

**MOLECULAR STRUCTURE AND VIBRATIONAL AND
CHEMICAL SHIFT ASSIGNMENTS OF CIS-1,2-
DIHYDROXY-TRANS-3-METHOXY-1,5,5-
TRIMETHYLCYCLOHEXANE AND CIS-2,3-
DIHYDROXY-TRANS-1-METHOXY-1,5,5-
TRIMETHYLCYCLOHEXANE BY DFT AND AB INITIO
HF CALCULATIONS**

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ABSTRACT

The molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO) ¹H NMR and ¹³C NMR chemical shift values and several thermodynamic parameters of cis-1,2-dihydroxy-trans-3-methoxy-1,5,5-trimethylcyclohexane (6) and cis-2,3-dihydroxy-trans-1-methoxy-1,5,5-trimethylcyclohexane (7) in the ground state have been calculated by using the Hartree-Fock (HF) and density functional method (B3LYP) with 6-31G(d) basis set. The results of the optimized molecular structure are presented and compared with the experimental X-ray diffraction. The computed vibrational frequencies were used to determine the types of molecular motions associated with each of the experimental bands observed. In addition, calculated results were related to the linear correlation plot of experimental ¹H NMR and ¹³C NMR chemical shifts values.

Keywords: cis-1,2-Dihydroxy-trans-3-methoxy-1,5,5-trimethylcyclohexane; cis-2,3-Dihydroxy-trans-1-methoxy-1,5,5-trimethylcyclohexane; DFT; HF; GIAO; ¹H; ¹³C NMR; IR spectra; Structure elucidation; Vibrational assignment

CİS-1,2-DİHİDROKSİ-TRANS-3-METOKSİ-1,5,5-TRİMETİLSİKLOHEKZAN VE CİS-2,3-DİHİDROKSİ-TRANS-1-METOKSİ-1,5,5-TRİMETİLSİKLOHEKZAN MOLEKÜLÜNÜN MOLEKÜL YAPISINI, TİTREŞİM FREKANSINI VE KİMYASAL KAYNAKLARINI YOĞUNLUK FONKSİYON TEORİSİ(DFT) VE AB İNİTİO HF YÖNTEMİYLE İNCELENMESİ

ÖZET

cis- 1,2-dihidroksi-trans-3-metoksi-1,5,5-trimetilsikloheksana ve cis- 2,3-dihidroksi-trans-1-metoksi-1,5,5-trimetilsikloheksan moleküllerinin geometrik titreşim frekansları, atomik orbitalleri içeren (GIAO) ¹H ve ¹³C NMR kimyasal kaymaları ve birçok termodinamik parametreleri yoğunluk fonsiton teorisi(DFT) ve ab initio HF yöntemleri ve 6-31g(d) temel ş efi kullanılarak hesaplandı. Kararlı hale getirilmiş molekül yapısı ile deneysel x-ışınları spektrumu karşılaştırıldı. Teorik olarak hesaplanan titreşim frekansları ile deneysel titreşim frekansları karşılaştırıldı. İlave olarak hesaplanan sonuçlar ile deneysel ¹H ve ¹³C NMR sonuçlarına uygunluk grafikleri çizildi.

Anahtar kelimeler: *cis- 1,2-dihidroksi-trans-3-metoksi-1,5,5-trimetilsikloheksana, cis- 2,3-dihidroksi-trans-1-metoksi-1,5,5-trimetilsikloheksan, DFT, HF, GIAO, ¹H NMR, ¹³C NMR, IR spektrum, yapı izahı, titreşim işaretlemesi*

1. INTRODUCTION

A number of papers have recently appeared in the literature concerning the calculation of NMR chemical shift (c.s.) by quantum-chemistry methods [1-6]. These papers indicate that geometry optimization is a crucial factor in an accurate determination of computed NMR chemical shift. Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or

electron lone pairs. However, considering that as molecular size increases, computing-time limitations are introduced for obtaining optimized geometries at the DFT level, it was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometry-optimization procedure at the molecular mechanics level [5].

The gauge-including atomic orbital (GIAO) method is one of the most common approaches for calculating nuclear magnetic shielding tensors [7-8]. It has been shown to provide results that are often more accurate than those calculated with other approaches, at the same basis set size [9]. In most cases, in order to take into account correlation effects, post-Hartree-Fock calculations of organic molecules have been performed using (i) Møller-Plesset perturbation methods, which are very time consuming and hence applicable only to small molecular systems, and (ii) density functional theory (DFT) methods, which usually provide significant results at a relatively low computational cost [10]. In this regard, DFT methods have been preferred in the study of large organic molecules [11], metal complexes [12] and organometallic compounds [13] and for GIAO ^{13}C c.s. calculations [9] in all those cases in which the electron correlation contributions were not negligible.

