Research Article

Molecular Structure, NMR, HOMO, LUMO, and Vibrational Analysis of O-Anisic Acid and Anisic Acid Based on DFT Calculations

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This work deals with the vibrational spectroscopy of O-Anisic acid (OAA) and Anisic acid (AA). The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) with standard B3LYP/6-31G** method and basis set combinations. The vibrational spectra were interpreted, with the aid of normal coordinate analysis based on a scaled quantum mechanical force field. The infrared and Raman spectra were also predicted from the calculated intensities. The effects of carbonyl and methyl substitutions on the structure and vibrational frequencies have been investigated. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. The ¹³C and ¹H NMR chemical shifts of the DFA and CA molecules were calculated using the gauge-invariant-atomic orbital (GIAO) method in DMSO solution using IEF-PCM model and compared with experimental data.

1. Introduction

Aromatic acids have all the properties characteristic of the carboxylic acids of the aromatic series. In medicine, aromatic acids are employed as weak antiseptics, and their salts as carriers of specific cations [1]. Benzoic acid derivatives substituted by hydroxyl group or ether containing oxygen atom have active bacteriostatic and fragrant properties. They are typically used in pharmaceutical and perfumery industry.

Anisic acid or methoxy benzoic acid is an organic compound which is a carboxylic acid. Anisic acid is a part of cresol class antiseptic compounds. It is also used as an insect repellent. Anisic acid and its derivatives are also widely used in chemical reaction as intermediates to obtain target materials such as dyes, pharmaceuticals, perfumes, photoinitiators, and agrochemicals. O-Anisic acid is used in organic synthesis and antiseptic disinfectant [2].

The vibrational assignments of the compounds can be proposed on the basis of the wavenumber agreement between the computed harmonics and the observed fundamentals.

Quantum chemical computational methods have proven to be an essential tool for interpretations and prediction of vibrational spectra [3, 4]. A significant advent in this area was made by the scaled quantum mechanical (SQM) force field method [5–8]. In the SQM approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which were found to be well transferable between chemically related molecules [4, 9–11].

In this study, we recorded FTIR and FT-Raman spectra and calculated the vibrational frequencies of O-Anisic acid and Anisic acid in the ground state to distinguish fundamentals from experimental vibrational frequencies and geometric parameters using DFT/B3LYP (Becke3-Lee-yang-Parr) method. Natural bond orbital (NBO) analysis of the title molecules was also carried out. In addition, the gauge-invariant-atomic orbital (GIAO) ¹³C and ¹H chemical shifts calculations of the title compounds were calculated by using B3LYP/6-31G** basis set [12]. The calculated quantum chemical parameters are E_{HOMO} , E_{LUMO} , ΔE , and those parameters that give valuable information about the reactive behavior

such as chemical potential (P_i), global hardness (η), and the softness (σ) [13]. A detailed quantum chemical study will aid in making definite assignments to fundamental normal modes of OAA and AA to clarify the experimental data for these important molecules.

2. Experimental

The pure crystalline samples of OAA and AA were obtained from Lanchester chemical company, UK, and used without further purification for the spectral measurements. The room-temperature Fourier-transform (FT) infrared spectra of the title compounds were measured in the region 4000–400 cm^{-1} at a resolution of $\pm 1 \text{ cm}^{-1}$ using BRUKER IFS-66V Fourier-transform spectrometer, equipped with an MCT detector, a KBr beam splitter, and a global source. The FT-Raman spectra were recorded on the same instrument with an FRA-106 Raman accessory in the region 4000–50 cm^{-1} . The 1064-nm line of a Nd:YAG laser was used as excitation source, and the laser power was set to 200 mw.

The ^1H and ^{13}C NMR spectra were taken in CDCl_3 , and $\text{DMSO}-d_6$ solution and all signals were referenced to TMS on a BRUKER FT-NMR spectrometer. All NMR spectra were measured at room temperature.

3. Computational Details

All the calculations were performed by using Gaussian 03 program [14] package on the personal computer. The Becke's three-parameter hybrid density functional, B3LYP, was used to calculate both harmonic and anharmonic vibrational wavenumbers with 6-31G** basis set. It is well known in the quantum chemical literature that the B3LYP functional yields a good description of harmonic vibrational wavenumbers for small and medium sized molecules. The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming C_s point group symmetry, respectively, for OAA and AA. The theoretical DFT force field was transformed from Cartesian coordinates into the local coordinates and then scaled empirically according to the SQM procedure [5]

$$F_{ij}^{\text{Scaled}} = (C_i C_j)^{1/2} F_{ij}^{\text{B3LYP}}, \quad (1)$$

where C_i is the scale factor of coordinate i , F_{ij}^{B3LYP} is the B3LYP/6-31G** force constant in local coordinate, and F_{ij}^{Scaled} is the scaled force constant.

