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Molecular structure, vibration properties and quantum chemical calculations of 4-(chloromethyl)-7-methoxycoumarin and 4-(chloromethyl)-7-methyl-coumarin

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Abstract

Objective: This study presents the quantum chemical calculations of 4-(Chloromethy)-7-methoxycoumarin (1) and 4-(Chloromethy)-7-methylcoumarin (2).

Material and Methods: The solid phase FT-IR spectra of compounds 1 and 2 have been recorded in the region 4000–500 cm-1. The molecular geometry, vibrational frequency of compounds 1 and 2 in the ground state have been calculated by utilizing the density functional method (DFT/B3LYP) with the 6-311G+ (d, p) basis set. The calculated vibrational frequencies are compared with experimental obtained by FT-IR spectra. On the other hand, frontier molecular orbitals (FMOs) and molecular electrostatic potentials (MEP) of compounds 1 and 2 were calculated at the B3LYP/6-311G+ (d, p) level of theory.

Results: With the aid of the theoretical calculations, the vibrational frequencies are precisely assigned to their molecular structure.

Conclusion: The theoretical and experimental results support each other.

Keywords: 4-(Chloromethy)-7-methoxycoumarin; 4-(Chloromethy)-7-methylcoumarin; FT-IR spectra ; DFT; Vibrational frequencies

Introduction

Coumarin is an aromatic compound that has a bicylic structure with lactone carbonyl (1). The substitution of coumarins represents one of the most biologically active classes of compounds, possessing a wide spectrum of activities, including analgesic, antimicrobial, anticancer, anti-viral, anti-inflammatory (2). Coumarins are used as drug. They have also used as photosensitizers, fluorescens and laser dyes (3). Coumarins which contain an electron-releasing group in the 4-position, recognized as fluorescent dyes that suitable for application to synthetic fibers (4). In addition to analytical techniques involving the use of fluorescent coumarin derivatives are of considerable importance search for the development of new diagnostic methods providing a useful tool and new biologically-active compounds (5). Widely used methods for their preparation are Perkin, Knoevenagel, Wittig reactions, Reformatsky and von Pechmann (6-10). The density functional theory (DFT) is a very good method to compute the electronic structure of matter. In this way, DFT procedures may not be regarded as a pure ab initiation method. In the recent years, DFT procedure has seen a quick rising in several types of implementations, especially since the displaying of certainty non-local arrangements. In the DFT the exchange–coordination energy is the major point among all of the approaches; consequently, the certainity of DFT is directly connected on the approximate nature of the exchange–coordination energy functional. Thus DFT methods were frequently utilized in a large number of theoretical researches and several scientists have broadly researched the distinct attitude of coumarin derivatives (11-20).

The work with DFT method for this compounds has not been reported so far. In this work, the molecular geometry was determined using DFT method and using these molecular structure, vibrational frequencies, HOMO–LUMO energies, molecular electrostatic potentials (MEPs) are determined for further researchers of coumarin derivatives.

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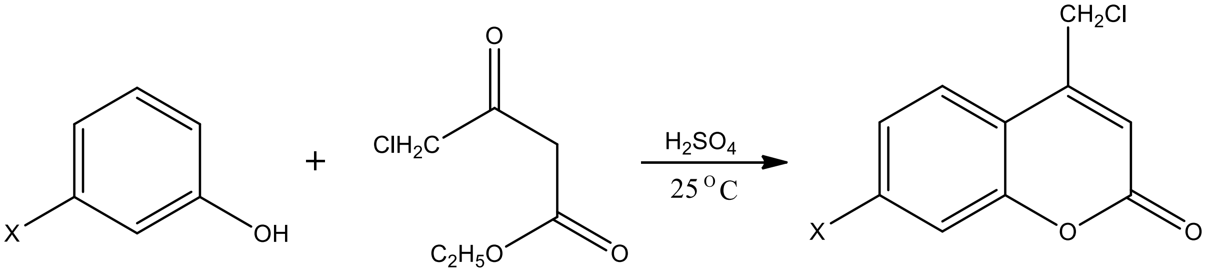
Material and Methods

