

**MOLECULAR STRUCTURE AND VIBRATIONAL AND
CHEMICAL SHIFT ASSIGNMENTS OF 2 α ,8-
DIHYDROXY-1 β -METHOXY-P-MENTHANE BY DFT
AND AB INITIO HF CALCULATIONS**

C. UYANIK^a, K. ESMER^e, D. AVCI^c, E. TARCAN^b, T. ÇELİK^d
and Y. ATALAY^c

^a Kocaeli University Department of Chemistry KOCAELİ

^b Kocaeli University Department of Physics KOCAELİ

^c Sakarya University Department of Physics SAKARYA

^b Beykent University Department of Civil Engineering İSTANBUL

^e Marmara University Department of Physics İSTANBUL

E-mail: yatalay@sakarya.edu.tr

ABSTRACT

The molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO) ¹H and ¹³C chemical shift values and several thermodynamic parameters of 2 α ,8-Dihydroxy-1 β -methoxy-p-menthane in the ground state were 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 were 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 geometric parameters, IR, ¹H NMR and ¹³C NMR chemical shifts values.

Keywords: 2 α ,8-Dihydroxy-1 β -methoxy-p-menthane; DFT; HF; NMR; IR spectra

**2 α ,8-DİHİDROKSİ-1 β -METOKSİ-P-METHAN
MOLEKÜLÜNÜN GEOMETRİK, TİTREŞİM VE
KİMYASAL KAYMALARININ YOĞUNLUK
FONKSİYON TEORİSİ(DFT) VE AB İNİTİO HF
YÖNTEMİYLE HESAPLANMASI**

ÖZET

2 α ,8-Dihidroksi-1 β -metoksi-p-metan molekülünün moleküler geometri, titreşim frekansları, gauge atomik orbitalleri içeren(GIAO) ¹H ve ¹³C kimyasal kaymaları ve birçok termodinamik parametresi temel durumda yoğunluk fonksiyon teorisi(DFT) ve Hartree-Fock(HF) metoduyla 6-31G(d) temel seti kullanılarak hesaplandı. Teorik olarak hesaplanan titreşim frekansları molekülün deneysel titreşim frekanslarıyla karşılaştırıldı. İlave olarak teorik olarak hesaplanan titreşim spektrumu(IR), NMR(¹H ve ¹³C) kimyasal kaymalar ve geometrik parametreler, deneysel sonuçlarla uyum grafikleri çizildi.

Anahtar Kelimeler: 2 α ,8-Dihidroksi-1 β -metoksi-p-metan, DFT, HF, NMR, IR spektrum.

1. INTRODUCTION

2 α ,8-Dihydroxy-1 β -methoxy-p-menthane [1] was prepared from the tetracyanoethylene catalysed (TCNE) methanolysis of mixed 1,2-epoxy-8-hydroxy methanes. The stereochemistry of the compound was established by X-ray crystallography.

In this paper, the molecular structure, vibrational properties and chemical shifts on 2 α ,8-dihydroxy-1 β -methoxy-p-menthane crystalline-structure were described and characterized. A number of papers have recently appeared in the literature concerning the calculation of NMR chemical shift (c.s.) by quantum-chemistry methods [2-7]. 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 [6].

The gauge-including atomic orbital (GIAO) [8,9] method is one of the most common approaches for calculating nuclear magnetic shielding tensors. It has been shown to provide results that are often more accurate than those calculated with other approaches, at the same basis set size [10]. 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 [11]. In this regard, DFT methods have been preferred in the study of large organic molecules [12], metal complexes [13] and organometallic compounds [14] and for GIAO ^{13}C c.s. calculations [10] in all those cases in which the electron correlation contributions were not negligible.

In previous publication, ^1H and ^{13}C NMR spectra (in the CDCl_3 solution), the crystal structure and vibrational spectra of $2\alpha,8$ -dihydroxy- 1β -methoxy- p -menthane had been studied [1]. The best of our knowledge, no estimates of theoretical results for $2\alpha,8$ -dihydroxy- 1β -methoxy- p -menthane have been reported so far. In this study geometrical parameters, fundamental frequencies and GIAO ^1H and ^{13}C NMR chemical shifts of $2\alpha,8$ -dihydroxy- 1β -methoxy- p -menthane in the ground state were calculated 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. These calculations are valuable for providing insight into molecular analysis.