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (S_i) calculated by the Gaussian 03 program and adjusted during the scaling procedure with the MOLVIB program were converted to relative Raman intensities (I_i) using

the following relationship derived from the basic theory of Raman scattering [15–17]:

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i [1 - \exp(-hcv_i/KT)]}, \quad (2)$$

where v_o is the exciting frequency (in cm^{-1} units); v_i the vibrational wavenumber of the i th normal mode; h , c , and k are the fundamental constants, and f is the suitably chosen common normalization factor for all the peak intensities.

The calculated quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), chemical potential (P_i), global hardness (η), and the softness (σ) were calculated. The concept of these parameters is related to each other [18–21], where

$$\begin{aligned} P_i &= -\chi, \\ P_i &= \frac{(E_{\text{HOMO}} + E_{\text{LUMO}})}{2}, \\ \eta &= \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2}. \end{aligned} \quad (3)$$

The inverse values of the global hardness are designated as the softness σ , as follows:

$$\sigma = \frac{1}{\eta}. \quad (4)$$

For NMR calculations, the title molecules are firstly optimized and after optimization, ^1H and ^{13}C NMR chemical shifts (H and C) were calculated using the GIAO method in CDCl_3 at B3LYP method with 6-31G** basis set [22, 23]. Absolute isotropic magnetic shielding was transformed into chemical shifts by referring to the shielding of a standard compound (TMS) computed at the same level. It has been shown that B3LYP applications were successful in shielding calculations on carbon and hydrogen atoms [23].

4. Results and Discussion

4.1. Molecular Geometry. The molecular structures of OAA and AA with C_s symmetry are shown in Figures 1(a) and 1(b), respectively. The optimized bond lengths and angles for OAA and AA using DFT methods are given in Table 1. The global minimum energies obtained by the DFT structure optimization for OAA and AA are calculated as -535.3530 and -535.3627 Hartrees, respectively. The substitution of OCH_3 with COOH group in the OAA and AA leads to strong intermolecular hydrogen bonding and +I effect, respectively.

4.2. Vibrational Force Constants. Quantum mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/Bohr² units. These force constants were transformed to the force fields in internal local-symmetry coordinates. The local-symmetry coordinates defined in terms of the internal valence coordinates

FIGURE 1: (a) Molecular structure of O-Anisic acid along with numbering of atoms. (b) Molecular structure of Anisic acid along with numbering of atoms.

TABLE 1: Optimized geometrical parameters O-Anisic acid (OAA) and Anisic acid (AA) obtained by B3LYP/6-31G** density functional calculations.

Bond length ^a	Value (Å)		Bond angle ^a	Value (°)	
	OAA	AA		OAA	AA
C1-C2	1.39	1.39	C1-C2-C3	119.99	119.99
C2-C3	1.39	1.39	C2-C3-C4	119.99	119.99
C3-C4	1.39	1.39	C3-C4-C5	120.00	120.00
C4-C5	1.39	1.39	C4-C5-C6	119.99	119.99
C5-C6	1.39	1.39	C2-C1-C7	120.01	120.01
C1-C7	1.54	1.54	C1-C7-O8	130.07	130.07
C7-O8	1.23	1.23	C1-C7-O9	112.29	112.29
O9-C7	1.35	1.35	C7-O9-H10	110.60	110.60
O9-H10	0.97	0.94	C3-C2-O11(H11)	119.98	119.98
C2-O11(H11)	1.43	1.09	C2-O11-C12 (C4-C3-H12)	109.50	120.01
C11-C12 (H12-C2)	1.43	1.00	O11-C12-H13 (C5-C4-O13)	109.47	119.98
C12-H13 (O13-C3)	1.07	1.43	O11-C12-H14 (C4-O13-C14)	109.47	109.50
C12-H14 (C14-O13)	1.07	1.43	O11(O13)-C12(C14)-H15	109.47	109.47
C12(C14)-H15	1.07	1.07	C4(O13)-C3(C14)-H16	120.01	109.47
C3(C14)-H16	1.09	1.07	C5(O13)-C4(C14)-H17	119.98	109.47
C4(C14)-H17	1.09	1.07	C6-C5-H18	120.00	120.00
C5-H18	1.09	1.09	C1-C6-H19	119.99	119.99
C6-H19	1.09	1.09			

^aThe atoms indicated in the parenthesis belongs to AA.
For numbering of atoms refer to Figures 1(a) and 1(b).

following the IUPAC recommendations [24, 25] are given in Tables 4 and 5 for the title compounds.

The bonding properties of OAA and AA are influenced by their rearrangements of electrons during substitutions and addition reactions. The stretching force constants of C1-C7 in OAA and AA are found to be lower than the values of stretching force constant of other C-C atoms. The force

constant of C1-C7 in OAA is found to be greater than AA due to steric effect (i.e., bulky groups in OAA). The most important diagonal force constants (stretching only) of OAA and AA are listed in Table 6.

4.3. Assignment of Fundamentals. The molecules OAA and AA are disubstituted aromatic system. The vibrational bands

TABLE 2: Definition of internal coordinates of O-Anisic acid (OAA).