Cis-1,2-dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane (6) and *cis*-2,3-dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane (7) have been prepared from the tetracyanoethylene catalysed (TCNE) methanolysis of the epoxides [14]. ^1H NMR and ^{13}C NMR spectra (in the CDCl_3 solution), and vibrational spectra of 6 and 7 were studied. The stereochemistries of the compounds have been established by X-ray crystallography. The best of our knowledge, no estimates of theoretical results for 6 and 7 were reported so far. In this study, we calculated geometrical parameters, fundamental frequencies and GIAO ^1H and ^{13}C NMR chemical shifts of 6 and 7 in the ground state to distinguish the fundamental from the experimental ^1H and ^{13}C NMR chemical shifts (in the CDCl_3 solution), vibrational frequencies and geometric parameters, by using the HF and DFT (B3LYP) method with 6-31G(d) basis set. A

comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift-molecular structure relationship. And so, these calculations are valuable for providing insight into molecular analysis. The aim of the present work was to describe and characterize the molecular structure, vibrational properties and chemical shifts on *cis*-1,2-dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane (6) and *cis*-2,3-dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane (7) crystalline-structure.

2. COMPUTATIONAL DETAILS

The molecular structures of 6 and 7 in the ground state (in vacuo) are optimized HF and B3LYP with 6-31G(d) basis set. Vibrational frequencies for optimized molecular structures have been calculated. The geometry of the title compounds, together with that of tetramethylsilane (TMS) is fully optimized. ^1H and ^{13}C NMR chemical shifts are calculated within GIAO approach [7,8] applying B3LYP and HF method [15] with 6-31G(d) basis set [16]. The theoretical NMR ^1H and ^{13}C chemical shift values were obtained by subtracting the GIAO calculated [17-18]. ^1H and ^{13}C isotropic magnetic shielding (IMS) of any X carbon atom, to the average ^{13}C IMS of TMS: $\text{CS}_x = \text{IMS}_{\text{TMS}} - \text{IMS}_x$. Molecular geometry is restricted and all the calculations are performed by using Gauss-View molecular visualisation program [19] and Gaussian 98 program package on personal computer [20].

3. RESULTS AND DISCUSSION

3.1. Geometrical Structure

The atomic numbering scheme for 6 and 7 crystal and the theoretical geometric structure of 6 and 7 are shown in Figure 1a-d. The crystal structures of 6 and 7 are monoclinic, triclinic, and space groups are $\text{P}\bar{1}$ and the space group. The crystal structure parameters of 6 and 7 are $a = 13.0204(6) \text{ \AA}$, $b = 6.1954(3) \text{ \AA}$, $c = 26.6900(11) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 92.167(3)^\circ$ and $V = 2151.45(17) \text{ \AA}^3$ [14].

The optimized parameters of **6** and **7** (bond lengths and angles) by HF, B3LYP methods with 6-31G(d) as the basis set are listed in Table 1 and compared with the experimental crystal structure for **6** and **7**. The O(2)-C(10) and O(1)-C(9) which are consist of O-CH₃ bond lengths were found to be 1.4141(17) and 1.422(3)Å [14]. Here in these bond lengths have been calculated at 1.3986 Å (for HF/6-31G(d)), 1.4191 Å (for B3LYP/6-31G(d)), and 1.399 Å (for HF/6-31G(d)), 1.419 Å (for B3LYP/6-31G(d)). Moreover, we take into account the important bonds which are consist of O(1)-C(1), O(2)-C(2), O(3)-C(6) for **6** and O(1)-C(5), O(2)-C(4), O(3)-C(3) for **7** bond lengths, these bond lengths were observed to be 1.4307(13) Å, 1.4439(14) Å, 1.4314(17) Å and 1.447(3) Å, 1.428(3) Å, 1.442(3) Å, respectively [14]. In present paper, we have calculated at 1.4012 Å, 1.4033 Å using HF/6-31G(d) method, 1.4226 Å, 1.4234 Å, 1.4491 Å using B3LYP/6-31G(d) method for **6**, .422 Å, 1.404 Å, 1.397 Å using HF/6-31G(d) method, 1.452 Å, 1.426 Å, 1.416 Å using B3LYP/6-31G(d) method for **7** and the data are shown in Table 1. Furthermore, C(10)-O(2)-C(2) and C(9)-O(1)-C(5) bond angles for **6** and **7** were observed to be 114.2(11)° and 115.6(19)° [14], these angle values have been calculated at 119.91°, 115.65 for **6** 119.8°, 118.4 for **7** by using HF and B3LYP with 6-31G(d) basis set, respectively, as can be seen in Table 1. Additionally, the C(3)-C(2)-C(1) and C(6)-C(5)-C(4) bond angles were found to be 110.85(11)° and 108.9(2)° [14], and these angles have been calculated at 110.01°, 109.8° by HF/6-31G(d) level and 109.59°, 109.9° by B3LYP/6-31G(d) level and the data are listed Table 1. The difference results from crystal structure of **6** and **7**, as can be seen Figure 1a-d. The optimized geometric parameter other values of **6** and **7** are shown in Table 1.