2. COMPUTATIONAL DETAILS

The molecular structures of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane 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 compound, together with that of tetramethylsilane (TMS) is fully optimized. ^1H and ^{13}C NMR chemical shifts are calculated within GIAO approach [8,9] applying B3LYP and HF method [15] with 6-31G(d) [16] basis set. 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 (I.M.S.) of any X carbon atom, to the average ^{13}C IMS of TMS: $\text{CS}_x = \text{IMS}_{\text{TMS}} - \text{IMS}_x$. Molecular

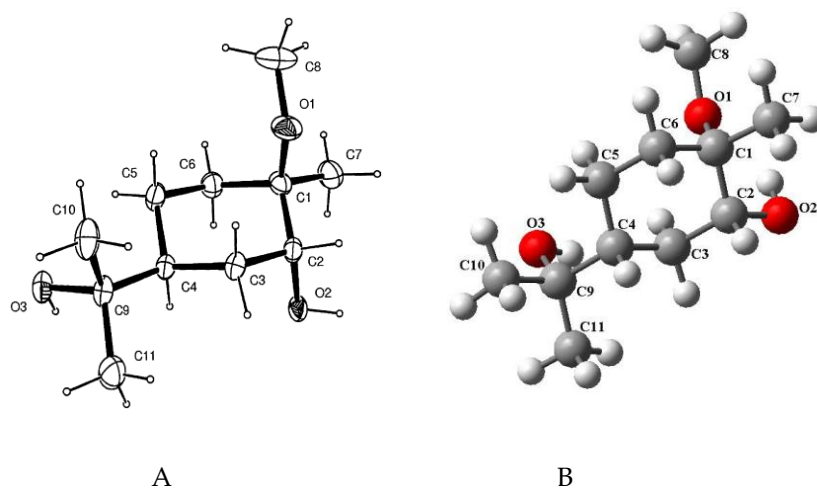


Figure 1. (a) The experimental geometric structure of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane ($\text{C}_{11}\text{H}_{22}\text{O}_3$) [14] (b) The theoretical geometric structure of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane ($\text{C}_{11}\text{H}_{22}\text{O}_3$).

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 the 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane crystal¹ and the theoretical geometric structure of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane are shown in Fig. 1a-b. Its geometric structure is orthorhombic, and the space group is *Pbca*, with the cell dimensions $a = 8.0065(2)$ Å, $b = 14.5231(4)$ Å, $c = 19.9634(7)$ Å, $\alpha = \beta = \gamma = 90^\circ$ and $V = 2321.33(12)$ Å³ [1,4].

The optimized parameters of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (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 2 α ,8-Dihydroxy-1 β -methoxy-*p*-menthane. The O(1)-C(8) consist of O-CH₃, this bond length were found to be 1.409(3) Å [1]. Herein this bond length has been calculated at 1.397 Å (for HF/6-31G(d)), 1.415 Å (for B3LYP/6-31G(d)). Moreover, we take into account the important bonds in the structure which consist of O(1)-C(1), O(2)-C(2), O(3)-C(9) bond lengths, these bond lengths were observed to be 1.446(3) Å, 1.440(3) Å, 1.449(3) Å [1]. In present paper, we have calculated at 1.421 Å, 1.401 Å, 1.416 Å using HF/6-31G(d) method, 1.448 Å, 1.423 Å, 1.439 Å using B3LYP/6-31G(d) method, and the data are shown in Table 1. Furthermore, C(8)-O(1)-C(1) bond angle in the structure were observed to be 117.4(2)°,¹ this angle value has been calculated at 119.8°, 118.3 by using HF and B3LYP with 6-31G(d) basis set, respectively, as can be seen in Table 1. Additionally, the O(1)-C(1)-C(7), C(10)-C(9)-C(4) and C(11)-C(9)-C(4) bond angles were found to be 110.7(19)°, 113.33(19)° and 110.38(17)° [1], and these angles were calculated at 111.3°, 111.5° by HF/6-31G(d) level, 111.2°, 111.6°, 111.5° by B3LYP/6-31G(d) level and the data are listed Table 1. The difference result from crystal structure of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane, can be seen Fig. 1a-b. The optimized geometric parameter other values of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane were 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. The correlation between the experimental and calculated geometric parameters obtained by the several methods was shown in Fig. 2. Owing to our calculations, HF method correlates well for the bond length compared with the other method (Table 1, Fig. 2). As a result, the B3LYP method leads to geometric parameters, which are much closer to experimental data.