No. (i)	Symbol	Type	Definition
Stretching			
1-4	r_i	C-H	C3-H16, C4-H17, C5-H18, C6-H19
5-11	r_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C1-C7
12-14	r_i	C-O	C7-O8, C7-O9, C2-O11
15	r_i	O-C	O11-C12
16	r_i	O-H	O9-H10
17-19	r_i	C-H(methyl)	C12-H13, C12-H14, C12-H15
Bending			
20-21	β_i	C-C-C	C2-C1-C7, C6-C1-C7
22-29	β_i	C-C-H	C2-C3-H16, C4-C3-H16, C3-C4-H17, C5-C4-H17, C4-C5-H18, C6-C5-H18, C5-C6-H19, C1-C6-H19
30-32	β_i	C-C-H(methyl)	O11-C12-H13, O11-C12-H14, O11-C12-H15
33-35	β_i	H-C-H	H13-C12-H14, H13-C12-H15, H14-C12-H15
36-37	β_i	C-C-O	C1-C7-O8, C1-C7-O9
38	β_i	C-O-H	C7-O9-H10
39-40	β_i	C-C-O	C1-C2-O11, C3-C2-O11
41	β_i	C-O-C	C2-O11-C12
42-47	β_i	C-C-C (Ring)	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
Out-of-plane bending			
48-51	ω_i	C-H	H16-C3-C2-C4, H17-C4-C5-C3, H18-C5-C6-C4, H19-C6-C1-C5
52	ω_i	C-C	C7-C1-C6-C2
53	ω_i	C-O	O11-C2-C1-C3
Torsion			
54-55	τ_i	C-O	C2-C1-C7-O8, C2-C1-C7-O9
56-57	τ_i	C-O-C	C1-C2-O11-C12, C3-C2-O11-C12
58-60	τ_i	C-H(methyl)	C2-O11-C12-H13, C2-O11-C12-H14, C2-O11-C12-H15
61	τ_i	O-H	C1-C7-O9-H10
62-67	τ_i	tring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3

For numbering of atoms refer to Figure 1(a).

observed in the IR region are very sharp, broad, and less intense. The title compounds belong to C_s point group. The 19 atoms present in OAA and AA molecular structure, each has 51 fundamental modes of vibrations. For molecules of C_s symmetry, group theory analysis indicates that the 51 fundamental vibrations are distributed among the symmetry species as

$$\Gamma_{\text{vib}} = 35A' (\text{in-plane}) + 16A'' (\text{out-of-plane}) \quad (5)$$

for both OAA and AA, respectively. From the structural point of view of the molecules, OAA and AA have 18 stretching vibrations 33 bending vibrations, respectively. All the vibrations were found to be active both in Raman scattering and infrared absorption.

The observed and calculated wave numbers, calculated IR and Raman intensities, and normal mode descriptions (characterized by potential energy distribution (PED)) for

the fundamental vibrations of OAA and AA are depicted in Tables 7 and 8. For visual comparison, the observed and simulated FTIR and FT-Raman spectra of the compounds are presented in Figures 2, 3, 4, and 5, which help to understand the observed spectral features. The root mean square (RMS) error of the observed and calculated wavenumbers (unscaled/B3LYP/6-31G**) of OAA and AA was found to be 84.3 cm^{-1} and 89.1 cm^{-1} , respectively. This is understandable since the mechanical force fields usually differ appreciably from the observed ones. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. However for reliable information on the vibrational properties, the use of selective scaling is necessary. The calculated wavenumbers are scaled using the set of transferable scale factors recommended by Fogarasi and Pulay [7]. The SQM treatment has resulted in an RMS deviation of 9.67 cm^{-1} and 11.3 cm^{-1} for OAA and AA,

TABLE 3: Definition of internal coordinates of Anisic acid (AA).

No. (i)	Symbol	Type	Definition
Stretching			
1-4	r_i	C-H	C2-H11, C3-H12, C5-H18, C6-H19
5-10	r_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1
11	r_i	C-Cfn	C1-C7
12-14	r_i	C-O	C7-O8, C7-O9, C4-O13
15	r_i	O-C	O13-C14
16	r_i	O-H	O9-H10
17-19	r_i	C-H(methyl)	C14-H15, C14-H16, C14-H17
Bending			
20-21	β_i	C-C	C2-C1-C7, C6-C1-C7
22-29	β_i	C-C-H	C1-C2-H11, C3-C2-H11, C2-C3-H12, C4-C3-H12, C4-C5-H18, C6-C5-H18, C5-C6-H19, C1-C6-H19
30-35	β_i	C-C-H(methyl)	O13-C14-H15, O13-C14-H16, O13-C14-H17, H17-C14-H15, H15-C14-H16, H17-C14-H16
36-37	β_i	C-C-O	C3-C4-O13, C5-C4-O13
38	β_i	C-O-H	C7-O9-H10
39-40	β_i	C-C-O	C1-C7-O8, C1-C7-O9
41	β_i	C-O-C	C4-O13-C14
42-47	β_i	C-C-C (Ring)	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
Out-of-plane bending			
48-51	ω_i	C-H	H11-C2-C3-C1, H12-C3-C4-C2, H18-C5-C6-C4, H19-C6-C1-C5
52	ω_i	C-C	C7-C1-C6-C2
53	ω_i	C-O	O13-C4-C5-C3
Torsion			
54-55	τ_i	C-O	C2-C1-C7-O8, C2-C1-C7-O9
56-57	τ_i	C-O-C	C3-C4-O13-C14, C5-C4-O13-C14
58-60	τ_i	C-H(methyl)	C4-O13-C14-H15, C4-O13-C14-H16, C4-O13-C14-H17
61	τ_i	O-H	C1-C7-O9-H10
62-67	τ_i	tring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3