For the optimized geometric parameters, various methods including HF method estimated some bond lengths well to some extent [21-24]. We noted that the experimental results belong to the solid phase and theoretical calculations belong to the gaseous phase. As a result, the HF method leads to geometric parameters, which are much closer to experimental data.

3.2 Assignments of the vibration modes

We have not found theoretical results for **6** and **7** in the literature and the experimental vibrational spectra of **6** and **7** used in this study have been taken by C.Uyanik et al [14]. We have calculated the theoretical vibrational spectra of **6** and **7** by using HF and B3LYP methods with 6-31G(d) basis set. We have compared our calculation of **6** and **7** with their experimental results. The bands calculated in the measured region 4000-400cm⁻¹ arise from the vibrations of hydroxyl stretching, methyl asymmetric and symmetric stretching, and the internal vibrations of the title compound. The vibrational bands assignments have been made by using Gauss-View molecular visualisation program [19]. Theoretical and experimental results of **6** and **7** are shown in Table 2. Most bands observed in infrared spectra of **6** and **7** belong to diaxial structure modes, only some of them may be assigned to group CH₂ (symmetric/asymmetric stretching). These bands have been calculated at 2902-2846 cm⁻¹ for HF/6-31G(d) level and 2969-2882 cm⁻¹ for B3LYP/6-31G(d) level.

Other reliable group vibrations of **6** and **7** are O-H, CH₃ and C-H stretching. The bands at 3659-2840 cm⁻¹ for **6** (HF/6-31G(d)), 3590-2875 cm⁻¹ for **6** (B3LYP/6-31G(d)), and 3637-2851 cm⁻¹ for **7** (HF/6-31G(d)), 3500-2908 cm⁻¹ for **7** (B3LYP/6-31G(d)), these were attributed to diaxial interaction. For other assignment of internal vibrations of **6** and **7** can be seen Table 2.

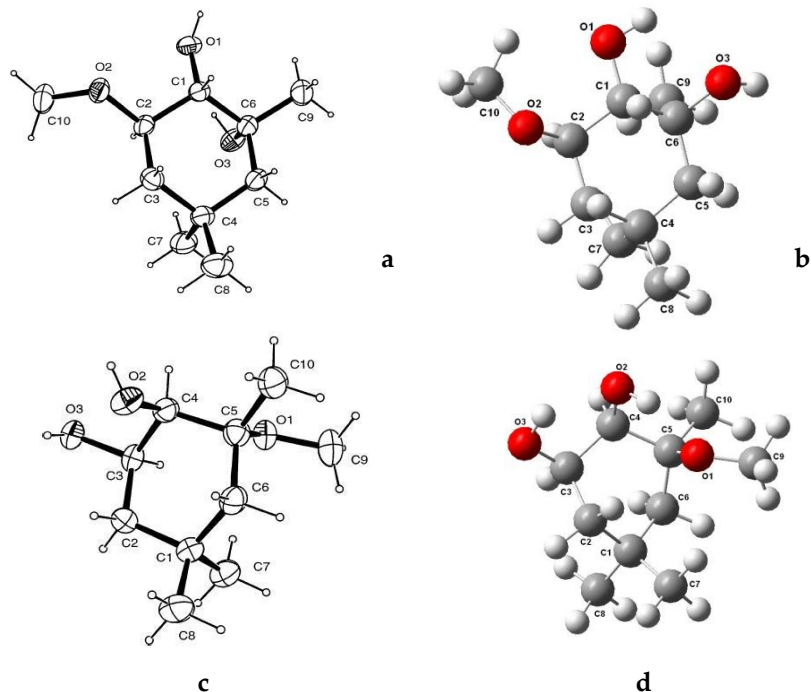


Figure 1. (a) The experimental geometric structure of *cis*-1,2-Dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane ($C_{10}H_{20}O_3$) (**6**) [14], (b) The theoretical geometric structure of *cis*-1,2-Dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane ($C_{10}H_{20}O_3$) (**6**), (c) The experimental geometric structure of *cis*-2,3-Dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane ($C_{10}H_{20}O_3$) [14] (**7**) (d) The theoretical geometric structure of *cis*-2,3-Dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane ($C_{10}H_{20}O_3$) (**7**)