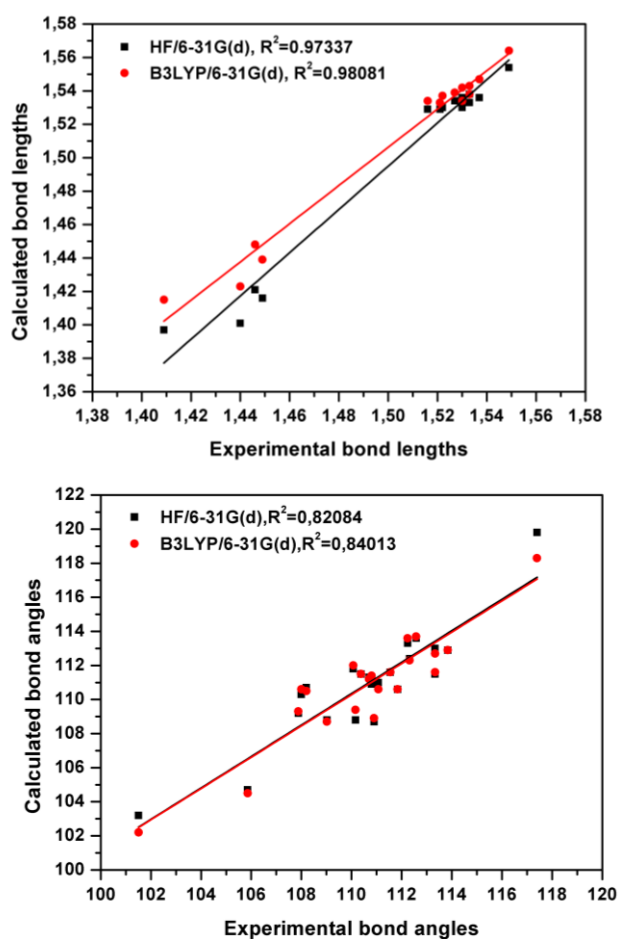


Figure 2. (a) Correlation graphics of calculated and experimental molecular bond lengths of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (C₁₁H₂₂O₃) (b) Correlation graphics of calculated and experimental molecular bond angles of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (C₁₁H₂₂O₃).

Table 1. Optimized and experimental geometries parameters of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (C₁₁H₂₂O₃) in the ground state

Parameters	Exp. [1]	Calculated	
		HF	B3LYP
6-31G(d)			
Bond lengths (Å)			
O(1)-C(8)	1.409(3)	1.397	1.415
O(1)-C(1)	1.446(3)	1.421	1.448
O(2)-C(2)	1.440(3)	1.401	1.423
O(3)-C(9)	1.449(3)	1.416	1.439
C(1)-C(7)	1.521(3)	1.529	1.533
C(1)-C(6)	1.533(3)	1.533	1.538
C(1)-C(2)	1.537(3)	1.536	1.547
C(2)-C(3)	1.522(3)	1.530	1.537
C(3)-C(4)	1.533(3)	1.538	1.543
C(4)-C(5)	1.530(3)	1.536	1.542
C(4)-C(9)	1.549(3)	1.554	1.564
C(5)-C(6)	1.530(3)	1.530	1.534
C(9)-C(10)	1.516(3)	1.529	1.534
C(9)-C(11)	1.527(3)	1.534	1.539
Bond angles (°)			
C(8)-O(1)-C(1)	117.4(2)	119.8	118.3
O(1)-C(1)-C(7)	110.70(19)	111.3	111.2
O(1)-C(1)-C(6)	111.55(17)	111.6	111.6
C(7)-C(1)-C(6)	110.8(2)	110.9	111.4
O(1)-C(1)-C(2)	101.51(18)	103.2	102.2
C(7)-C(1)-C(2)	111.84(18)	110.6	110.6
C(6)-C(1)-C(2)	110.16(17)	108.8	109.4
O(2)-C(2)-C(3)	108.00(17)	110.3	110.6
O(2)-C(2)-C(1)	111.07(18)	111.0	110.6
C(3)-C(2)-C(1)	112.32(16)	112.4	112.3
C(2)-C(3)-C(4)	112.24(18)	113.3	113.6
C(5)-C(4)-C(3)	109.02(17)	108.8	108.7
C(5)-C(4)-C(9)	113.84(16)	112.9	112.9
C(3)-C(4)-C(9)	113.33(17)	113.0	112.7
C(6)-C(5)-C(4)	110.07(17)	111.8	112.0
C(5)-C(6)-C(1)	112.58(19)	113.6	113.7
O(3)-C(9)-C(10)	105.86(16)	104.7	104.5
O(3)-C(9)-C(11)	107.88(19)	109.2	109.3
C(10)-C(9)-C(11)	110.9(2)	108.7	108.9
O(3)-C(9)-C(4)	108.20(16)	110.7	110.5
C(10)-C(9)-C(4)	113.33(19)	111.5	111.6
C(11)-C(9)-C(4)	110.38(17)	111.5	111.5