For numbering of atoms refer to Figure 1(b).

respectively. The RMS values of wavenumbers were obtained in this study using the following expression

$$\text{RMS} = \sqrt{\frac{1}{n-1} \sum_i^n (v_i^{\text{calc}} - v_i^{\text{exp}})^2}. \quad (6)$$

4.3.1. CH Vibrations. Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm⁻¹ [26] due to aromatic C-H stretching vibrations. According to the PED analysis, the bands observed in experimental spectrum at 3098, 3083, 3069, 3020 cm⁻¹ in OAA and 3085, 3034, 3029, and 3002 cm⁻¹ in AA were assigned to stretching vibrations of

C-H bond. According to these studies, all the C-H stretching vibrations are not mixed with other types of vibrations.

The C-H in-plane deformation vibrations are assigned in the region 1100–1400 cm⁻¹ [27]. The in-plane deformations of C-H groups are noticed on PED analysis at 1494, 1439, 1288, and 1182 in OAA and 1518, 1301, 1181 and 1131 cm⁻¹ in AA. There is slight increase in the C-H in-plane deformation frequency because of steric effect in OAA and inductive effect (+I) in AA. These values of calculated frequencies are typical and in very good agreement with experimental data. The in-plane C-H deformation vibrations are slightly mixed in both OAA and AA.

The C-H out-of-plane deformation vibrations are assigned in the region 900–600 cm⁻¹ [26]. The bands

TABLE 4: Definition of natural internal coordinates of O-Anisic acid (OAA).

No. (i)	Symbol ^a	Definition ^b
1-4	C-H stretch	r_1, r_2, r_3, r_4
5-11	C-C stretch	$r_5, r_6, r_7, r_8, r_9, r_{10}, r_{11}$
12-14	C-O stretch	r_{12}, r_{13}, r_{14}
15	O-C stretch	r_{15}
16	O-H stretch	r_{16}
17	CH ₃ ss	$(r_{17} + r_{18} + r_{19}) / \sqrt{3}$
18	CH ₃ ips	$(2r_{17} - r_{18} - r_{19}) / \sqrt{6}$
19	CH ₃ ops	$(r_{18} - r_{19}) / \sqrt{2}$
20	bC-C-C	$(\beta_{20} - \beta_{21}) / \sqrt{2}$
21-24	bC-C-H	$(\beta_{22} - \beta_{23}) / \sqrt{2}, (\beta_{24} - \beta_{25}) / \sqrt{2}, (\beta_{26} - \beta_{27}) / \sqrt{2}, (\beta_{28} - \beta_{29}) / \sqrt{2}$
25	CH ₃ sb	$(-\beta_{30} - \beta_{31} - \beta_{32} + \beta_{33} + \beta_{34} + \beta_{35}) / \sqrt{6}$
26	CH ₃ ipb	$(-\beta_{33} - \beta_{34} - 2\beta_{35}) / \sqrt{6}$
27	CH ₃ opb	$(\beta_{33} - \beta_{34}) / \sqrt{2}$
28	CH ₃ ipr	$(2\beta_{30} - \beta_{31} - \beta_{32}) / \sqrt{6}$
29	CH ₃ opr	$(\beta_{31} - \beta_{32}) / \sqrt{2}$
30	bC-C-O	$(\beta_{36} - \beta_{37}) / \sqrt{2}$
31	bC-O-H	β_{38}
32-33	bC-C-O	β_{39}, β_{40}
34	bC-O-C	β_{41}
35	Rtrigd	$(\beta_{42} - \beta_{43} + \beta_{44} - \beta_{45} + \beta_{46} - \beta_{47}) / \sqrt{6}$
36	Rsymd	$(-\beta_{42} - \beta_{43} + \beta_{44} - \beta_{45} - \beta_{46} + 2\beta_{47}) / \sqrt{12}$
37	Rasymd	$(\beta_{42} - \beta_{43} + \beta_{45} - \beta_{46}) / 2$
38-41	ω C-H	$\omega_{48}, \omega_{49}, \omega_{50}, \omega_{51}$
42	ω C-C	ω_{52}
43	ω C-O	ω_{53}
44-45	tC-O	τ_{54}, τ_{55}
46	tC-O-C	$1/2 (\tau_{56} + \tau_{57})$
47	tCH ₃	$1/3 (\tau_{58} + \tau_{59} + \tau_{60})$
48	tO-H	τ_{61}
49	Ttrigd	$(\tau_{62} - \tau_{63} + \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67}) / \sqrt{6}$
50	Tsymd	$(\tau_{62} - \tau_{63} + \tau_{65} + \tau_{66}) / 2$
51	Tasymd	$(-\tau_{62} + 2\tau_{63} - \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67}) / \sqrt{12}$

^aThese symbols are used for description of the normal modes by PED in Table 7.