3.3. Assignments of the chemical shift values

Initially, molecular structures of **6** and **7** are optimized by using B3LYP method with 6-31G(d). Then, GIAO ^{13}C and 1H c.s. calculations of the title compound have been made by using B3LYP and HF method with 6-31G(d) basis set. The 1H and ^{13}C chemical shift values (with respect to TMS) have been calculated for the optimized structures of **6** and **7** and compared to the experimental 1H and ^{13}C chemical shift values [14]. These results are shown in Table 3a-b. Taking into account that the range of ^{13}C NMR chemical shifts for **6** and **7** are 78.8-27.2 and 78.9-27.2 ppm [14]. In the present paper, these chemical shift values 74.2-23.8 ppm and 67.3-23.5 ppm for **6**, **7** (HF/6-31G(d)), and 92.8-35.7 ppm and 87.1-35.3 ppm for **6**, **7** B3LYP/6-31G(d), and so the accuracy ensures reliable

interpretation of spectroscopic parameters. As can be seen from Fig. 1, molecular structure of **6** and **7** includes C atoms bounded hydroxyl and methoxy groups. These groups include oxygen atom which shows electronegative property. Therefore, the chemical shift values of C1 and C6 atoms bounded hydroxyl for **6** and C4 and C3 atoms bounded hydroxyl for **7** have been calculated at 74.2, 54.4 ppm and 92.8, 68.6 ppm for **6** and 75.3, 58.5 ppm and 83.4, 66.2 ppm for **7** by using HF and B3LYP method with 6-31G(d) basis set, respectively (in Table 3a-b), and those were observed 78.8, 73.5 and 78.8, 72.7 ppm. Similarly, the chemical shift values of C2 and C5 atoms bounded methoxy group for **6** and **7** have been calculated at 67.1, 85.6 ppm for **6** and 67.3, 87.1 ppm for **7** by using HF and B3LYP method with 6-31G(d) basis set, respectively (in Table 3a-b), and those were observed 78.6 and 78.9 ppm. Besides, ^1H chemical shift values were experimentally observed [14]. These values compared to theoretical results.

In addition to this, we have calculated ^1H chemical shift values (with respect to TMS) of 4.20–0.55 ppm and 3.37–0.72 ppm and for **6** and **7** (HF/6-31G(d)), and 4.77–0.62 ppm and 3.91–1.16 ppm for **6** and **7** (B3LYP/6-31G(d)), whereas the experimental results were observed to be 4.17–0.93 ppm and 3.40–0.94 ppm, these values are shown in Table 3a-b. As can be seen from Table 3a-b, there is a good agreement between experimental and theoretical ^1H and ^{13}C NMR chemical shift results for **6** and **7**. To make comparison with experiment, we present correlation graphic in Figure 2 based on our calculations. As one can easily see from correlation graphic in Figure 2, the experimental ^1H and ^{13}C NMR chemical shift values are in better agreement with the calculated ^1H and ^{13}C NMR chemical shift values and are found to have a good correlation for B3LYP and HF.

Table 1. Optimized and experimental geometries parameters of *cis*-1,2-dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane (C₁₀H₂₀O₃) (6) and *cis*-2,3-dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane (C₁₀H₂₀O₃) (7) in the ground state