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

3.2 Assignments of the vibration modes

In the literature there is no theoretical results for 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane in the literature and the experimental vibrational spectra of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane used in this study have been taken by C.Uyanik et al [1].

We have calculated the theoretical vibrational spectra of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane by using HF and B3LYP methods with 6-31G(d) basis set. We have compared our calculation of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane with their experimental results. The bands calculated in the measured region 4000-400 cm⁻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 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane are shown in Table 2 and Fig. 3. Most bands observed in infrared spectra of title compound belong to diaxial structure modes, only some of them may be assigned to group CH₂ (symmetric/asymmetric stretching). These bands were calculated at 2955-2854 cm⁻¹ for HF/6-31G(d) level and 3010-2903 cm⁻¹ for B3LYP/6-31G(d) level.

Other reliable group vibrations of the title compound are O-H, CH₃ and C-H stretching. The bands at 3673-2823 cm⁻¹ for HF/6-31G(d), 3336-2877 cm⁻¹ for B3LYP/6-31G(d), these were attributed to diaxial interaction. For other assignment of internal vibrations of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane can be seen Table 2 and Fig. 3. The theoretical and experimental IR spectra of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane are shown in Fig. 3. To make comparison with experiment, correlation graphic was presented in Fig. 4 based on our calculations. As one can easily see from correlation graphic in Fig. 4, the experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for B3LYP than HF.

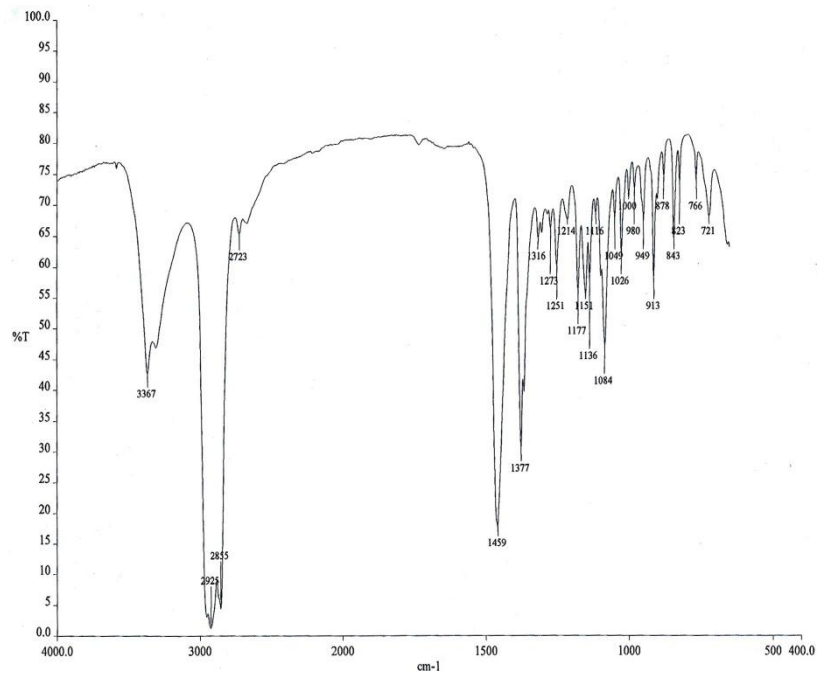
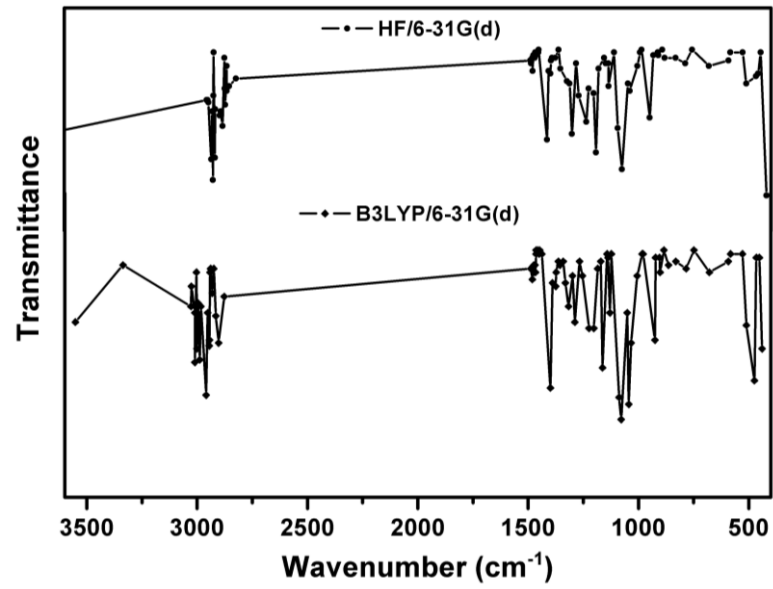


