Molecular Structure, Vibrational Spectra and Chemical Shift Properties of $C_{12}H_9ClO_4$ and $C_{12}H_9BrO_4$ Crystals by Density Functional Theory and *ab initio* Hartree-Fock Calculations

Nergin Günay^a, Erdogan Tarcan^a, Davut Avcı^b, Kadir Esmer^a, and Yusuf Atalay^b

^a Department of Physics, Kocaeli University, Umuttepe Campus, Izmit, 41380, Kocaeli, Turkey

^b Department of Physics, Sakarya University, Esentepe Campus, Adapazari, 54140, Sakarya, Turkey

Reprint requests to Y. A.; Fax: +90 264 295 59 50; E-mail: yatalay@sakarya.edu.tr

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The molecular geometry, vibrational spectra, and gauge including atomic orbital (GIAO), individual gauges for atoms in molecules (IGAIM), and continuous set of gauge transformations (CSGT) ¹H and ¹³C chemical shift values of ethyl 6-chloro-2-oxo-2*H*-chromene-3-carboxylate ($C_{12}H_9CIO_4-(I)$) and ethyl 6-bromo-2-oxo-2*H*-chromene-3-carboxylate ($C_{12}H_9BrO_4-(II)$) in the ground state have been calculated by using the Hartree-Fock (HF) and density functional method (B3LYP) with 6-31G+(d,p) 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 the spectra of the experimental bands observed. Also, calculated ¹H and ¹³C chemical shift values were compared with the experimental ones.

Key words: Ethyl 6-chloro-2-oxo-2*H*-chromene-3-carboxylate; Ethyl 6-bromo-2-oxo-2*H*-chromene-3-carboxylate; DFT; HF; ¹H (¹³C) NMR; Structure Elucidation; Vibrational Assignment.

1. Introduction

Coumarins represent a class of organic compounds which has extensive and diverse applications [1]. Firstly, coumarins possess distinct biological activity [2] and have been described as agents with potential for anti-cancer and anti-coagulant activity [1]. They have demonstrated a great variety of biological properties as anti-inflamatories [3], anti-bacterials [4] and anti-helmintics [5]. Coumarin and its derivatives are known to exhibit photosensitizing properties [6]. They have been proposed in HIV [7] and cancer [8] treatment, as well as being inhibitors of monoaminooxidase [9, 10]. Particularly, furocoumarins (psoralen and its derivatives) have been reported to photoinduce skin erythema [11, 12] and skin cancer in mice [13]. On the other hand, furocoumarins are important drugs used in the photochemotherapy of skin diseases such as psoriasis [14] and vitiligo [15]. The skin photosensitizing ability of furocoumarins has been correlated with their photoreactivity toward pyrimidine bases of DNA to form cyclobutane-type adducts and interstrand crosslinks with two pyrimidine bases on separate strands of DNA double helix [16, 17]. In order to understand the photosensitizing mechanism of furocoumarins, it is important to obtain information on the structures and dynamics of the excited states and photolytically generated transient species of coumarin. Due to its structural similarities with psoralen, coumarin serves as a useful model for elucidating spectroscopic characteristics of the transient species of psoralen and its derivatives [6]. Non-covalent interactions are involved in most of the molecular recognition processes [18]. Particularly, hydrogen bonding and π -stacking interactions are responsible for the self-association of coumarin derivatives in the solid state [19, 20]. Coumarin derivatives are known to be important laser dyes [21], whereas unsubstituted coumarin will hardly emit fluorescence [22]. In addition, coumarin itself is also known to show interesting photochemical behaviours, particularly the dimerization to form cis and trans head-to-head dimers through excited singlet and triplet states in polar and nonpolar solvents [23].

In previous publication, Santos-Contreras et al. worked with isostructural ethyl 6-chloro- and 6-bromo-2-oxo-1*H*-benzopyran-3-carboxylates. It was characterized by elemental analyses, IR, ¹H and

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Fig. 1. The molecular structures of isostructural ethyl 6chloro- and 6-bromo-2-oxo-1*H*-benzopyran-3-carboxylates, viz. (I) and (II), respectively [18].

¹³C NMR, and X-ray diffraction [18]. In recent years, the *ab initio* and the density functional theory (DFT) has become a powerful tool in the investigation of chemical shift, vibrational spectra, and molecular structure [24]. So in this study, we have calculated the vibrational frequencies, geometric parameters, and GIAO, IGAIM, CSGT ¹H and ¹³C chemical shift of the title compounds in the ground state using HF (Hartree-Fock) and B3LYP (Becke-3-Lee-Yang-Parr) methods with 6-31G+(d,p) basis set.