4-(Chloromethyl)-7-methoxycoumarin

For the synthesis of 4-(Chloromethyl)-7-methoxycoumarin (1), a mixture of 3-methoxyphenol (1.24 g, 10 mmol) and ethyl 4-chloro-3-oxobutanoate (1.64 g, 10mmol) in sulfuric acid (6 ml) was refluxed two hours. The reaction mixture allowed to cool to room temperature and then poured into crushed ice (40ml), stirred for 20min. The solid precipitate was filtered off and recrystallized with ethanol. Yield 52 %;IR (ν, cm-1): 1736 (C=O lacton) , 1274 (C-O), 1063 (COC methoxy).

4-(Chloromethy)-7-methylcoumarin

For the synthesis of 4-(Chloromethyl)-7-methylcoumarin (2), a mixture of 3-methylphenol (1.08g, 10 mmol) and ethyl 4-chloro-3-oxobutanoate (1.64 g, 10mmol) in sulfuric acid (6 ml) was refluxed two hours. The reaction mixture allowed to cool to room temperature and then poured into crushed ice (40ml), stirred for 20min. The solid precipitate was filtered off and recrystallized with ethanol. Yield 48%;IR (ν, cm-1): 2925 and 2985 (C-H:methyl), 1739 (C=O lacton) , 1276 (C-O). The reactions for the synthesis of 1 and 2 are shown in Fig. 1.



1-2

X: OCH_3 (1), CH_3 (2)

Figure 1: The synthesis route of compounds 1-2.

Computational methods

Using the density functional theory (DFT) applications with B3LYP levels using 6-311G+(d, p) as a principle set using the Gaussian 09W (21). Using the vibrational wave number, the optimized molecular structures were predicted, these calculations were carried out using the B3LYP protocol. By solving the self-consisting field equation iteratively, the optimized geometry corresponding to the minima on the potentials were obtained. The molecular structure for compounds 1 and 2 are shown in Fig. 2. For the optimized structure, the harmonic vibration frequencies were studied at the same level of theory using the Gauss-View molecular visualization program (22). The molecular electrostatic potentials were dtermined using the B3LYP/6–311G+(d,p) method to investigate the reactive sites of compounds 1 and 2. Furthermore, frontier molecular orbitals (FMOs) for the title compounds were carried out by the density functional theory (DFT) applications with B3LYP levels using 6-311G+(d,p) as a principle set using the Gaussian 09W program package.

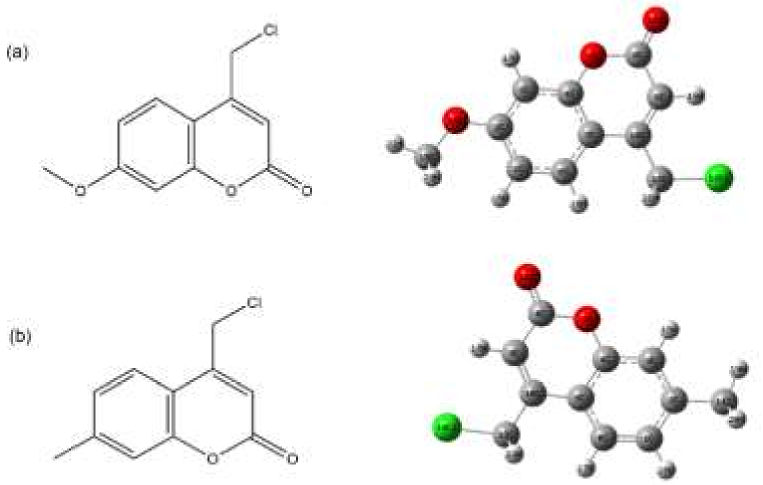


Figure 2: The optimized geometric structures of compound 1 (a) and 2 (b).