Parameters (6)	Exp. [14]	Calculated		Parameters (7)	Exp. [14]	Calculated	
		HF	B3LYP			HF	B3LYP
		6-31G(d)				6-31G(d)	
Bond lengths (Å)				Bond lengths (Å)			
O(1)-C(1)	1.4307(10)	1.4012	1.4226	O(1)-C(9)	1.422(3)	1.399	1.419
O(2)-C(10)	1.4141(17)	1.3986	1.4191	O(1)-C(5)	1.447(3)	1.422	1.452
O(2)-C(2)	1.4439(15)	1.4012	1.4234	O(2)-C(4)	1.428(3)	1.404	1.426
O(3)-C(6)	1.4314(17)	1.4233	1.4491	O(3)-C(3)	1.442(3)	1.397	1.416
C(1)-C(2)	1.5165(18)	1.5251	1.5326	C(1)-C(7)	1.531(4)	1.535	1.540
C(1)-C(6)	1.5383(18)	1.5349	1.5449	C(1)-C(8)	1.535(4)	1.538	1.543
C(2)-C(3)	1.5179(19)	1.5291	1.5357	C(1)-C(2)	1.544(3)	1.547	1.554
C(3)-C(4)	1.5400(19)	1.5408	1.5474	C(1)-C(6)	1.544(3)	1.556	1.564
C(4)-C(7)	1.526(2)	1.5397	1.5444	C(2)-C(3)	1.519(3)	1.523	1.531
C(4)-C(8)	1.537(2)	1.5378	1.5429	C(3)-C(4)	1.522(3)	1.543	1.556
C(4)-C(5)	1.5397(19)	1.5469	1.5542	C(4)-C(5)	1.545(3)	1.559	1.568
C(5)-C(6)	1.5276(18)	1.5382	1.5428	C(5)-C(10)	1.519(4)	1.530	1.534
C(6)-C(9)	1.524(2)	1.5311	1.5345	C(5)-C(6)	1.527(3)	1.534	1.538
Bond angles (°)				Bond angles (°)			
C(10)-O(2)-C(2)	114.20(11)	116.91	115.65	C(9)-O(1)-C(5)	115.6(19)	119.8	118.4
O(1)-C(1)-C(2)	109.24(10)	109.52	110.31	C(7)-C(1)-C(8)	108.5(2)	107.9	108.2
O(1)-C(1)-C(6)	109.48(11)	111.0	110.59	C(7)-C(1)-C(2)	110.4(2)	109.5	109.3
C(2)-C(1)-C(6)	111.15(10)	112.94	112.74	C(8)-C(1)-C(2)	108.8(2)	110.0	110.1
O(2)-C(2)-C(3)	109.30(11)	106.39	105.77	C(7)-C(1)-C(6)	112.0(2)	111.3	110.9
O(2)-C(2)-C(1)	107.70(10)	110.72	111.76	C(8)-C(1)-C(6)	107.5(2)	108.0	108.1
C(3)-C(2)-C(1)	110.85(11)	110.01	109.59	C(2)-C(1)-C(6)	109.7(2)	110.1	110.1
C(2)-C(3)-C(4)	114.04(11)	115.22	115.45	C(3)-C(2)-C(1)	113.15(19)	111.6	111.9
C(7)-C(4)-C(8)	108.11(12)	107.13	107.29	O(3)-C(3)-C(2)	110.69(19)	112.4	112.6
C(7)-C(4)-C(5)	112.83(13)	113.14	113.06	O(3)-C(3)-C(4)	110.22(19)	110.2	109.5
C(8)-C(4)-C(5)	108.15(12)	107.77	107.82	C(2)-C(3)-C(4)	109.8(2)	111.6	111.5
C(7)-C(4)-C(3)	110.59(12)	110.73	110.52	O(2)-C(4)-C(3)	108.87(19)	110.3	109.9
C(8)-C(4)-C(3)	108.72(13)	108.81	108.78	O(2)-C(4)-C(5)	109.0(2)	110.9	110.5
C(5)-C(4)-C(3)	108.34(11)	109.12	109.22	C(3)-C(4)-C(5)	110.71(19)	113.2	113.4
C(6)-C(5)-C(4)	116.65(11)	117.39	109.22	O(1)-C(5)-C(10)	111.0(2)	111.1	111.3
O(3)-C(6)-C(9)	108.75(12)	107.49	107.65	O(1)-C(5)-C(6)	112.8(2)	110.3	110.3
O(3)-C(6)-C(5)	108.16(10)	108.52	109.01	C(10)-C(5)-C(6)	111.0(2)	111.2	111.8
C(9)-C(6)-C(5)	110.22(11)	114.34	114.38	O(1)-C(5)-C(4)	102.46(18)	104.9	103.9
O(3)-C(6)-C(1)	110.17(11)	103.32	102.49	C(10)-C(5)-C(4)	110.3(2)	109.2	109.4
C(9)-C(6)-C(1)	109.94(11)	112.85	112.76	C(6)-C(5)-C(4)	108.9(2)	109.8	109.9
C(5)-C(6)-C(1)	109.57(11)	115.22	109.78	C(5)-C(6)-C(1)	117.5(2)	115.6	115.7

Bond lengths in angstrom, bond angles and dihedral angles in degrees.

3.4 Thermodynamic parameters of 6 and 7

Several thermodynamic parameters have been calculated using HF and B3LYP with 6-31G(d) basis set. Calculated these parameters of 6 and 7 are given in Table 4. For zero-point vibrational energy (ZPVE) and the entropy (S_{vib}(T)) which are an accurate prediction are multiplied the data

[25]. According to the appropriate scale factors of ZPVE and $S_{\text{vib}}(T)$, the results of B3LYP method has shown better than HF method. The total energies and the change in the total entropy of **6** and **7** at room temperature at different theoretical methods are also presented. In Table 4 demonstrates several thermodynamic parameters of **6** and **7** without of results of experimental.

4. CONCLUSIONS

In this study, we calculated the geometric parameters, vibrational frequencies, chemical shifts and several thermodynamic parameters of **6** and **7** by using HF and B3LYP methods with 6-31G(d) basis set. To fit the theoretical frequencies results with experimental ones for HF and B3LYP methods, we multiplied the data by 0.8929 and 0.9613. Multiplication factors results gained seemed to be in a good agreement with experimental ones. According to the appropriate scale factors, the results of B3LYP method for fundamental frequencies and thermodynamic parameters should be shown better fit to experimental ones than HF. Herein, vibrational frequencies and ^1H chemical shifts of **6** and ^{13}C chemical shifts of **7** for HF have shown better fit to experimental ones than B3LYP. Unlike, vibrational frequencies and ^1H chemical shifts of **7** and ^{13}C chemical shifts of **6** for B3LYP have shown better fit to experimental ones than HF. In these state, geometric parameters, vibrational frequencies, chemical shifts and thermodynamic parameters for diverse molecular structure analysis change with respect to the different theoretical approaches. More commonly, however, the NMR spectrum is used in conjunction with other forms of spectroscopy and chemical analysis to determinate the structures of complicated organic molecules.