2. Computational Details

The approximate geometries at three dimensions of title compounds (I, II) are drawn in GaussView 3.07 package programme [25] on personal computer. With the assistance of this programme in the ground state (in vacuo) the title molecules are optimized by Hartree-Fock (HF) and the density functional method (B3LYP) with the 6-31G+(d,p) basis set using Gaussian 03W package programme [26]. Vibrational frequencies for optimized molecular structures have been calculated and all the calculated vibrational frequencies are scaled by 0.89 for HF and 0.96 for B3LYP for 6-31G+(d,p) basis set, respectively [27]. ¹H and ¹³C NMR chemical shifts are calculated within GIAO, IGAIM, and CSGT approach applying B3LYP and HF method with 6-31G+(d,p) basis set.

3. Results and Discussion

3.1. Geometrical Structure

The title compounds (I) and (II) were synthesized as reported by Bonsignore et al. (1995), starting from 5-chloro- or 5-bromosalicylaldehyde with diethyl malonate in equimolor amounts. Santos-Contreras et al. determined the molecular and supramolecular structures of the isostructural ethyl 6-



Fig. 2. (a) and (c) the experimental [18], (b) and (d) the theoretical (with HF/6-31+G(d,p) level) geometric structures of the title compounds (I,II).

chloro- and 6-bromo-2-oxo-1*H*-benzopyran-3-carboxylates ($C_{12}H_9CIO_4$ and $C_{12}H_9BrO_4$), viz. (I) and (II), respectively [18]. For the molecular structure see Figure 1.

The title compounds (I, II) are isomorphous and crystallize in the monoclinic space group P2₁/c with four molecules in the unit cell. The crystal structure parameters of the title compounds are a = 5.7982(5) Å, b = 13.0702(12) Å, c =

	Experim	ental [18]	HF	B3LYP	HF	B3LYP
Parameters				6-310	G+(d,p)	
	(I)	(II)		(I)	-	(II)
Bond Lengths (Å)						
Cl1-C6	1.736(2)	_	1.741	1.755	-	-
Br1-C6	-	1.888 (3)	_	_	1.891	1.904
O1-C2	1.382(2)	1.379(3)	1.360	1.408	1.361	1.409
O1-C9	1.366(2)	1.366(3)	1.346	1.358	1.345	1.357
O2-C2	1.188(2)	1.189(4)	1.180	1.204	1.180	1.204
011-C11	1.200(3)	1.198(4)	1.195	1.221	1.195	1.221
C2-C3	1.470(3)	_	1.479	1.474	-	_
C3-C4	1.342(3)	1.341(4)	1.339	1.363	1.339	1.363
Bond Angles (°)						
C2-O1-C9	122.98(15)	123.1(2)	124.84	124.14	124.9	124.2
O1-C2-C3	115.78(15)	115.6(2)	115.45	115.14	115.4	115.1
C3-C4-C10	121.38(17)	121.3(3)	121.50	122.20	121.5	122.2
Cl1-C6-C5	119.20(17)	-	119.92	119.79	-	-
Br1-C6-C5	-	119.0 (2)	-	_	119.9	119.8
O11-C11-O12	124.10(18)	124.4(3)	124.32	124.03	124.3	124.0
O11-C11-C3	121.72(17)	-	121.54	121.91	-	-
O12-C11-C3	114.18(16)	114.1(2)	114.09	114.05	114.2	114.1
Torsion Angles (°)						
O2-C2-C3-C11	5.4(3)	6.1(5)	5.61	1.20	5.1	-0.02
C2-C3-C11-O11	-156.44(19)	-155.0(3)	-159.23	-174.81	-160.5	179.9

Table 1. Optimized and experimental geometric parameters of the title compounds (I, II) in the ground state.

15.5540(12) Å, V = 1119.83(17) Å³ and a = 5.8432(6) Å, b = 13.2073(14) Å, c = 15.6959(15) Å, V = 1143.0(2) Å³, respectively [18]. The atomic numbering scheme for the title compound crystals and their theoretical geometric structures are shown in Figures 2a-d.