Figure 3. (a) Calculated (HF,B3LYP) IR spectra of $2\alpha,8$ -dihydroxy- 1β -methoxy- p -menthane ($\text{C}_{11}\text{H}_{20}\text{O}_3$) (b) FT-IR spectra of $2\alpha,8$ -dihydroxy- 1β -methoxy- p -menthane¹ ($\text{C}_{11}\text{H}_{20}\text{O}_3$).

Table 2. Comparison of the observed and calculated vibrational spectra of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (C₁₁H₂₂O₃)

Assignments	Experimental [1] (cm ⁻¹)		Scaled frequencies (6-31G(d)) (cm ⁻¹)		
	IR with KBr	HF	Rel. Intensity (KM/mol)	B3LYP	Rel. Intensity (KM/mol)
ν O-H str.	-	3673	0,17	3336	0,04
ν O-H str.	3367	3645	0,35	3552	0,21
ν_{as} CH ₃ asym str.	-	2956	0,2	3028	0,16
ν_{as} CH ₃ asym str.	-	2951	0,2	3026	0,1
ν_{as} CH ₃ asym str.	-	2948	0,21	3010	0,18
ν_{as} CH ₂ asym str.	-	2935	0,5	3010	0,35
ν_{as} CH ₂ asym str.	-	2931	0,25	3003	0,06
ν_{as} CH ₂ asym str.	-	2927	0,63	3001	0,3
ν_{as} CH ₂ asym str.	2925	2925	0,18	2996	0,15
ν_{as} CH ₂ asym str.	-	2924	0,01	2988	0,34
ν_{as} CH ₂ asym str.	-	2918	0,49	2983	0,16
ν_{as} CH ₂ asym str.	-	2917	0,24	2959	0,48
ν_s CH ₂ sym str.	-	2896	0,27	2952	0,18
ν CH str.	2855	2892	0,25	2945	0,29
ν_s CH ₂ sym str.	-	2884	0,32	2944	0,27
ν_s CH ₃ sym str.	-	2875	0,03	2942	0,06
ν_s CH ₃ sym str.	-	2874	0,15	2939	0,05
ν_s CH ₂ sym str.	-	2872	0,22	2931	0,12
ν_s CH ₃ sym str.	-	2865	0,06	2925	0,05
ν_s CH ₃ sym str.	-	2865	0,16	2915	0,19
ν_s CH ₂ sym str.	-	2854	0,14	2903	0,28
ν CH str.	2723	2823	0,11	2877	0,13
β CH ₃ bend.	-	1490	0,04	1488	0,05
β CH ₃ bend.	-	1487	0,05	1481	0,08
β CH ₃ bend.	-	1481	0,03	1474	0,04
β CH ₂ bend.	-	1480	0,08	1473	0,06
β CH ₂ bend.	-	1476	0,02	1469	0,04
β CH ₃ bend.	-	1470	0,03	1467	0,06
β CH ₃ bend.	-	1468	0,01	1464	0,01
β CH ₃ bend.	-	1465	0,02	1464	0
β CH ₂ bend.	-	1462	0,01	1456	0
β CH ₂ bend.	1459	1460	0,01	1450	0,01
ρ_w O-CH ₃ wag.	-	1453	0,01	1448	0
β CH ₃ bend.	-	1452	0	1438	0,01
ρ O-H + C-H rock.	-	1414	0,39	1399	0,45
ρ_w CH ₃ wag.	-	1407	0,08	1390	0,09
ρ_w CH ₃ wag.	-	1399	0,09	1375	0,1
ρ_w CH ₃ wag.	-	1396	0,04	1373	0,06
β CH + CH ₂ bend.	-	1392	0,03	1363	0,03
β CH + CH ₂ bend.	1377	1378	0,03	1356	0,04
β CH bend.	-	1362	0	1341	0,03
β CH bend.	-	1354	0,07	1331	0,09

