 5.4 and 4.0°, respectively. On the other hand, larger differences of dihedrals HO–C₃–C₂–C₁₀ and C₂–C₇–C₆–O were 6.4 and 3.3°, respectively, but smaller than the experimental value. From this set of data, it is possible to consider the results with and without solvent effect as similar in view of the geometry optimization.

3.3. Calculated chemical shifts

3.3.1. ¹H Chemical shifts of alcohols **1**, **2** and **3**

The NMR absolute isotropic shielding tensors were accomplished by GIAO calculation from each of the three geometries obtained before, using the same level of theory and basis set. The geometry achieved at the RHF theory was also used to perform the NMR calculation at the B3LYP and B3PW91 density functionals. The ¹H absolute isotropic shielding tensors were converted to chemical shift relative

to TMS using the corresponding absolute isotropic shielding tensor. The results of these calculations are given in the [Tables 6, 7 and 8](#).

Comparing each experimental ¹H chemical shift for alcohol **1** with the respective calculated value in [Table 6](#), it becomes evident that the GIAO//RHF/6-31G(d,p) approach applied to the optimized RHF/6-31G(d,p) geometry generate results with a shielding effect up to 0.8 ppm (hydrogen H₆). This particular calculation presents the largest disagreement with the experiment. Considering a hydrogen scale of 10 ppm, this deviation represents an error of almost 10%, being considered as unsatisfactory. The GIAO//B3PW91/6-31G(d) approach applied to the B3PW91/6-31G(d) geometry furnishes more values matching the experimental data, with an average difference of 0.21 ppm, representing an error of approximately 2% on the hydrogen scale. Observing these results in view of the basis set, we found that the two combinations of density functionals with 6-31G(d,p) basis set for geometry and NMR calculation, provides a slightly more accurate description of the hydrogen chemical shifts with an average error of about 1%. In fact, the utilization of any of these calculations for chemical shifts as an auxiliary tool for the interpretation of the ¹H-NMR spectrum of alcohol **1**, provides a good assignment. Nevertheless, once the spectroscopic data are known, the best choice for the computational procedure

Table 5

Mulliken charge distribution for carbon C₁₀ of alcohols **1**, **2** and **3** using 6-31G(d) basis set

	Alcohol 1	Alcohol 2	Alcohol 3
RHF	–0.2052	–0.1933	–0.2051
B3LYP	–0.1399	–0.1396	–0.1400
B3PW91	–0.1651	–0.1612	–0.1653

¹ See supplementary material.

Table 6
Experimental and calculated ^1H chemical shifts of alcohol **1** (ppm)

Basis set		6-31G(d)				6-31G(d,p)			
Geometry		RHF			B3LYP	B3PW91	RHF	B3LYP	B3PW91
NMR	Experimental	RHF	B3LYP	B3PW91	B3LYP	B3PW91	RHF	B3LYP	B3PW91
H ₁	1.82	1.59	1.56	1.60	1.67	1.69	1.55	1.72	1.73
H ₃	4.63	4.10	4.69	4.67	4.74	4.70	4.07	4.81	4.78
H ₄	6.38	6.07	5.82	5.92	5.77	5.88	6.15	6.00	6.13
H ₆	4.43	3.70	4.09	4.09	4.15	4.15	3.63	4.21	4.21
H ₇	2.42	1.85	2.18	2.22	2.22	2.22	1.79	2.23	2.23
H ₈	2.25	1.71	1.77	1.82	1.81	1.82	1.69	1.88	1.89
H ₉	4.43	4.17	4.17	4.21	4.19	4.20	4.00	4.31	4.32
H ₁₀	1.31	1.42	1.41	1.47	1.48	1.50	1.39	1.53	1.55
H _{11a}	1.74	1.42	1.60	1.60	1.61	1.61	1.36	1.63	1.63
H _{11b}	1.74	1.42	1.62	1.63	1.64	1.64	1.37	1.66	1.66

seems to be the density functionals with 6-31G(d,p) basis set for geometry and NMR parameters calculation.