The optimized parameters of the title compounds (bond lenghts, bond angles, and dihedral angles) by HF and B3LYP methods with 6-31G+(d,p) as the basis set are listed in Table 1 and compared with the experimental crystal structure for the title compounds. Based on our calculations, the result of HF method has shown a better fit to experimental data than B3LYP in evaluating bond lenghts, bond angles, and dihedral angles for both two title compounds. The largest difference between experimental and calculated HF bond length is about 0.023 Å for (I) and 0.021 Å for (II).

It is well known that the HF calculation underestimates bond lengths and the inclusion of the electron correlation makes them longer [29]. This elongation usually makes the agreement better between the optimized and the experimental geometric parameters. This pattern is also observed here. Most of the bond distances and angles in (I) and (II) are very similar to the values reported for the isomorphic ethyl coumarin-3-carboxylate, (III) [18], except for the O1-C9 bond length, which is slightly shorter; the mean value is 1.366(2) Å for (I) and (II), compared with 1.377(2) Å in (III) [20]. This is probably due to the inductive negative effect of the halogen atom on the lactone O atom (O1) lone pair of electrons [18]. Compounds (I) and (II) present an anti-conformation between the 3-carboxy and the lactone carbonyl groups, in contrast to the previously reported syn arrangement in (III). In both title molecules, the lactone and the carboxylate carbonyl groups are out of the plane defined by atoms O1/C3-C10 by 8.37(6)° and 17.57(6)°, respectively, for (I), and by $9.07(8)^{\circ}$ and $18.96(18)^{\circ}$, respectively, for (II) [18]. The above mentioned carbonyl derivations from planarity seem to be related to intermolecular interactions. It is interesting to note that the replacement of Cl by Br does not alter the molecular packing [18]. It is noted that the experimental results belong to the solid phase and the theoretical calculations belong to the gaseous phase.

3.2. Assignments of the Vibration Modes

The title molecules (I) and (II) have 26 atoms and 72 normal modes of vibrations. Optimized ground state vibrational modes for studied molecular structures were obtained by *ab initio* HF and DFT (B3LYP) with 6-31G+(d,p) levels. The experimental vibrational spectra of the title compounds were