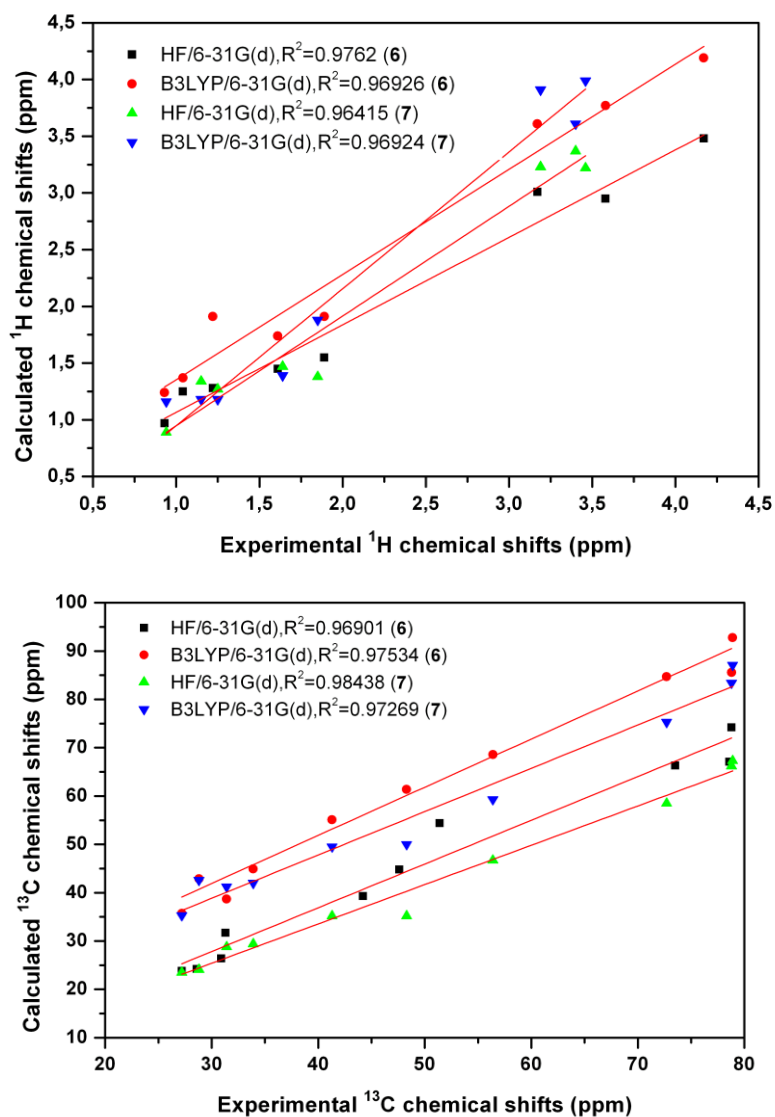


Figure 2. (a) Correlation graphics of calculated and experimental ^{13}C and ^1H isotropic chemical shifts for cis-1,2-dihydroxy-trans-3-methoxy-1,5,5-trimethylcyclohexane (6) (b) Correlation graphics of calculated and experimental ^{13}C and ^1H isotropic chemical shifts for cis-2,3dihydroxy-trans-1-methoxy-1,5,5-trimethylcyclohexane (7)

Table 2. Comparison of the observed and calculated vibrational spectra of *cis*-2,3-dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane (C₁₀H₂₀O₃) (6) and *cis*-1,2-Dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane (C₁₀H₂₀O₃) (7)