Result and Discussion

Vibrational assignments

Usually, the experimental ones are lower than the calculated harmonic vibrational wavenumbers because of the anharmonicity of the incomplete treatment of electron correlation and of the use of finite one-particle basis set. For this reason, calculated frequencies are scaled by a proper scale factor. The experimental and theoretical FT-IR spectra for compounds 1 and 2 are shown in Figs. 3 and 4 and experimentally observed and theoretical calculated harmonic vibrational frequencies were listed in Table 1. From the calculations, the observed values are in good coherence with the computed values. The vibrational bands assignments have been made by using the animation option of Gauss View 5.0 graphical interface for Gaussian programs.

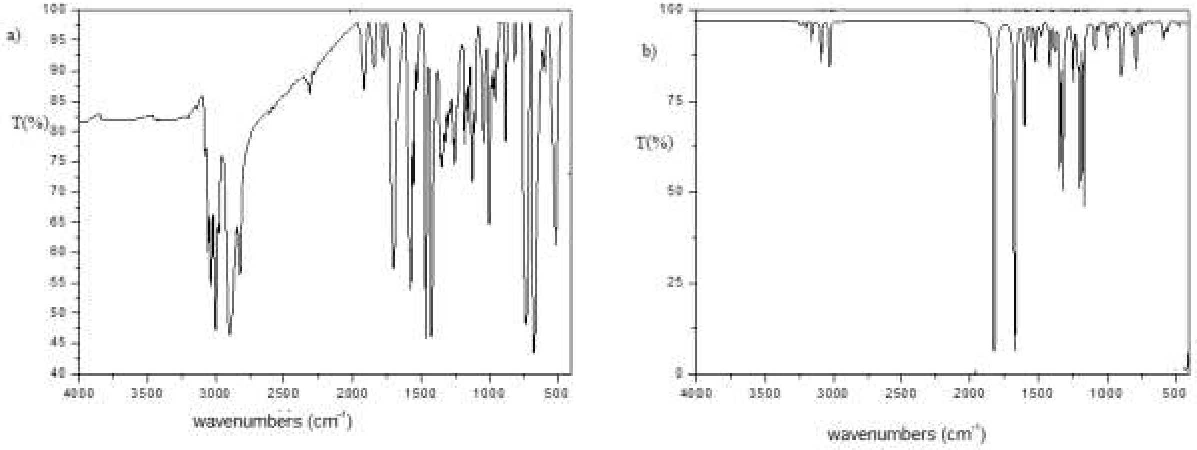


Figure 3: (a) FT-IR spectrum of the title compound (1), (b) Simulated B3LYP level IR spectra.

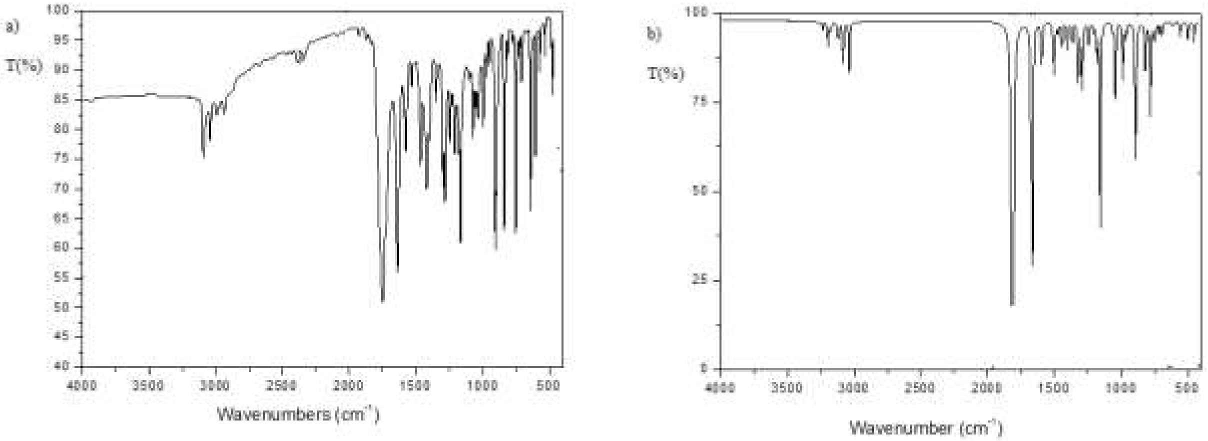


Figure 4: (a) FT-IR spectrum of the title compound (2) . (b) Simulated B3LYP level IR spectra.