Having achieved the results described above, the three geometries accomplished for alcohol **2** were also submitted to the GIAO absolute isotropic shielding tensor calculation. Using the RHF geometry, the GIAO calculation was performed at the RHF, B3LYP and B3PW91 levels of theory using the 6-31G(d) basis set. The B3LYP geometry was submitted to the GIAO calculation employing the same density functional with the 6-31G(d) basis set. The B3PW91 geometry was submitted to the GIAO calculation also employing the same density functional with the 6-31G(d) basis set. The chemical shifts relative to TMS calculated at the corresponding levels of theory and basis set are given in Table 7. These data present the RHF//B3PW91 and B3LYP//B3LYP approaches as best results, presenting more values matching the experimental data set.

It should be noted that the hydrogens H_{11a}, H_{11b}, H_{12a} and H_{12b} are accumulated between 1.57 and 1.72 ppm. Consequently, the respective chemical shift values were

estimated by ^{13}C – ^1H correlation experiments. The calculated chemical shifts for these hydrogens at the RHF//B3PW91, B3LYP//B3LYP and B3PW91//B3PW91 approaches are in accordance with the experimental interval. Thus, the GIAO calculation of magnetic shielding tensors is considered as successful in the prediction of hydrogen chemical shifts of alcohol **2**.

Table 8 shows the chemical shifts for alcohol **3** obtained from the same type of calculation. Here, again, the DFT levels of theory used for geometry and shielding tensor calculations provided the best results.

In fact, the GIAO method at the DFT levels of theory achieved more accurate ^1H results for alcohols **1**, **2** and **3**, although it is mentioned in the literature [25] that this method does not furnish good results for hydrogen nuclei. In addition, such results point to some significant influence of the electron correlation on the ^1H chemical shifts calculation in these molecules. Thus, the accuracy of the ^1H chemical shifts achieved by using the DFT computations for geometry and NMR parameters was sufficient to use it as a tool in

Table 7
Experimental and calculated ^1H chemical shifts of alcohol **2** (ppm)

Basis set		6-31G(d)			
Geometry		RHF			B3PW91
NMR	Experimental	RHF	B3LYP	B3PW91	B3PW91
H ₁	1.36	1.16	0.96	1.34	1.47
H ₃	4.51	4.02	4.26	4.60	4.67
H ₄	6.31	5.98	5.37	5.83	5.68
H ₆	4.14	3.44	3.44	3.79	3.87
H ₇	2.52	1.90	1.87	2.28	2.26
H ₈	1.89	1.34	1.23	1.60	1.63
H ₉	4.32	3.92	3.66	4.06	4.08
H ₁₀	1.36	1.40	1.17	1.59	1.60
H _{11a}	1.72	1.46	1.24	1.57	1.66
H _{11b}	1.72	1.45	1.21	1.53	1.63
H _{12a}	1.62	1.34	1.17	1.51	1.57
H _{12b}	1.62	1.30	1.10	1.44	1.51

The bold chemical shifts were estimated from HMQC experiments.

Table 8
Experimental and calculated ^1H chemical shifts of alcohol **3** (ppm)

Basis set		6-31G(d)				
Geometry		RHF			B3LYP	B3PW91
NMR	Experimental	RHF	B3LYP	B3PW91	B3LYP	B3PW91
H ₁	1.77	1.55	1.56	1.60	1.66	1.68
H ₃	4.58	4.06	4.65	4.62	4.69	4.15
H ₄	6.02	5.87	5.76	5.87	5.70	5.82
H ₅	6.02	6.15	6.00	6.09	5.98	6.08
H ₆	4.33	3.67	4.12	4.11	4.16	4.66
H ₇	2.21	1.77	2.08	2.11	2.12	2.11
H ₈	2.25	1.67	1.74	1.78	1.78	1.79
H ₉	4.33	3.95	4.12	4.15	4.14	4.15
H ₁₀	1.23	1.36	1.37	1.43	1.45	1.46
H _{11a}	1.70	1.40	1.58	1.59	1.60	1.60
H _{11b}	1.70	1.38	1.58	1.59	1.60	1.60

the structural elucidation, at least for the mentioned compounds.