^bThe internal coordinates used here are defined in Table 2.

appearing at 960, 937, 865, and 755 cm⁻¹ in OAA and 929, 854, 846, and 774 cm⁻¹ in AA were assigned to out-of-plane deformation type of vibration (ω) of C-H groups. There is slight increase in the C-H out-of-plane deformation frequency because of strong intermolecular hydrogen bonding in OAA. In these bands, the pronounced participation of other types of vibrations is observed. These are also supported by the literature.

4.3.2. Carboxylic Acid Vibrations. Due to the presence of strong intermolecular hydrogen bonding, the FT-IR spectra exhibits spectra exhibit a broad band due to the O-H stretching vibrations and a strong band due to C=O stretching vibrations. The carboxylic acid dimers display a very broad and intense O-H stretching absorption in the region of 3300–2500 cm⁻¹ [28]. The title molecules both exhibit intermolecular hydrogen bonding. In our case, the bands at 3390 cm⁻¹

in OAA and 3435 cm⁻¹ in AA are assigned as O-H stretching vibrations. There is a slight increase in the O-H frequency because of steric effect in OAA and +I effect in AA. The O-H out-of-plane bending vibration occurs near the region of 920 cm⁻¹ [27]. The bands appearing at 595 cm⁻¹ in OAA and 505 cm⁻¹ in AA are assigned to O-H out-of-plane bending vibration. The O-H out-of-plane bending vibrations in OAA and AA decrease due to intermolecular hydrogen bonding.

The carbonyl stretching vibrations are expected in the region 1720 cm⁻¹–1680 cm⁻¹ [28]. The IR band at 1670 cm⁻¹ in OAA and FT-Raman band at 1688 cm⁻¹ in AA are assigned as C=O stretching vibrations. The C-O bond appears strongly in the 1320–1210 cm⁻¹ region [29]. The bands observed at 1049, and 795 cm⁻¹ in OAA and 1267, and 1100 cm⁻¹ in AA are assigned to C-O stretching mode. The C-O stretching vibrational frequency is lower than general range. In the case of carboxylic acid dimers like OAA and AA, the OH

TABLE 5: Definition of natural internal coordinates of Anisic acid (AA).

No. (i)	Symbol ^a	Definition ^b
1–4	C–H stretch	r_1, r_2, r_3, r_4
5–10	C–C stretch	$r_5, r_6, r_7, r_8, r_9, r_{10}$
11	C–Cfn stretch	r_{11}
12–14	C–O stretch	r_{12}, r_{13}, r_{14}
15	O–C stretch	r_{15}
16	O–H stretch	r_{16}
17	CH ₃ ss	$(r_{17} + r_{18} + r_{19}) / \sqrt{3}$
18	CH ₃ ips	$(2r_{17} - r_{18} - r_{19}) / \sqrt{6}$
19	CH ₃ ops	$(r_{18} - r_{19}) / \sqrt{2}$
20	bC–C–C	$(\beta_{20} - \beta_{21}) / \sqrt{2}$
21–24	bC–C–H	$(\beta_{22} - \beta_{23}) / \sqrt{2}, (\beta_{24} - \beta_{25}) / \sqrt{2}, (\beta_{26} - \beta_{27}) / \sqrt{2}, (\beta_{28} - \beta_{29}) / \sqrt{2}$
25	CH ₃ sb	$(-\beta_{30} - \beta_{31} - \beta_{32} + \beta_{33} + \beta_{34} + \beta_{35}) / \sqrt{6}$
26	CH ₃ ipb	$(-\beta_{33} - \beta_{34} - 2\beta_{35}) / \sqrt{6}$
27	CH ₃ opb	$(\beta_{33} - \beta_{34}) / \sqrt{2}$
28	CH ₃ ipr	$(2\beta_{30} - \beta_{31} - \beta_{32}) / \sqrt{6}$
29	CH ₃ opr	$(\beta_{31} - \beta_{32}) / \sqrt{2}$
30	bC–C–O	$(\beta_{35} - \beta_{36}) / \sqrt{2}$
31	bC–O–H	β_{38}
32–33	bC–C–O	β_{39}, β_{40}
34	bC–O–C	β_{41}
35	Rtrigd	$(\beta_{42} - \beta_{43} + \beta_{44} - \beta_{45} + \beta_{46} - \beta_{47}) / \sqrt{6}$
36	Rsymd	$(-\beta_{42} - \beta_{43} + \beta_{44} - \beta_{45} - \beta_{46} + 2\beta_{47}) / \sqrt{12}$
37	Rasymd	$(\beta_{42} - \beta_{43} + \beta_{45} - \beta_{46}) / 2$
38–41	ω C–H	$\omega_{48}, \omega_{49}, \omega_{50}, \omega_{51}$
42	ω C–C	ω_{52}
43	ω C–O	ω_{53}
44–45	tC–O	τ_{54}, τ_{55}
46	tC–O–C	$1/2 (\tau_{56} + \tau_{57})$
47	tCH ₃	$1/3 (\tau_{58} + \tau_{59} + \tau_{60})$
48	tO–H	τ_{61}
49	Ttrigd	$(\tau_{62} - \tau_{63} + \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67}) / \sqrt{6}$
50	Tsymd	$(\tau_{62} - \tau_{63} + \tau_{65} + \tau_{66}) / 2$
51	Tasymd	$(-\tau_{62} + 2\tau_{63} - \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67}) / \sqrt{12}$