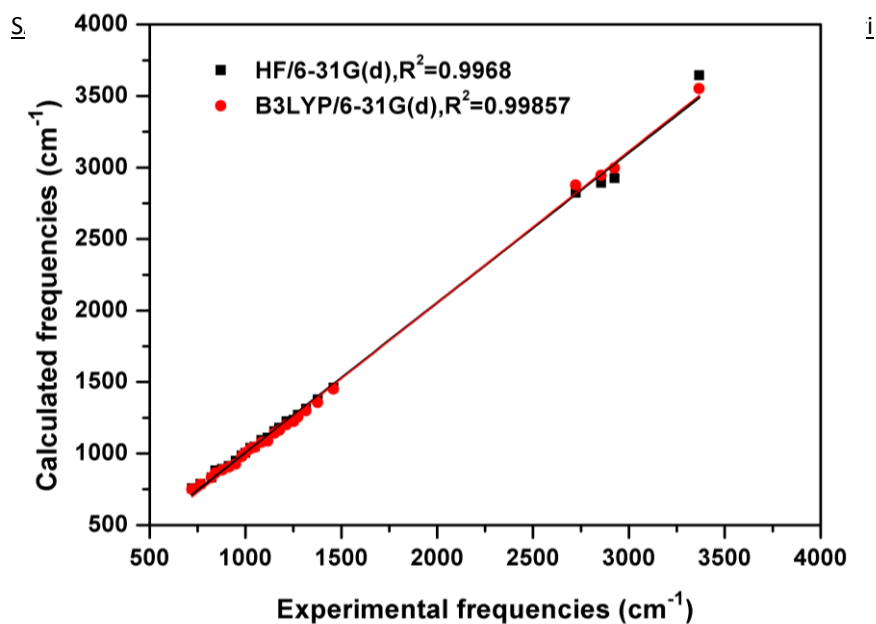


Figure 4. Correlation graphics of calculated and experimental frequencies of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (C₁₁H₂₂O₃).

3.3. Assignments of the chemical shift values

Initially, molecular structure of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane is optimized by using B3LYP method with 6-31G(d). Then, GIAO ¹³C 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 ¹³C chemical shift values (with respect to TMS) have been calculated for the optimized structures of the title compound and compared to the experimental ¹H and ¹³C chemical shift values.¹ These results are shown in Table 3. Taking into account that the range of ¹³C NMR chemical shifts for the title compound is 73.9-22.6 ppm [1]. In the present paper, these chemical shift values 67.2-19.3 ppm for HF/6-31G(d) and 85.7-33.2 ppm for B3LYP/6-31G(d), and so the accuracy ensures reliable interpretation of spectroscopic parameters. As can be seen from Fig. 1, molecular structure of the title compound includes C atoms bounded hydroxyl and methoxy groups. These groups include oxygen atom which shows electronegative property. Therefore, the chemical shift values of C8 and C9 have been calculated at 44.9, 62.8 ppm and 57.9, 81.6 ppm by using HF and B3LYP method with 6-31G(d) basis set, respectively (in Table 3), and those were

observed 49.8, 73.3 ppm. Besides, ^1H chemical shift values were experimentally observed [1]. These values compared to theoretical results. In addition to this, we have calculated ^1H chemical shift values (with respect to TMS) of 3.39–0.53 ppm by using HF method with 6-31G(d) basis set and of 3.78–0.59 ppm by using B3LYP method with 6-31G(d) basis set, whereas the experimental results were observed to be 3.44–0.74 ppm, these values are shown in Table 3. As can be seen from Table 3, there is a good agreement between experimental and theoretical ^1H and ^{13}C NMR chemical shift results for the title compound.