CO vibrations

The coumarins and its derivatives are observed two diverse type CO stretching vibrations. The first one is C=O and the second one is C-O stretching vibrations. The C=O stretching vibrations are viewed in the part of 1780-1700 cm-1 (23). In this study, the bands appeared 1736 cm-1 (1) and 1739 (2) experimentally are belong to C=O group and the corresponding calculated wave numbers are 1767 cm-1 (1) and 1766 (2). The reported value of stretching mode of COC in the ring (C4-O7) was 1216 cm-1 for 3-(bromoacetyl) coumarin (23). this vibration was appeared at 1274 cm-1(1) and 1276 (2) experimentally and calculated at 1282 cm-1 (1) and 1283 (2) for B3LYP. In addition to this, the methoxy group COC stretching vibrations (C15-O14) was appeared 1063 (1) experimentally, and calculated at 1067cm-1 (1) for B3LYP.

Table 1: Comparison of the experimental and calculated vibrational frequencies of 4-(Chloromethyl)-7-methoxycoumarin (1) and 4-(Chloromethyl)-7-methylcoumarin (2)

Assignments	Experimental FT-IR (cm^{-1}) with KBr		Calculated B3LYP	
	1	2	1	2
υ pyron C-H	3063	3116	3165	3163
υ_s aromatic ring C-H	3023	3035	3152	3127
υ_{as} aromatic ring C-H	-	-	3122	3104
υ_{as} methoxy C-H3	-	-	3079	-
υ_{as} chloromethyl C-H	-	-	3056	3057
υ_{as} methyl C-H3	-	2985	-	3048
υ_s chloromethyl C-H	2983	-	3009	3010
υ_s methyl C-H3	-	2925	-	2967
υ_s methoxy C-H3	2943	-	2951	-
υ pyron C=O	1736	1739	1767	1766
υ pyron C=C + υ aromatic ring	1616	1618	1628	1632
C=C	1455	-	1471	-
δ methoxy C-H3	-	1558	-	1464
δ methyl C-H3	1425	1447	1435	1436
δ chloromethyl C-H	-	1397	-	1385
α methyl C-H3	1274	1276	1282	1283
υ pyron C_4- O_7 + δ aromatic	1163	1196	1180	1190
ringHCO+CH3	1153	1156	1175	1173
β chloromethyl C-H	1063	-	1067	-
δ aromatic ring C-H	1023	1045	1124	1124
υ methox C_{15}-O_{14}	-	985	1168	-
υ pyron C-O + β aromatic ring	-	985	-	1036
C=C	993	894	936	946
α methox C-H3	852	834	865	867
α methyl C-H3	812	824	784	796
δ chloromethyl C-H+ δ aromatic ring C-H	741	693	756	756
υ pyron O-C + C-C				
α aromatic ring C-H				
υ chloromethyl C-Cl				

υ,stretching; δ,in-plane bending;α,out of-plane bending;β,rocking;s,symetric;as,asymetric

CH vibrations

The aromatic CH stretching, CH in-plane bending and CH out-of-plane bending vibrations appearing 2900-3150 cm-1,1100-1500 cm-1 and 700-1000 cm-1 frequency ranges, respectively (24). The C-H aromatic stretching modes were observed at 3023 cm-1 (1), 3035 (2) experimentally and calculated 3152 cm-1 (1), 3127 (2) for B3LYP. The C-H in-plane bending vibrations were observed at 1153 cm-1 (1), 1156 (2) experimentally and calculated at 1175 cm-1(1) , 1173 (2) for B3LYP. The C-H out-of-plane bending vibrations were observed at 812cm-1(1), 824 (2) experimentally and calculated at 784 cm-1(1) 796 (2) for B3LYP. The most useful diagnostic band to determine the methyl in a sample is the C-H stretching vibrations that this group exhibit. These vibrations typically fall between 2800 and 3000 cm-1 (25). For the methyl group vibrations appeared at 2925 and 2985 cm-1 (2) experimentally and calculated at 2967 and 3048 cm-1 (2) for B3LYP.