^aThese symbols are used for description of the normal modes by PED in Table 8.

^bThe internal coordinates used here are defined in Table 3.

in-plane bending and C–O stretching bands involve some interaction between them, they are referred to as coupled OH in-plane bending and C–O stretching vibrations [26]. The C–O bending vibration occurs in the region of 580–340 cm^{−1} [30]. The band observed at 380 cm^{−1} in OAA and 440 cm^{−1} in AA are assigned to C–O bending mode. The present assignments agree very well with the values available in the literature.

4.3.3. Methyl Group Vibrations. The title molecules OAA and AA under consideration possess one CH₃ group. For the assignments of CH₃ group one can expect that 9 fundamentals can be associated with each CH₃ group, namely, the symmetrical stretching (CH₃ symmetric stretch) and asymmetrical stretching (CH₃ asymmetric stretch), in-plane stretching modes (i.e., in-plane hydrogen stretching modes),

and the symmetrical (CH₃ symmetric deform) and asymmetrical (CH₃ asymmetric deform) deformation modes; in-plane rocking (CH₃ ipr), out-of-plane rocking (CH₃ opr), and twisting (tCH₃) bending modes.

For the methyl group compounds, the asymmetric stretching mode appeared in the range 2965–3005 cm^{−1}, and the symmetric stretching mode appeared in the range of 2815–2860 cm^{−1} [30]. The FT-Raman band at 2983 cm^{−1} for OAA, and IR band at 2941 cm^{−1} for AA are symmetric stretching. The symmetric stretching vibrational frequency is higher in OAA and AA due to steric effect and +I effect. The asymmetric methyl stretching band appeared at 3003, 3018 cm^{−1} in OAA and 2990, 2956 cm^{−1} in AA, respectively. The asymmetric deformation mode appeared in the range 1445–1485 cm^{−1} and symmetric deformation mode appeared in the range of 1420–1460 cm^{−1} [30]. The IR band at 1466,

FIGURE 2: FTIR spectra of O-Anisic acid (a) observed and (b) calculated with B3LYP/6-31G**.

TABLE 6: Diagonal force constants (10^2 Nm^{-1}) of O-Anisic acid (OAA) and Anisic acid (AA).

Description ^a	Force constants ^b	
	OAA	AA
C1-C2	6.21	6.30
C2-C3	6.33	6.96
C3-C4	6.77	6.26
C4-C5	6.75	6.28
C5-C6	6.82	6.63
C6-C1	6.44	6.48
C1-C7	4.65	2.22
C7-O8	5.32	5.22
C7-O9	10.30	11.28
C2-O11(C4-O13)	4.49	5.76
O11-C12(O13-C14)	4.13	4.99
O9-H10	6.44	6.61
C12-H13(C14-H15)	4.98	5.08
C12-H14(C14-H16)	5.26	4.70
C12-H15(C14-H17)	4.98	5.07
C3-H16(C2-H11)	5.14	4.98
C4-H17(C3-H12)	5.01	4.96
C5-H18	5.05	5.00
C6-H19	5.32	5.22

^aThe atoms indicated in the parenthesis belong to AA.

^bStretching force constants are given in $\text{mdyn } \text{\AA}^{-1}$.

For numbering of atoms refer to Figures 1(a) and 1(b).

and 1435 cm^{-1} in OAA and 1468 , and 1461 cm^{-1} in AA are assigned as asymmetric deformation vibrations. The IR band at 1411 cm^{-1} for OAA and 1429 cm^{-1} for AA are symmetric deformation mode. The CH_3 deformation absorption occurs at 1466 cm^{-1} and 1429 cm^{-1} ; this vibration is known as umbrella mode that overlaps with CC ring stretching vibrations for the title compounds. These are also supported by the literature.