Assignments	FT-IR [14]	FT-IR [14]	Calculated (cm ⁻¹)			
	(cm ⁻¹) (6)	(cm ⁻¹) (7)	HF (6)	B3LYP (6)	HF (7)	B3LYP (7)
	IR with KBr	IR with KBr	6-31G(d)			
ν O-H str.	-	-	3659	3590	3637	3500
ν O-H str.	3458	3383	3654	3569	3630	3483
ν_{as} CH ₃ asym str.	2973	-	2982	3046	2955	3017
ν_{as} CH ₃ asym str.	-	-	2962	3017	2948	3016
ν_{as} CH ₃ asym str.	-	-	2951	3017	2936	3011
ν_{as} CH ₃ asym str.	-	-	2938	3008	2934	3009
ν_s CH ₃ sym str.	-	2925	2925	2990	2929	2990
ν_s CH ₃ sym str.	-	-	2918	2987	2916	2983
ν_s CH ₃ sym str.	-	-	2913	2981	2913	2978
ν_s CH ₃ sym str.	-	-	2905	2978	2907	2975
ν_{as} CH ₂ asym str.	-	-	2902	2969	2905	2971
ν_{as} CH ₂ asym str.	-	-	2891	2952	2899	2953
ν_s CH ₂ sym str.	-	-	2872	2934	2888	2946
ν_s CH ₂ sym str.	-	-	2868	2930	2877	2940
ν_s CH ₂ sym str.	-	-	2864	2925	2876	2938
ν CH str.	-	-	2861	2919	2874	2925
ν CH str.	-	-	2856	2906	2869	2918
ν_s CH ₃ sym str.	-	-	2853	2889	2860	2916
ν_s CH ₂ sym str.	-	2855	2846	2882	2855	2912
ν CH str.	2168	2172	2840	2875	2851	2908
ρ_s CH ₃ sci.	1732	1668	1491	1490	1491	1487
ρ_s CH ₃ sci.	1652	-	1490	1488	1484	1481
ρ_s CH ₃ + CH ₂ sci.	-	-	1479	1475	1482	1477
ρ_s CH ₃ + CH ₂ sci.	-	-	1475	1473	1479	1475
ρ_s CH ₃ + CH ₂ sci.	-	-	1471	1469	1476	1471
ρ_s CH ₃ sci.	-	-	1469	1461	1473	1468
ρ_s CH ₃ sci.	-	-	1469	1457	1467	1462
ρ_w O-CH ₃ out of plane wag.	-	-	1461	1454	1465	1460
ρ_w O-CH ₃ in plane wag.	-	-	1460	1452	1462	1458
ρ_s CH ₃ + CH ₂ sci.	-	-	1457	1450	1460	1451
ρ_s CH ₃ + CH ₂ sci.	1445	1459	1457	1442	1455	1440
ρ_r CH + OH rock.	-	-	1431	1407	1424	1414
ρ_w CH ₃ wag.	-	-	1410	1395	1410	1401
ρ_w CH ₃ wag.	-	-	1407	1386	1406	1393
ρ_w CH ₃ wag. + ρ_r CH rock.	1373	-	1392	1373	1399	1379
ρ_w CH ₃ wag. + ρ_r CH rock.	-	-	1390	1356	1397	1377
ρ_r CH + OH rock.	-	-	1372	1348	1389	1370
ρ_r CH + OH rock. + t CH ₂ twist.	-	1377	1352	1335	1370	1341
ρ_r CH + OH + CH ₂ rock.	-	1339	1336	1318	1341	1317
ρ_r CH + OH rock.	-	1314	1331	1306	1320	1302
ρ_r CH + OH rock.	-	1284	1300	1286	1285	1273
ρ_r CH + OH rock.	-	-	1289	1277	1268	1254
ρ_r CH + OH rock. + t CH ₃ twist.	1247	1258	1268	1257	1246	1235
ν C-O str. + t CH ₃ twist.	-	-	1242	1226	1239	1227
ρ_r CH + OH rock. + t CH ₃ twist.	-	1213	1218	1192	1219	1207
ν ring C-C str. + ρ_r CH+OH rock.	1180	-	1191	1174	1209	1192

Table 2 (continued)

Assignments	FT-IR [14]	FT-IR [14]	Calculated (cm ⁻¹)			
	(cm ⁻¹) (6)	(cm ⁻¹) (7)				
	IR with KBr	IR with KBr	HF (6)	B3LYP (6)	HF (7)	B3LYP (7)
			6-31G(d)			
v ring C-C str.	-	-	1173	1161	1199	1178
v C-CH ₃ str.	-	-	1160	1156	1189	1169
ρ _r CH + OH rock. + t CH ₃ twist.	1149	1174	1156	1144	1156	1139
t CH ₃ twist.	-	1144	1150	1134	1151	1138
v O-CH ₃ str. + ρ _r CH + OH rock.	1115	-	1140	1112	1129	1103
v C-OH str. + t CH ₂ twist.	-	-	1118	1095	1117	1094
v C-OH str.	1088	1105	1091	1066	1101	1073
ρ _r CH + OH rock. + t CH ₃ twist.	-	-	1072	1062	1089	1065
ρ _r CH + OH rock. + t CH ₂ twist.	1043	1066	1040	1026	1057	1041
ρ _r CH + OH rock. + t CH ₂ twist.	-	1033	1026	1019	1036	1024
t CH ₃ + CH ₂ twist.	-	997	999	984	1010	1000
ρ _r CH rock. + t CH ₃ twist.	964	978	971	957	974	969
t CH ₃ twist.	947	942	960	947	945	940
t CH ₃ twist.	931	924	941	930	944	933
t CH ₃ twist.	-	-	931	923	918	914
β ring bend. + t CH ₃ twist.	-	902	913	910	912	909
t CH ₂ twist.	-	875	905	896	886	880
t CH ₂ twist.	857	833	867	863	853	849
β ring bend.	814	809	849	845	816	807
v C-CH ₃ str. + ρ _r CH ₂ rock.	781	754	763	768	753	758
v ring H ₂ C-(CCH ₃) ₂ -CH ₂ str.	718	720	749	754	739	727
β ring H ₂ C-(CCH ₃) ₂ -CH ₂ bend.	-	-	623	622	660	660
τ ring tor.	-	-	551	552	587	599
β ring bend.+ ρ _r CH ₃ rock.	-	-	505	507	552	584
ρ _r OH + CH + CH ₂ rock.	-	-	494	488	511	551
ρ _r OH + CH + CH ₂ rock.	-	-	461	463	475	475
β ring H ₃ C-C-CH ₃ bend.	-	-	451	451	462	463
ρ _r OH rock.	-	-	-	437	-	449
ρ _r OH + CH + CH ₂ rock.	-	-	410	410	420	415