Table 3. Theoretical and experimental ^{13}C and ^1H isotropic chemical shifts (with respect to TMS, all values in ppm) for 2 α ,8-Dihydroxy-1 β -methoxy-*p*-menthane ($\text{C}_{11}\text{H}_{20}\text{O}_3$) (all calculations performed with the 6-31G(d) basis set)

Atom	Exp. (ppm) [1] (CDCl_3)	Calculated chemical shift (ppm)	
		HF/6-31G(d)	B3LYP/6-31G(d)
C2	77.2	67.2	85.4
C1	73.9	66.7	85.7
C9	73.3	62.8	81.6
C8	49.8	44.9	57.9
C4	43.2	38.4	56.2
C3	31.5	28.1	42.5
C6 and C11	29.1	27.2	41.5, 39.5
C10	28.8	26.3	37.7
C7	24.1	21.1	32.0
C5	22.6	19.3	33.2
$\text{H}_3(-\text{OMe})$	2.84	3.39, 3.03, 2.99	3.73, 3.64, 3.56
$\text{H}(\text{C}2)$	3.44	2.98	3.78
$\text{H}_2(\text{C}6)$	2.20-0.74	1.81, 0.72	2.50, 1.44
$\text{OH}(\text{C}2)$	-	1.81	1.81
$\text{H}_3(\text{C}7)$	1.29	1.69, 1.19, 0.66	2.06, 1.58, 1.09
$\text{H}_2(\text{C}5)$	2.20-0.74	1.65, 1.29	2.23, 1.81
$\text{H}_2(\text{C}3)$	2.20-0.74	1.62, 1.15	3.78, 2.07
$\text{H}_3(\text{C}10)$	0.97	1.60, 1.30, 0.89	1.94, 1.58, 1.17
$\text{H}_3(\text{C}11)$	0.95	1.29, 1.26, 0.85	1.63, 1.58, 1.44
$\text{H}(\text{C}4)$	1.29	0.83	1.81
$\text{OH}(\text{C}9)$	-	0.53	0.59

3.4 Thermodynamic parameters of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane

Several thermodynamic parameters have been calculated using HF and B3LYP with 6-31G(d) basis set. Calculated these parameters of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane are given in Table 4. For zero-point vibrational energy (ZPVE) and the entropy ($S_{\text{vib}}(T)$) which are an accurate prediction are multiplied the data [25]. The total energies and the change in the total entropy of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane at room temperature at different theoretical methods are also presented.

4. CONCLUSIONS

In this study, we have calculated the geometric parameters, vibrational frequencies, chemical shifts and thermodynamic parameters of 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane by using HF and B3LYP methods with 6-31G(d) basis set. To fit the theoretical frequencies results with

Table 4. Calculated energies (a.u), zero-point vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹ K⁻¹) and dipole moment (D) for 2 α ,8-dihydroxy-1 β -methoxy-*p*-menthane (C₁₁H₂₀O₃)

Parameters		HF	B3LYP
		6-31G(d)	
Dipole moment		1.5743	1.5496
Zero-point vibrational energy		199.9862	200.1507
Total energy		-653.92785574	-658.07511658
Rotational constants		1.20230	1.18526
		0.42055	0.41684
		0.38470	0.38137
Entropy			
	Rotational	28.532	31.859
	Translational	37.542	41.878
	Vibrational	41.597	50.104
	Total	107.671	123.841

experimental ones for HF and B3LYP methods, we have multiplied the data by 0.8929 and 0.9613. Multiplication factors results gained seemed to be in a good agreement with experimental ones. In particular, the results of B3LYP method has shown better fit to experimental ones than HF in

evaluating vibrational frequencies and geometric parameters. Unlike, chemical shift values for HF method have shown better fit to experimental ones than B3LYP.

To test the different theoretical approaches (HF, DFT/B3LYP) reported here, these and experimental ones depending on geometric parameters, vibrational frequencies and chemical shift values of the title compound have been compared.