Frontier molecular orbitals (FMOs)

Frontier molecular orbitals called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are one of the most important orbitals in a molecule. The main orbital take part in chemical stability are not only the highest occupied molecular orbital but also lowest unoccupied molecular orbital (26). Frontier Molecular orbitals and their properties are very useful parameters for quantum chemistry. Frontier Molecular orbitals play an important role in the UV–Visible spectra and chemical reaction, as well as in the electric and optical properties (27). The HOMO and LUMO represent the ability to donate an electron and the ability to obtain an electron, respectively. The orbital energy of HOMO and LUMO and the energy gap between

LUMO and HOMO are calculated using B3LYP/6- 311G+ (d, p) method. 3D plots of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals for both the compounds are shown in Fig. 5. It can be seen that from the Fig. 5, the molecular orbitals are localized on almost the whole molecules and is more located over the coumarin ring for both the compounds. Besides, while the HOMO-1 is localized on the benzene ring, LUMO+1 is localized on almost the pyrone ring The positive phase is shown as red , but the negative one is shown as green. The energies of HOMO–1, HOMO, LUMO and LUMO+1 orbitals of the compound 1 in gas phase are – 7.26, -6.61, -2.19 and -0.92 eV, respectively. The energies of HOMO–1, HOMO, LUMO and LUMO+1 orbitals of the compound 2 in gas phase are – 7.41, -6.83, -2.26 and -1.01 eV, respectively. Also, the value of energy separation between the HOMO and LUMO of compound 1 and 2 is 4.41 and 4.56 eV, while the value of energy gap between the HOMO–1 and LUMO+1 is 6.34 and 6.40 eV in gas, respectively. In the recent, the energy gap between HOMO and LUMO has been used to found the bioactivity from intra molecular charge transfer (ICT) (28, 29) and describes kinetic stability, the chemical reactivity, chemical softness-hardness, optical polarizability and of a molecule.