3.3.2. ^{13}C Chemical shifts of alcohols **1**, **2** and **3**

The systematics applied to the hydrogen chemical shifts generates the results given in Table 9 for ^{13}C analysis. All chemical shifts presented are relative to the carbon atoms of TMS.

The RHF ab initio calculations were unable to provide good results for most of the carbons, e.g. C₅, RHF/RHF/6-31G(d,p). Carbon C₅ presents the largest observed differences in all calculations. These differences were traduced as deshielding effect with respect to the experimental value. The best calculation for carbon C₅, provides a deshielding effect of 11.3 ppm with respect to the experimental value. Carbon C₄, is best represented by the RHF ab initio calculation, but shieldings of up to 5.6 ppm were observed (C₄, RHF/B3LYP/6-31G(d)), depending on the calculation approach.

Table 10 shows the experimental and calculated chemical shifts for these two carbons of alcohols **2** and **3**.

For alcohol **2** similar discrepancies for the carbons C₄ and C₅ were observed.

In contrast, alcohol **3** exhibits a much better value of chemical shift of carbon C₅. Although the RHF ab initio approach provided the best results for carbons C₄ and C₅, this methodology produces less satisfactory results for the other carbons. For the carbon atoms, with exception of C₁ and C₁₀, the DFT calculations give equivalent reasonable results as much as the mixed ab initio/DFT approaches.

Considering the chemical shifts of C₄ and C₅ presented in Tables 9 and 10, the employed approaches seem to be unable to describe correctly the experimental data.

It is well known that the presence of a heavy atom attached to a carbon shields this carbon and deshields the beta carbon due to a diamagnetic shielding produced by the large number of electrons close to the heavy atom. These effects are observed experimentally for alcohols **1** and **2**. In this way, the calculations seem to treat the presence of the bromine atom more in terms of an inductive effect, which actually should deshield the alpha carbon. Thus, experimentally, the effect can be understood in terms of the heavy

Table 9
Experimental and calculated ^{13}C chemical shifts of alcohol **1** (ppm)

Basis set		6-31G(d)					6-31G(d,p)		
Geometry		RHF			B3LYP	B3PW91	RHF	B3LYP	B3PW91
NMR	Experimental	RHF	B3LYP	B3PW91	B3LYP	B3PW91	RHF	B3LYP	B3PW91
C ₁	18.3	14.5	19.9	20.2	21.2	20.8	15.0	22.1	21.6
C ₂	29.0	18.7	28.0	27.8	27.2	26.9	20.2	29.8	28.9
C ₃	65.8	57.7	64.7	65.2	66.1	65.6	58.5	67.4	66.8
C ₄	137.8	136.4	132.2	133.1	133.2	134.2	137.3	134.4	135.4
C ₅	127.8	139.1	141.0	140.9	143.5	141.7	140.7	145.7	143.9
C ₆	79.6	69.7	78.4	78.2	80.0	79.0	70.6	81.3	80.3
C ₇	49.1	42.0	51.1	51.0	51.4	50.2	42.9	52.4	51.3
C ₈	43.1	36.5	43.6	43.4	44.5	43.5	37.2	45.6	44.5
C ₉	83.0	71.4	80.0	80.3	81.7	81.0	72.1	82.9	82.1
C ₁₀	17.5	14.1	21.1	21.3	21.4	21.0	14.7	22.4	22.0
C ₁₁	30.1	27.4	31.2	31.4	31.3	31.1	27.7	31.8	31.5

Table 10

Experimental and calculated ^{13}C chemical shifts for C_4 and C_5 of alcohols **2** and **3** (ppm)

	Alcohol 2		Alcohol 3	
	C_4	C_5	C_4	C_5
Experimental	136.1	125.7	137.8	129.8
RHF//RHF/6-31G(d)	134.7	137.8	133.3	128.9
RHF//B3LYP/6-31G(d)	130.7	140.1	131.7	125.3
RHF//B3PW91/6-31G(d)	131.3	139.6	132.7	126.4
B3LYP//B3LYP/6-31G(d)	131.2	142.3	132.6	126.3
B3PW91//B3PW91/6-31G(d)	132.2	140.6	133.5	127.3

atom effect over the double bond carbons. The calculated result carries a large inductive effect that does not describe correctly the experimental data.