The tensional modes appeared in the range of 265 – 185 cm^{-1} [30]. This modes are strongly coupled with other

vibrations that are observed at 280 cm^{-1} in OAA and 165 cm^{-1} in AA which are in agreement with the calculated results also.

4.3.4. Ring Vibrations. The ring C–C stretching vibrations occur in the region of 1600 – 1400 cm^{-1} [29]. The bands appear at 1600 , 1579 , 1312 , 1184 , 1153 , 1062 , and 698 cm^{-1} in OAA and 1608 , 1580 , 1416 , 1307 , 1107 , 1028 , and 825 cm^{-1} in AA were assigned to C–C stretching vibrations. The shift in the frequency of C–C vibrations towards lower wave number may be due to the COOH and OCH_3 groups. Many ring modes are affected by the substitutions in the aromatic ring. The bands at 180 cm^{-1} and 285 cm^{-1} for OAA and AA were assigned to C–C bending vibrations. The out-of-plane and in-plane deformations of the phenyl ring are observed below 1000 cm^{-1} , and these modes are sensitive by the addition of functional groups. The out-of-plane bending vibrations were observed at 170 cm^{-1} and 111 cm^{-1} for OAA and AA. Small changes in the wavenumbers were observed due to the presence of +I effect in AA and steric effect in OAA. The computed wavenumbers are in good agreement with experimental data.

5. Electronic Properties

Atomic charges on the various atoms of OAA and AA obtained by Mulliken population analysis [31] are given in Table 9. From the listed atomic charge values, the oxygen [O8, O9] and O11 in OAA and O13 in AA atoms had a large negative charge and behaved as electron acceptor. It was also observed that there is a large accumulation of charge on O11 in OAA, O13 in AA molecules. Therefore, C7 and O11 in OAA and C7 and O13 in AA had a greater ionic character.

Natural bond orbital analysis provides an efficient method for studying steric effect and intermolecular bonding and interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Natural charge analysis is given in Table 10 for the title compounds. The results show that substitution of COOH and CH_3 group in OAA and AA leads to a redistribution of electron density. The C7 atom in OAA and AA is more positive charge ($+0.8091$, $+0.8139$). In the

TABLE 7: Detailed assignment of fundamental vibrations of O-Anisic acid (OAA) by normal mode analysis based on SQM force field calculations.

Sl. no.	Symmetry species C_s	Observed wavenumbers cm^{-1}		Calculated wavenumbers B3LYP/6-31G** force field cm^{-1}		IR intensity	Raman activity	Characterization of normal modes with PED (%)
		FTIR	Raman	Unscaled	Scaled			
1	A'	3390	—	3771	3390	72.652	155.385	νOH (100)
2	A'	—	3098	3273	3098	16.124	99.564	νCH (99)
3	A'	—	3083	3233	3083	1.700	135.114	νCH (99)
4	A'	3069	—	3207	3069	10.674	70.382	νCH (99)
5	A'	—	3020	3186	3024	17.253	137.201	νCH (99)
6	A'	3018	—	3157	3018	38.987	58.202	νCH_3 (99)
7	A''	3003	—	3085	3003	5.946	78.409	νCH_3 (99)
8	A'	—	2983	3020	2983	52.626	120.657	νCH_3 (99)
9	A'	1670	—	1822	1670	358.567	54.628	νCO (53), νCC (14), bCCO (14), bCOH (12)
10	A'	1600	—	1656	1600	15.061	16.343	νCC (60), bCH (20), Rasynd (10)
11	A'	1579	—	1630	1579	61.364	48.880	νCC (69), bCH (19)
12	A'	1494	—	1539	1494	58.214	10.686	bCH (48), νCC (37)
13	A'	1466	—	1513	1466	6.534	6.058	bCH ₃ (43), bCH (25), νCC (16)
14	A'	—	1439	1506	1439	22.318	5.639	bCH (39), bCH ₃ (37), νCC (17)
15	A''	1435	—	1500	1435	36.525	10.814	bCH ₃ (88)
16	A'	1411	—	1475	1411	11.849	19.713	bCH ₃ (74)
17	A'	—	—	1382	1367	4.497	1.268	bCOH (35), νCO (32), bCCO (13), νCC (11)
18	A'	—	1312	1350	1312	2.182	8.877	νCC (67)
19	A'	1288	—	1320	1288	63.194	1.648	bCH (33), Rtrigd (20), νCO (13), νCC (12)
20	A'	—	1287	1302	1287	19.694	0.449	Rtrigd (26), νCC (25), bCH (20), νCO (12)
21	A'	—	1184	1210	1184	228.252	32.980	νCC (31), bCH (19), bCH ₃ (17), νCO (17)
22	A'	1182	—	1201	1182	162.989	27.136	bCH (42), νCC (34), bCH ₃ (10)
23	A'	1170	—	1193	1170	1.576	4.576	bCH ₃ (57), bCH (24)
24	A'	—	1173	1173	1153	7.419	1.097	νCC (31), bCH (29), bCH ₃ (25)
25	A'	1140	—	1168	1140	0.662	4.253	bCH ₃ (96)
26	A'	1049	—	1087	1050	107.304	7.809	νCO (29), νCC (27), Rtrigd (12)
27	A'	—	1062	1077	1060	104.848	21.650	νCC (41), νCO (22), bCH (12)
28	A''	960	—	1060	960	0.609	0.057	ωCH (91)
29	A'	—	974	989	974	207.871	0.836	νOC (62), νCC (12), νCO (11)
30	A''	937	—	965	935	1.244	1.294	ωCH (91)
31	A''	—	865	869	865	3.148	3.432	ωCH (64), ttrigd (19)
32	A'	—	795	830	795	12.200	4.238	νCO (29), Rasynd (21), νOC (15), νCC (15)
33	A''	761	—	795	761	1.002	0.207	tCO (32), ttrigd (28), ωCH (23), ωCC (11)
34	A''	—	755	770	755	41.473	1.456	ωCH (51), ttrigd (27), ωCO (14)
35	A''	695	—	747	698	64.512	0.469	ttrigd (52), ωCH (23), tCO (15)
36	A'	—	698	712	695	10.016	17.946	νCC (33), νCO (23), bCCO (21)
37	A'	—	602	639	602	13.503	2.683	Rasynd (36), bCCO (15), νCC (12), Rasynd (11)
38	A''	—	595	594	595	74.804	8.168	tOH (79)
39	A'	—	565	588	565	21.902	1.740	bCCO (28), νCC (17), bCO (15), Rasynd (14), bCCO (13)