Table 2.	Comparison o	f the observed :	and calculated	vibrational spectra	a of the title com	pounds (L.II).
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r i i i i i i i i i i i i i i i i i i i	Experi	mental		Calculated			
	(cm	$^{-1})$	HF	B3LYP HF		B3LYP	
Assignments	IR with 1	KBr [18]		6-31G+(d,p)			
	(I)	(II)		(I)		(II)	
C7-H and C8-H sym stretch	-	-	3023	3100	3024	3100	
C4-H and C5-H sym stretch	-	-	3012	3088	3013	3089	
C7-H and C8-H asym stretch	-	-	3010	3087	3010	3088	
C4-H and C5-H asym stretch	3070	3068	3008	3074	3009	3074	
C13-H ₂ and C14-H ₂ asym stretch	-	-	2933	3014	2933	3013	
C13-H ₂ and C14-H ₃ asym stretch	2975	2973	2909	3000	2909	2999	
C13-H stretch and C14-H ₃ asym stretch	2421	2335	2902	2986	2902	2985	
C13-H ₂ sym stretch	2246	2122	2881	2945	2881	2945	
C14-H ₃ sym stretch	1932	1962	2841	2930	2841	2930	
O2-C2 stretch	1743	1743	1798	1758	1799	1759	
O11-C11 stretch	1701	1718	1730	1682	1729	1682	
Coumarin C-C stretch	1613	1599	1627	1591	1626	1590	
Coumarin C-C stretch	1608	1580	1598	1578	1596	1576	
Coumarin C-C stretch	1556	-	1562	1532	1560	1531	
C13-H ₂ scissor	-	1469	1469	1458	1469	1458	
Benzene ring C-C stretch and C-H rock	-	-	1465	1451	1464	1451	
C14-H ₂ and C13-H ₂ scissor	-	-	1442	1442	1442	1442	
C14-H ₃ twist	-	-	1429	1430	1429	1430	
C14-H ₃ torsion + C13-H ₂ wag	-	1380	1402	1392	1402	1390	
C14-H ₃ torsion + C13-H ₂ wag + Coumarin C-C asym stretch	-	_	1392	1376	1391	1376	
C14-H ₃ torsion + C13-H ₂ wag	1365	_	1365	1344	1365	1344	
C2-C3 stretch + C4-H and C5-H rock and C13-H ₂ wag	_	_	1339	1328	_	_	
C2-C3 stretch + C4-H and C5-H rock	_	_	_	_	1339	1328	
O12-C11 stretch + C5-H + C4-H and C7-H rock	1288	_	1303	1314	1304	1314	
O1-C9 stretch + benzene ring C-H rock	_	_	1260	1264	_	_	
O1-C9 stretch + C7-H and C8-H scissor + C5-H rock	_	_	_	_	1263	1266	
C13-H ₂ twist and C14-H ₂ wag	_	_	1258	1243	1258	1242	
Benzene ring C-H rock and C-C stretch	1239	_	1232	1239	1234	1242	
Benzene ring C-C stretch + C7-H and C8-H scissor + C4-H rock	_	1203	1218	1223	1217	1224	
O1-C2 streth + C4-H and C5-H rock	_	_	1151	1187	1150	1188	
C14-H ₂ and C13-H ₂ twist	1142	_	1145	1130	1145	1130	
Benzene ring C-C stretch + C7-H and C8-H scissor	1126	_	1129	1110	1131	1115	
C14-H ₃ wag	_	_	1101	1106	1101	1106	
C7-H and C8-H scissor + benzene ring C-C stretch	1021	_	1091	1087	1093	1087	
Cll+C6 stretch and benzene ring C-H rock	995	-	1065	1056	-	-	
Br-C6 stretch and benzene ring C-H rock	-	_	_	_	1052	1048	
O12-C13-C14 asym stretch + O1-C2 and C3-C11 stretch	_	987	1028	998	1027	998	
Coumarin C-H out of plane bend + O1-C2 stretch and O12-C13-C14 asym stretch	_	_	996	959	_	_	
Coumarin C-H out of plane bend	-	-	-	-	999	966	
Coumarin C-H out of plane bend	_	-	984	934	-	-	
C7-H and C8-H twist	-	-	-	-	994	953	
Coumarin C-H out of plane bend	-	-	974	932	985	933	
Coumarin def	-	-	907	904	-	-	
C4-H and C5-H out of plane bend	-	-	_	_	924	897	
Coumarin C-H out of plane bend	-	-	905	872	-	-	
Coumarin def	_	-	_	_	901	883	
O12-C13-C14 sym stretch and Coumarin C-C stretch	860	_	880	856	_	_	
O12-C13-C14 sym stretch	_	_	_	_	878	871	
C11-O12-C13 bend + C14-H ₃ wag	_	834	855	839	853	837	
C7-H and C8-H wag	791	-	837	806	844	821	
C2-C3-C11 and C4-H out of plane bend	_	788	803	782	804	782	
O11-C11-O12 bend and Coumarin def	_	-	788	780	782	775	
C14-H2and C13-H2 twist	_	_	777	766	777	770	
Coumarin C-C and C-H + O11-C11-O12 out of plane bend	_	-	738	729	743	730	
Coumarin C-C and C-H + O11-C11-O12 out of plane bend	_	_	724	706	_	_	
Coumarin C-C and C-H out of plane bend	-	-	_	_	729	726	
Coumarin C-C and C-H + O11-C11-O12 out of plane bend	-	-	706	683	713	697	

N. Günay et al. \cdot Chemical Properties of $C_{12}H_9ClO_4$ and $C_{12}H_9BrO_4$ by DFT and HF calculation

Table 2 (continued).

	Experi	mental		Calculated				
	(cm	n^{-1})	HF	B3LYP	HF	B3LYP		
Assignments	IR with	KBr [18]		6-31G+(d,p)				
	(I)	(II)		(I)		(II)		
Benzene ring def	661	-	646	650	-	-		
Benzene ring def + Coumarin C-C and C-H out of plane bend	_	-	-	-	647	650		
Benzene ring def	605	_	589	590	-	-		
Benzene ring def + Coumarin C-C and C-H out of plane bend	-	_	-	-	634	641		
Coumarin C-C and C-H out of plane bend	-	_	564	560	-	-		
Coumarin def	_	-	-	-	583	586		
Coumarin C-C and C-H out of plane bend	-	_	557	548	-	-		
Coumarin def	_	-	-	-	557	558		
C11-C6 stretch and C2-O1-C9 + C3-C4-C10 ring bend	-	_	517	512	-	-		
Br1-C6 stretch and C2-O1-C9 + C3-C4-C10 ring bend	_	-	-	-	494	490		
Coumarin C-H and C-C out of plane bend	-	_	456	448	468	463		
O12-C13-C14 and C3-C11-O12 bend	_	-	419	405	418	403		
Coumarin ring C-C and C-H out of plane bend and C4-C3-C11bend	-	_	380	381	-	-		
Coumarin ring C-C and C-H out of plane bend and O12-C13-C14 bend	_	-	-	-	375	383		

Table 3. Theoretical and experimental ${}^{13}C$ and ${}^{1}H$ isotropic chemical shifts (with respect to TMS, all values in ppm) for the title compounds (I, II).