The same evaluation used for carbons C_4 and C_5 , was applied to the carbons C_1 and C_{10} . The best and the worst fitted chemical shift for carbon C_1 of alcohol **1** differs, in absolute values, respectively, from 1.6 (RHF//B3LYP/6-31G(d)) to 3.8 ppm (B3LYP//B3LYP/6-31G(d,p)) and from 2.8 (RHF//RHF/6-31G(d,p)) to 4.9 ppm (B3LYP//B3LYP/6-31G(d,p)) for carbon C_{10} from the experimental. Straighting this analysis to the 6-31G(d) basis set, it is found that the differences for carbon C_1 range from 1.6 (RHF//B3LYP/6-31G(d)) to 2.9 ppm (B3LYP//B3LYP/6-31G(d)). For carbon C_{10} , the variation is between 3.4 (RHF//RHF/6-31G(d)) and 3.9 ppm (B3LYP//B3LYP/6-31G(d)).

Alcohol **2** presents variations in absolute values from 2.2 (RHF//B3PW91/6-31G(d)) to 3.5 ppm (RHF//RHF/6-31G(d)) for carbon C_1 and from 2.8 (B3PW91//B3PW91/6-31G(d)) to 4.6 ppm (RHF//RHF/6-31G(d)) for carbon C_{10} . Alcohol **3** exhibit differences with the same magnitude already observed for alcohol **1**, 1.9 ppm (RHF//B3LYP/6-31G(d)) to 3.7 ppm (RHF//RHF/6-31G(d)) for carbon C_1 . Carbon C_{10} of alcohol **3** exhibit values comparable only with those observed for alcohol **1**, 3.2 ppm (RHF//RHF/6-31G(d)) and 4.1 ppm (RHF//B3LYP/6-31G(d)). The experimental and calculated chemical shifts for carbons C_1 and C_{10} of alcohols **2** and **3** are given in Table 11.

The deshielding observed for carbon C_{10} of alcohol **2** could be expected once the bond angle $\text{C}_9\text{--}\text{C}_{10}\text{--}\text{C}_1$ of alcohol **3** is very similar to that observed for alcohol **1** and about 9° minor than for alcohol **3**. This angle for each geometry calculation is given in Table 12. In alcohol **2**, evidences of

the enhancement of the p character of carbon C_{10} orbitals in accordance with the observed chemical shift are found.

It is noteworthy that the difference between the experimental chemical shifts of carbons C_1 and C_{10} of alcohols **1** and **3** is less than 1 ppm. Thus, the results attained via computational calculation not guarantee the correct assignment of these carbons. On the other hand, the larger difference between these carbons in alcohol **2** could clearly be distinguished by the calculations.

3.3.3. ^1H and ^{13}C Chemical shifts of alcohol **1** by IEF-PCM

Due to the rigidity of the carbocyclic ring system, only minor differences between the achieved geometry of alcohol **1** considering the solvent effect and the gas phase geometries were expected and observed.¹ However, one might expected a solvent effect on the chemical shift. Thus, comparing the calculated chemical shifts of ^{13}C achieved with B3LYP/6-31G(d,p), with and without the solvent effect the major difference is 5.8 ppm at the olefinic carbon C_4 (3% in a 200 ppm scale). When compared with the experimental value, the difference considering the solvent effect is 1.6 ppm, slightly lower than the corresponding gas phase value (3.4 ppm). These discrepancies are interpreted as not relevant. Thus, the IEF-PCM does not represent an auxiliary tool for spectral interpretation.

It should be noted the deshielding effect observed over the carbon C_5 , only 1 ppm smaller than the effect observed not considering solvent effect. Thus, the solvent consideration does not affect significantly the erroneous interpretation of the inductive effect over the carbon C_5 . In the same way, the carbons C_1 and C_{10} cannot be distinguished by the computation in solution due to the minor difference of 0.8 ppm between them.