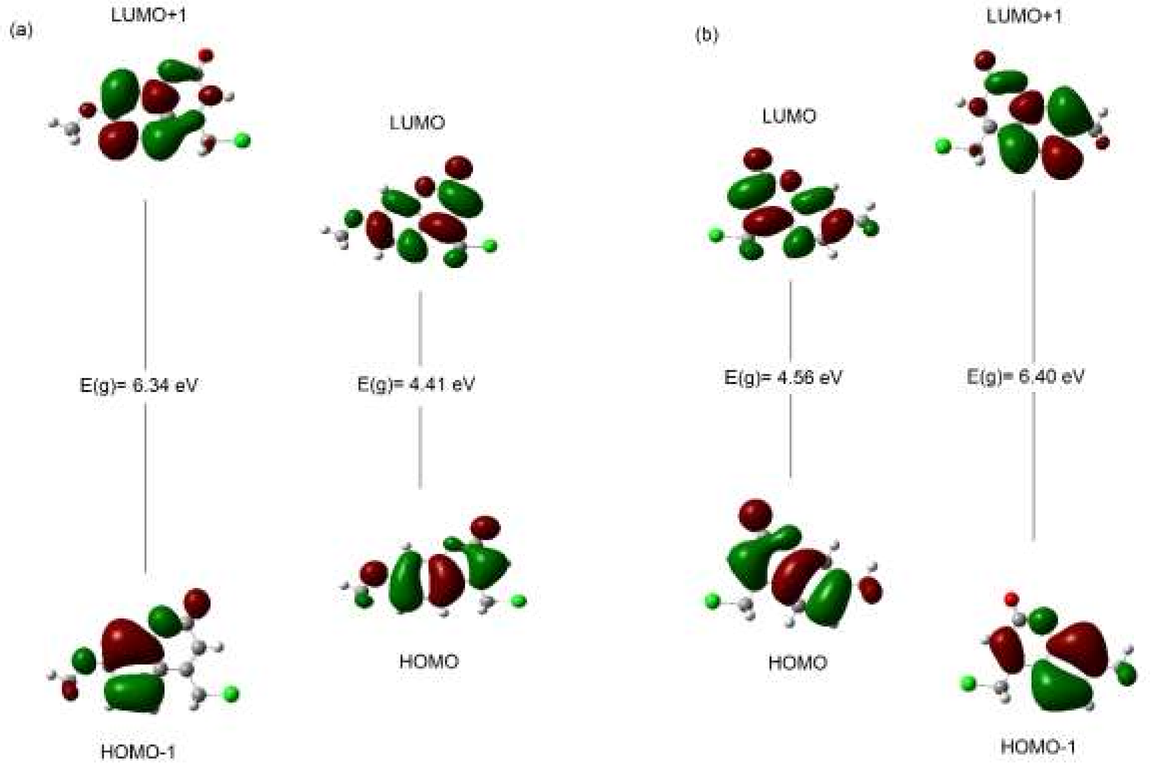


Figure 5: The Frontier Molecular Orbitals (FMOs) of compound 1(a) and 2 (b).

Molecular electrostatic potential surfaces

Molecular electrostatic potential (MEP) provides a visual method to understand the correlation between molecular structures containing drugs and biomolecules and its physiochemical property (30). The molecular electrostatic potential (MEP) surface and the electrostatic potential (ESP) have been plotted for the compound 1 and 2 at the B3LYP/6-311G+(d,p) basis set as shown in Figs. 6 and 7, respectively.

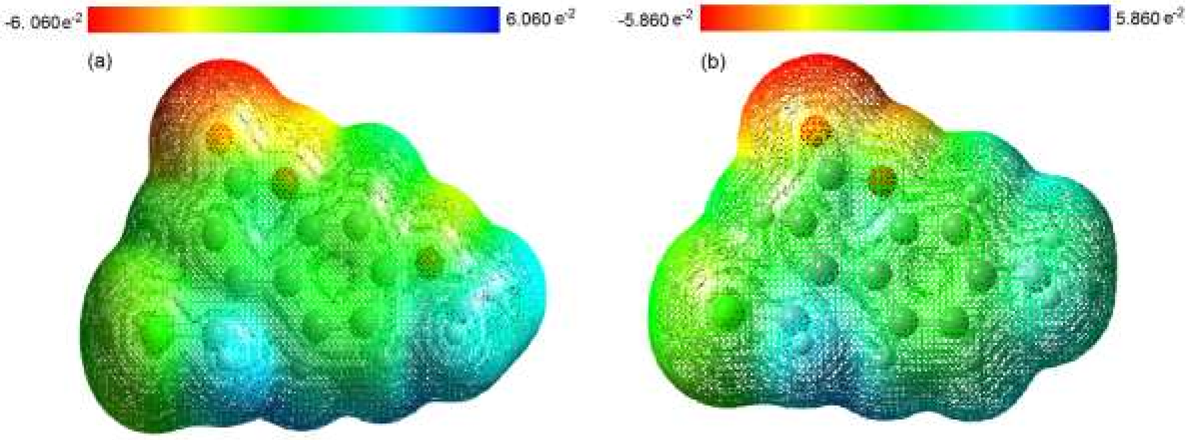


Figure 6: Molecular electrostatic potential (MEP) surfaces of compound 1 (a) and 2 (b).