NMR [18]			HF/6-31G+(d,p)			B3LYP/6-31G+(d,p)			HF/6-31G+(d,p)			B3LYP/6-31G+(d,p)		
Atom	(DMS	$SO-d_6$)	GIAO	IGAIM	CSGT	GIAO	IGAIM	CSGT	GIAO	IGAIM	CSGT	GIAO	IGAIM	CSGT
	(I)	(II)			(I)					(I	I)		
H (C4)	8.72	8.42	9.52	9.29	9.29	9.00	8.91	8.91	9.58	9.32	9.32	9.01	8.91	8.91
H (C5)	8.06	7.69	8.30	8.03	8.03	7.75	7.61	7.60	8.45	8.10	8.10	7.85	7.71	7.71
H (C7)	7.78	7.73	8.31	8.21	8.21	7.79	7.73	7.72	8.44	8.26	8.26	7.96	7.81	7.80
H (C8)	7.48	7.23	8.00	8.19	8.19	7.59	7.77	7.78	8.02	8.18	8.18	7.58	7.76	7.76
H (C13)	4.30	4.40	4.35	5.60	5.60	4.57	5.82	5.82	4.36	5.60	5.60	4.54	5.81	5.81
H (C13)	4.30	4.40	4.26	5.52	5.52	4.54	5.80	5.80	4.28	5.53	5.53	4.54	5.81	5.81
H (C14)	1.31	1.39	2.11	3.92	3.92	1.91	3.65	3.65	2.12	3.92	3.92	1.89	3.62	3.63
H (C14)	1.31	1.39	1.87	3.70	3.70	1.84	3.59	3.60	1.89	3.71	3.72	1.89	3.62	3.63
H (C14)	1.31	1.39	1.42	3.08	3.09	1.34	3.01	3.01	1.43	3.09	3.09	1.34	3.01	3.02
C2	155.4	155.9	147.3	152.0	152.0	140.3	142.6	142.6	147.2	151.9	151.9	140.1	142.5	142.5
C3	118.6	117.3	114.7	120.5	120.5	107.2	111.2	111.2	114.3	120.2	120.1	106.8	111.0	111.0
C4	147.3	147.0	151.4	155.8	155.8	138.4	139.7	139.7	151.8	156.1	156.2	138.4	139.9	139.9
C5	129.0	131.4	127.7	131.5	131.5	115.7	118.4	118.4	131.3	134.6	134.6	119.1	121.2	121.2
C6	128.3	119.3	127.2	128.5	128.5	124.7	125.0	125.0	123.2	126.8	126.8	122.1	124.5	124.4
C7	133.7	136.8	133.5	136.6	136.6	120.1	122.1	122.1	136.8	139.4	139.4	123.1	124.6	124.6
C8	118.2	118.4	112.9	117.9	117.9	104.8	107.3	107.3	112.9	117.7	117.7	105.1	107.3	107.3
C9	153.3	153.8	149.7	154.6	154.6	143.2	146.9	146.9	150.6	155.5	155.5	143.7	147.5	147.5
C10	119.1	119.2	111.5	116.7	116.7	108.7	111.1	111.0	111.7	116.8	116.8	108.8	111.3	111.3
C11	162.2	162.5	158.2	162.6	162.5	151.4	153.2	153.2	158.1	162.5	162.4	151.4	153.2	153.2
C13	61.3	62.1	53.1	54.6	54.6	54.8	54.1	54.1	53.1	54.6	54.6	54.8	54.1	54.1
C14	13.9	14.0	11.9	13.4	13.5	5.3	5.0	5.0	11.9	13.5	13.5	5.3	5.0	5.0

reported by Santos-Contreras and co-workers [18]. We have compared our calculations of the title compounds with their experimental results. Theoretical and experimental vibrational results are shown in Table 2.