Table 11

Experimental and calculated ^{13}C chemical shifts for C_1 and C_{10} of alcohols **2** and **3** (ppm)

	Alcohol 2		Alcohol 3	
	C_1	C_{10}	C_1	C_{10}
Experimental	13.9	20.9	18.1	17.3
RHF//RHF/6-31G(d)	11.0	16.3	14.4	14.1
RHF//B3LYP/6-31G(d)	16.4	24.3	20.0	21.1
RHF//B3PW91/6-31G(d)	16.1	24.0	20.2	21.2
B3LYP//B3LYP/6-31G(d)	17.4	24.2	21.2	21.3
B3PW91//B3PW91/6-31G(d)	16.7	23.7	20.8	20.9

Table 12
C₉–C₁₀–C₁ bond angle obtained from each geometry calculation at the 6-31G(d) basis set

Geometry	Alcohol 1	Alcohol 2	Alcohol 3
RHF	109.52	118.66	109.55
B3LYP	109.43	118.67	109.55
B3PW91	109.52	118.55	109.47

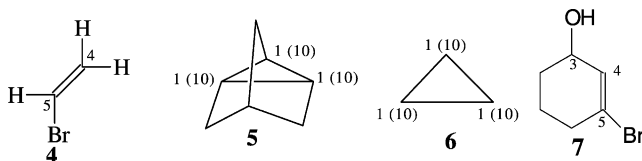


Fig. 2. Model compounds **4**, **5**, **6** and **7**.

The hydrogen chemical shift presents a major difference of 0.5 ppm between calculated chemical shift with and without solvent effect. The larger difference between calculated and experimental chemical shifts is 0.7 ppm at the hydrogen H₃ in the computation considering the solvent effect. This difference corresponds to 7% on a 10 ppm scale, but as the signal of H₃ is easily distinguishable in the experimental spectrum, the result is considered not to be relevant.

3.4. ¹³C Chemical shifts of model molecules **4** to **7**

To verify the conflicted results obtained for the carbons C₄ and C₅ of alcohols **1**, **2**, and **3**, the geometry of vinyl bromide **4** (Fig. 2) was optimized using the same approaches applied to alcohol **2**. The five batches of results were very consistent with the experimental data [26] and are presented in Table 13. The largest difference found in the calculated values with respect to the experiment is 4.13 ppm (C₅, B3PW91//B3PW91). It is worth to mention that in the vinyl bromide the inductive effect predominates over the heavy atom effect in the experimental data. Thus the agreement for the vinyl bromide data suggests that not only a bad interpretation of the diamagnetic shielding is responsible for the poor description of alcohol's **1** and **2** brominated vinyl systems. One possible explanation could be that a better geometry has been applied to proceed the calculation of the magnetic properties of vinyl bromide **4**. Thus, the 6-31G(d) basis set seems to be sufficiently complete to describe the vinyl bromide but not to describe alcohols

1 and **2**. Actually, even 6-31G(d,p) basis set seems not to be complete enough to describe alcohols **1** and **2**.

In attempts to clarify further this question, 1-bromo-cyclohexen-3-ol **7** was optimized and has its shielding tensors calculated at RHF//RHF/6-31G(d,p), B3LYP//B3LYP/6-31G(d,p) and B3PW91//B3PW91/6-31G(d,p) approaches. This data set shows the same inductive effect observed for carbon C₅ of alcohols **1** and **2** acting over the carbon C₅ of 1-bromo-cyclohexen-3-ol **7** that is more deshielded than carbon C₄ (C₄/C₅, respectively: RHF//RHF/6-31G(d,p) 134.7, 135.5 ppm; B3LYP//B3LYP/6-31G(d,p) 131.4, 140.0 ppm; B3PW91//B3PW91/6-31G(d,p) 132.4, 137.9 ppm) in all the theoretical approaches. Unfortunately, experimental NMR data for 1-bromo-cyclohexen-3-ol **7** were not found in the literature and the arguments presented here are only of computational character, but not very helpful in the experimental signal assignment.