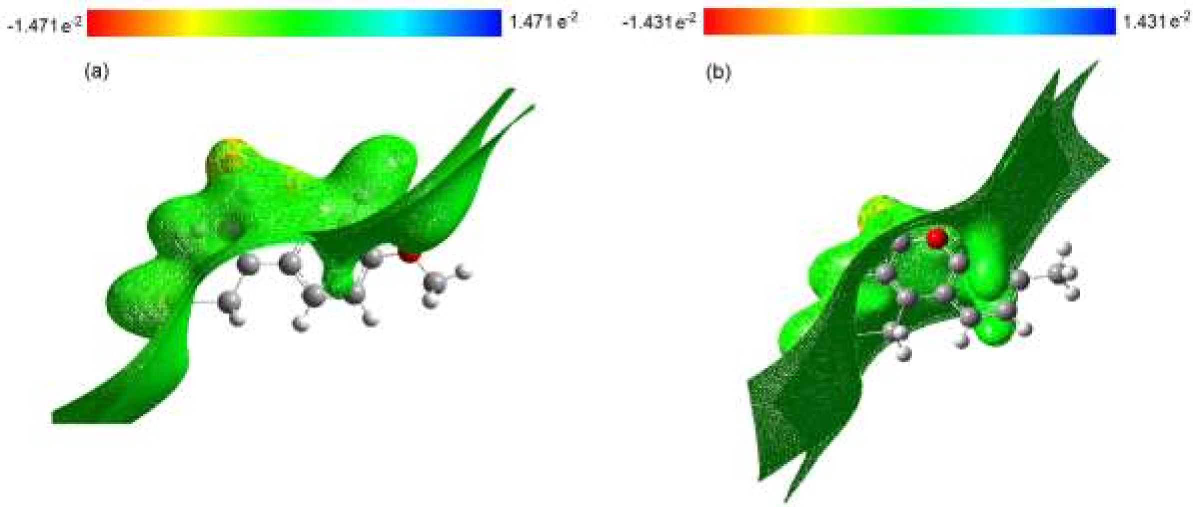


Figure 7: Electrostatic potential (ESP) surfaces of compound 1 (a) and 2 (b).

The MEP surfaces are very useful parameter to study reactivity given that an approaching electrophile will be attracted to negative areas. The different electrostatic potential values of the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. For compound 1, the color code of the MEP map were in the range between -0.0606 a.u (deepest red) and 0.0606 a.u (deepest blue), for compound 2, the color code of the MEP map were in the range between -0.0586 a.u (deepest red) and 0.0586 a.u (deepest blue), where blue colored area shows the strongest attraction and red colored area shows the strongest repulsion.

In the majority of the MEPs, the maximum positive area which favored site for nucleophilic attack as blue color, while the maximum negative area which favored site for electrophilic reactive as red and yellow color. The results show that the negative potential areas which are usually associated with the lone pair of electronegative atoms are mainly over the electronegative Oxygen atoms and positive potential areas are over the nucleophilic reactive hydrogen atoms. Red color shows the strongest repulsion and blue color shows the strongest attraction. From these results, we can say that the O (Oxygen) atoms show the strongest repulsion. As can be seen from the MEP map of the compounds 1 and 2, negative areas are mainly localized over the carbonyl (C=O) groups. The maximum positive areas are localized on the methyl (–CH3) groups. This result also gives information for the area from which the compounds can have intermolecular interaction.

Conclusion

A complete structural, vibrational and electronic investigations of the compounds 1 and 2 have been carried out using the FT-IR spectroscopic technique along with DFT/B3LYP method with 6-311G+ (d,p) basis sets. Vibrational frequencies were calculated using the B3LYP method using 6-311G+ (d) basis set shows the molecular geometry parameters. By mapping an electron density iso surface with molecular electrostatic potential surface, knowledge about the shapes, sizes, and site of high electronegativity and charge distributions of the compound 1 and 2 has been obtained. Using the B3LYP/6-311G+(d,p) method, which provide the nature of reactivity, the energies of HOMO and LUMO and their orbital energy gaps were calculated as well as the physical and structural properties of the molecules. 4.41 (1) and 4.56 (2) eV were found to be the frontier orbital energy gap (EHOMO- ELUMO). With the aid of the theoretical calculations at the B3LYP/6−311G+(d,p) level, the vibrational frequencies are precisely assigned to their molecular structure, in which the theoretical and experimental results support each other. It was noted that the theoretical calculation belonging to gaseous and the experimental outcomes belong to the solid phase. The positive potential sites are around the hydrogen atoms and the negative potential sites are on electronegative atoms, which are shown by the MEP map. The region from which the compound may have intermolecular interactions can be understood based on this information provided.

Conflict of interest: The authors declare they have no potential conflicts of interest with respect to the research, authorship, and/or publication of this article, and declare study has ethical permissions if required..

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