The C=O stretching calculated at B3LYP/6-31G+(d,p) after scalling down gives the values of 1821-1742 cm⁻¹ and 1821-1741 cm⁻¹ which are nearer to the observed values of 1743-1700 cm⁻¹ for compound (I) and 1743-1718 cm⁻¹ for compound (II) [18]. The asymmetric stretching for the CH_2 and CH_3 is a magnitude higher than the symmetric stretching. Other assignments of internal vibrations can be seen in Table 2. As can easily see from the tables, the experimental fundamentals are in a better agreement with the scaled fundamentals and are found to have a better correlation for B3LYP than HF. When the HF and B3LYP calculated frequencies are compared, almost all the frequencies are in good accord with each other.



Fig. 3. (a) and (b) plot of the calculated and experimental ${}^{1}H$ chemical shifts of $C_{12}H_9CIO_4$ -(I) and $C_{12}H_9BrO_4$ -(II) molecules.

3.3. Assignments of the Chemical Shift Values

750

For comparison of the calculated and the experimental NMR data, the shielding tensors of the molecules in question were calculated with the standard Gaussian 03W [26] program. The electronic structures of the molecules were treated by both HF and B3LYP methods with 6-31+G(d,p) basis set.

The NMR shielding tensors were computed with three different methods: the GIAO (gauge independent atomic orbital) [30], CSGT (continuous set of gauge transformations) [31], and IGAIM (individual gauges for atoms in molecules) [32] methods. Table 3 gives ¹³C and ¹H chemical shifts. HF/GIAO denotes the following procedure: the geometry minimized the corresponding HF energy and the wave function was calculated at the HF level, presuming the calculation of the optimum geometry. The NMR data were calculated by the GIAO method. The notations B3LYP/GIAO,

HF/IGAIM, B3LYP/IGAIM, etc. are similar. The results are presented in Table 3.

First of all, molecular structures of the title compounds are optimized by using HF and B3LYP method with 6-31G+(d,p). Then, GIAO, IGAIM and CSGT ¹H and ¹³C calculations of the title compounds (I, II) have been carried out using same methods with same basis set. In previous publication, IR and ¹H and ¹³C NMR spectra (DMSO- d_6) of the title compounds were studied [18]. We compared our calculations with their experimental chemical shift values. These results are shown in Table 3.

"Gauge-independent", or "gauge-invariant" atomic orbitals (GIAO), as they have been termed by several authors, guarantees that computed magnetic properties are left invariant in a translation of origin of the coordinate system [33]. In the gauge invariant atomic orbital (GIAO) method, each atomic orbital has its own local gauge origin placed on its center. Several other



Fig. 4. (a) and (b) plot of the calculated and experimental ${}^{13}C$ chemical shifts of $C_{12}H_9CIO_4$ -(I) and $C_{12}H_9BrO_4$ -(II) molecules.

methods have appeared in the literature, such as the individual gauge localized orbital (IGLO) method of Schindler and Kutzelnigg [34, 35] and the continuous set of gauge transformations (CSGT) method of Keith and Bader [31, 32]. In the CSGT method, the current density at every point of space is computed assuming that the same point is also the origin of the vector potential.

We can see in Table 3 that experimental ¹H and ¹³C chemical shift values are in better agreement with the theoretical values and are found to have better agreement with the B3LYP than the HF method.

Figure 3 and 4 show the correlation plot of the chemical shift values (with respect to TMS), calculated at HF and B3LYP level with 6-31G+(d,p) basis set versus the corresponding experimental data shown in Table 3. As we can see from the correlation graphic in the figures, experimental chemical shift values are in a better agreement with the theoretical chemical shift values.

4. Conclusions

In this study, the results of experimental and the HF and DFT level of theory with 6-31G+(d,p) basis set are reported. Computed and experimental geometric parameters, vibrational frequencies and chemical shifts of the title compounds have been compared. To fit the theoretical frequency results with the experimental ones for HF and B3LYP levels, we have multiplied the data. Multiplication factor gained results seemed to be in a good agreement with experimental ones. The B3LYP levels which include the effects of electron-correlation have shown better fit to the experimental ones than those of HF levels in terms of evaluate bond angles, vibrational frequencies, and chemical shifts. In these regard, geometric parameters, fundamental frequencies, and chemical shifts for diverse molecular structure analysis can change with respect to the different theoretical approaches.

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