In order to elucidate the small differences in the nortricyclic moiety of the target molecules, the geometry of nortricyclicene **5** (Fig. 2) was optimized at the three already used approaches. In this case, also additional basis sets not used previously were tested. Thus, the RHF//RHF, B3LYP//B3LYP and B3PW91//B3PW91 and the mixed RHF//B3LYP, RHF//B3PW91, RHF//MP2 approaches were combined with the 6-31G(d) basis set for the NMR calculation. The ab initio RHF//RHF approach was also applied to the combination with the 6-31G+(d), 6-31G++(d), 6-31G(d,p) and 6-311G(2df,2p). The DFT approaches were also combined with a 6-311G(2df,2p) basis set. Finally, a MP2//MP2 approach using the 6-31G(d) basis set was employed.

All these calculations exhibit a deficiency in describing the nortricyclicene molecule **5**. An exception is the RHF ab initio calculation performed with yhe6-31G(d,p) basis set. Considering an experimental [27] chemical shift of 9.9 ppm for cyclopropanic carbons, this computation has furnished, after treatment, a chemical shift of 8.02 ppm (1.88 ppm of difference). As already mentioned, this methodology applied to molecule **1** did not produce the same agreement with the experimental results.

Despite the much better result obtained for the cyclopropanic carbons at the RHF//RHF/6-31G(d,p) level for the nortricyclicene molecule **5**, the difference between theoretical and experimental chemical shift is almost 2 ppm. This result is not yet satisfactory enough to assign the carbons C₁ and C₁₀ of alcohols **1** and **3**. Thus, we used

Table 13
Experimental and calculated ¹³C chemical shifts of **4** using the 6-31G (d) basis set

	Experimental	RHF			B3LYP	
		RHF	B3LYP	B3PW91	B3LYP	B3PW91
C ₄	115	121.65	114.52	116.54	115.71	117.85
C ₅	122	124.71	124.54	125.56	126.44	126.13

cyclopropane **6** (Fig. 2) as a model for the search for the appropriated calculation approach. The carbon chemical shifts of this target were achieved via ab initio calculation using 6-31G(d), 6-31G(d,p), 6-311G(2df,2p) basis sets and via MP2//MP2 using 6-31G(d) basis set. The described experimental [28] carbon chemical shift of cyclopropane is -4.0 ppm and the calculated results were, respectively, -2.38 , -2.6 , -4.34 and 0.82 ppm. Another calculation described in the literature [28] uses B3LYP/6-31G(d) geometry and B3LYP/6-311G+(2d,p) for NMR calculation producing -6.7 ppm. Here, the best result was achieved by the RHF//RHF/6-311G(2df,2p) approach, which presents a difference of 0.34 ppm from the experimental result. As suggested earlier, the problem in describing the cyclopropanic ring seems to have more geometrical character than electronic nature, as demonstrated when the MP2 level of theory was applied to the geometry and magnetic properties calculation of **5** and **6**.

By simple comparison, it becomes evident that the best approach to the chemical shift calculation of **6**, does not generate the best result for **5**. In the same way, the best approach to the chemical shift calculation of **5**, does not provide a satisfactory result for alcohol **1**. This suggests that following these approaches, only poor results might be achieved for alcohol **2** and **3**.

Another aspect that might be considered is the higher computational cost involved in the use of large basis sets such as 6-31G(d,p), for alcohols **1**, **2** and **3**.

4. Conclusions

We have attained a set of geometry optimization and absolute magnetic shielding tensor calculations for molecules **1** to **7**. The deficiency in describing the chemical shifts of carbons C_4 and C_5 of alcohols **1** and **2** seems to have a stereo-electronic and not only geometric or only electronic character, as demonstrated by the calculations on the alcohol **3** and vinyl bromide **4**.

On the other hand, the differences concerning the carbons C_1 and C_{10} of the target alcohols seems to be more of geometrical than electronic character. We found consistency and good agreement between the experimental and calculated value was achieved for cyclopropane **6** with the large 6-311G(2df,2p) basis set. However, the same basis set failed for nortricylene **5** at the same combination of levels of theory. In addition, the geometric character seems predominate over the electronic character once the second order Moller–Plesset (MP2) level of theory with the 6-31G(d) basis set failed to describe the hydrocarbons **5** and **6**.

The solvent consideration in the computation of geometry and of magnetic shielding tensor does not affect significantly the results.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2004.12.024

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