Table 3a. Theoretical and experimental ^{13}C and ^1H isotropic chemical shifts (with respect to TMS, all values in ppm) for *cis*-2,3-Dihydroxy-*trans*-1-methoxy-1,5,5-trimethylcyclohexane ($\text{C}_{10}\text{H}_{20}\text{O}_3$)(6) (all calculations performed with the 6-31G(d) basis set)

Atom	Exp. (ppm) (CDCl_3) [14]	Calculated chemical shift (ppm)	
		HF/6-31G(d)	B3LYP/6-31G(d)
C1	78.8	74.2	92.8
C2	78.6	67.1	85.6
C6	73.5	66.3	84.7
C10	51.4	54.4	68.6
C5	47.6	44.8	61.4
C3	44.2	39.3	55.1
C8	31.3	31.7	44.9
C7	30.9	26.4	38.7
C4	28.6	24.2	42.9
C9	27.2	23.8	35.7
H ₃ (-OMe)	3.17	4.20, 3.48, 3.01	4.77, 3.88, 3.61
H(C1)	4.17	3.48	4.19
H(C2)	3.58	2.95	3.77
OH(C1)	-	2.11	2.23
H ₃ (C9)	1.22	1.79, 1.31, 1.28	2.23, 2.22, 1.91
H ₂ (C3)	1.89-1.61	1.55, 1.31	2.08, 1.91
H ₂ (C5)	1.89-1.61	1.45, 1.11	2.08, 1.74
H ₃ (C7)	1.04 and 0.93	1.31, 1.28, 1.25	1.91, 1.88, 1.37
H ₃ (C8)	1.04 and 0.93	1.01, 0.97, 0.83	1.47, 1.37, 1.24
OH(C6)	-	0.55	0.62

Table 3b. Theoretical and experimental ^{13}C and ^1H isotropic chemical shifts (with respect to TMS, all values in ppm) for *cis*-1,2-Dihydroxy-*trans*-3-methoxy-1,5,5-trimethylcyclohexane ($\text{C}_{10}\text{H}_{20}\text{O}_3$) (7) (all calculations performed with the 6-31G(d) basis set)

Atom	Exp. (ppm) (CDCl_3) [14]	Calculated chemical shift (ppm)	
		HF/6-31G(d)	B3LYP/6-31G(d)
C5	78.9	67.3	87.1
C4	78.8	66.2	83.4
C3	72.7	58.5	75.3
C9	56.4	46.7	59.3
C2	48.3	35.2	50.0
C6	41.3	35.2	49.5
C7	33.9	29.4	42.0
C8	31.4	28.8	41.2
C1	28.8	24.1	42.6
C10	27.2	23.5	35.3
H ₃ (-OMe)	3.40	3.37, 3.09, 3.05	3.70, 3.71, 3.61
H(C4)	3.19	3.23	3.91
H ₂ (C2)	1.85-1.64	1.38, 1.36	1.88, 1.81
H ₂ (C6)	1.85-1.64	1.47, 0.53	2.19, 1.39
H ₃ (C10)	1.25	1.59, 1.27, 0.72	1.92, 1.68, 1.18
H ₃ (C7)	1.15 and 0.94	1.34, 0.99, 0.77	1.77, 1.40, 1.18
H ₃ (C8)	1.15 and 0.94	1.16, 0.89, 0.82	1.62, 1.34, 1.16
H(C3)	3.46	3.22	3.99
OH(C3)	-	3.13	2.94
OH(C4)	-	3.21	3.02

Table 4. Calculated energies (a.u), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies ($\text{cal mol}^{-1} \text{K}^{-1}$) and dipole moment (D) for (6) and (7)

Parameters	HF (6)	B3LYP (6)	HF (7)	B3LYP (7)	
	6-31G(d)				
Dipole moment	2.730	2.715	4.428	4.339	
Zero-point vibrational energy	182.249	182.254	183.039	183.098	
Total energy	-614.888	-618.756	-614.883	-618.754	
Rotational constants	0.933	0.928	0.885	0.877	
	0.721	0.709	0.826	0.816	
	0.500	0.494	0.562	0.556	
Entropy					
	Rotational	28.044	31.315	27.864	31.116
	Translational	37.350	41.664	37.350	41.664
	Vibrational	35.856	43.587	33.307	40.692
	Total	101.250	116.566	98.521	113.472

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