REFERENCES

- [1]. Uyanik, C.; Hanson, J.R.; Hitchcock, P.B.; Meredith, L. *Tetrahedron* 6 (2005), p. 4323.
- [2]. Casanovas, J.; Namba, A.M.; Leon, S.; Aquino, G.L.B.; da Silva, G.V.J.; Aleman, C. *J. Org. Chem.* 66 (2001), p. 3775.
- [3]. Sebag, A.B.; Forsyth, D.A.; Plante, M.A. *J. Org. Chem.* 66 (2001), p. 7967.
- [4]. Chesnut, D.B. in *Reviews in Computational Chemistry*, vol. 8 (Eds: K. B. Lipkowitz, D. B. Boyd) VCH New York ch. 5: (1996), p. 245.
- [5]. De Dios, A.C. *Prog. Nucl. Magn. Reson. Spectrosc.* 29 (1996), p. 229.
- [6]. Forsyth, D.A.; Sebag, A.B. *J. Am. Chem. Soc.* 119, 99 (1997), p. 9483.
- [7]. Helgaker, T.; Jaszunski, M.; Ruud, K. *Chem. Rev.* (1999), p. 293.
- [8]. Ditchfield, R., *J. Chem. Phys.* 56(11) (1972), p. 5688.
- [9]. Wolinski, K.; Hinton, J.F.; Pulay, P., *J. Am. Chem. Soc.* 112(23) (1990), p. 8251.
- [10]. Cheeseman, J.R.; Trucks, G.W.; Keith, T.A.; Frisch, M.J. *J. Chem. Phys.* 104(14) (1996), p. 5497.
- [11]. Cimino, P.; Gomez-Paloma, L.; Duca, D.; Riccio, R.; Bifulco, G. *Magn. Reson. Chem.* 42 (2004), p. 26.
- [12]. Friesner, R.A.; Murphy, R.B.; Beachy, M.D.; Ringnalda, M.N.; Pollard, W.T.; Dunietz, B.D.; Cao, Y. *J. Phys. Chem. A.* 103(13) (1999), p. 1913.
- [13]. Rulisek, L.; Havlas, Z. *Int. J. Quantum Chem.* 91 (2003), p. 504.
- [14]. Ziegler, T. *Chem. Mater. Sci.* (1997), p. 69.
- [15]. Rauhut, G.; Puyear, S.; Wolinski, K.; Pulay, P. *J. Phys. Chem.*, 100(15) (1996), p. 6310.
- [16]. Ditchfield, R.; Hehre, W.J.; Pople, J.A. *J. Chem. Phys.* 54(2) (1971), p. 724.

- [17]. Ditchfield, R. *Mol. Phys.* 27(4) (1974), p. 789.
- [18]. Rohlfing, C.M.; Allen, L.C.; Ditchfield, R. *Chem. Phys.* 87(1) (1984), p. 9.
- [19]. Frisch A., Nielsen A.B., Holder A.J. *Gaussview User Manual*, Gaussian Inc., Pittsburg, (2001).
- [20]. *Gaussian 98*, (Revision A.9), Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A.; Jr. Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q., Morokuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Baboul, A.G.; Stefanov, B.B.; Liu G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P.M.W.; Johnson, B.G.; Chen, W.; Wong, M.W.; Andres, J.L.; Head-Gordon, M.; Replogle, E.S.; Pople, J.A. Gaussian Inc., Pittsburg PA, (2001).
- [21]. Lee, S.Y. *Bull. Korean Chem. Soc.* 19 (1) (1988), p. 93.
- [22]. Wheelless, C.J.M.; Zou, X.; Liu, R. *J. Phys. Chem.* 99(33) (1995), p. 12488.
- [23]. Lee, S.Y.; Boo, B.H.; *J. Phys. Chem.* 100(37) (1996), p. 15073; Lee, S.Y.; Boo, B.H.; *J. Phys. Chem.* 100(21) (1996), p. 8782.
- [24]. Atalay, Y.; Avcı, D.; Başoğlu, A.; Okur, İ. *J. Mol. Struct. THEOCHEM* 713 (2005), p. 21.
- [25]. Scott, A.P.; Radom, L. *J. Phys. Chem.* 100 (1996), p. 16502.