TABLE 7: Continued.

Sl. no.	Symmetry species C_s	Observed wavenumbers cm^{-1}		Calculated wavenumbers B3LYP/6-31G** force field cm^{-1}		IR intensity	Raman activity	Characterization of normal modes with PED (%)
		FTIR	Raman	Unscaled	Scaled			
40	A'	540	—	548	540	5.598	4.848	bCCO (40), bCC (16), ν CC (13), Rasynd (10)
41	A''	480	—	540	480	0.946	0.860	ω CO (40), ω CH (16), trigrd (14), tsym (14)
42	A''	—	401	435	401	3.585	0.792	tsym (14), ω CC (15)
43	A'	—	380	388	380	4.805	4.133	bCO (64), bCCO (16)
44	A'	—	303	383	303	1.180	4.980	Rsymd (59), bCOC (17), ν CC (15)
45	A''	—	280	283	280	0.092	0.016	tCH ₃ (79)
46	A'	—	240	280	240	0.927	0.935	bCOC (40), bCC (30), bCCO (18)
47	A''	—	180	229	180	0.018	2.096	ω CC (30), tCO (20), tsym (18) tsym (11) ω CH (10)
48	A'	—	170	190	170	3.092	0.715	bCC (42), bCOC (29), bCO (12)
49	A''	—	115	119	115	4.502	0.508	tCOC (47), tsym (15), tCH ₃ (12)
50	A''	—	110	96	96	0.922	3.779	tsym (35), tCO (25) tCOC (21), tCH ₃ (13)
51	A''	—	—	17	30	1.260	0.037	tCO (99)

R: ring; b: bending; deform: deformation; sym: symmetric; asy: asymmetric; ω : wagging; t: torsion; trig: trigonal; ν : stretching; ips: in-plane stretching; ipb: in-plane bending; ops: out-of-plane stretching; opb: out-of-plane bending; sb: symmetric bending; ipr: in-plane rocking; opr: out-of-plane rocking.
Only contributions larger than 10% are given.

TABLE 8: Detailed assignment of fundamental vibrations of Anisic acid (AA) by normal mode analysis based on SQM force field calculations.

Sl. no.	Symmetry species C_s	Observed wavenumbers cm^{-1}		Calculated wavenumbers B3LYP/6-31G** force field cm^{-1}		IR intensity	Raman activity	Characterization of normal modes with PED (%)
		FTIR	Raman	Unscaled	Scaled			
1	A'	3435	—	3768	3435	79.523	164.209	νOH (100)
2	A'	—	3085	3232	3085	21.438	120.058	νCH (89)
3	A'	—	3034	3224	3034	7.547	126.718	νCH (99)
4	A'	3029	—	3218	3029	3.520	99.229	νCH (99)
5	A'	3002	—	3209	3002	5.141	52.552	νCH (99)
6	A'	2990	—	3155	2990	2.423	53.071	νCHops (99)
7	A''	2956	—	3087	2956	45.319	94.074	νCHips (51), νCHss (36), νCHops (12)
8	A'	2941	—	3022	2941	42.847	91.231	νCHss (56), νCHips (44)
9	A'	1688	—	1813	1688	302.139	74.665	νCO (72), bCCO (17),
10	A'	1608	—	1666	1608	216.104	153.242	νCC (62), bCH (22), Rsymd (11)
11	A'	1580	—	1624	1580	34.785	12.359	νCC (66), bCH (14)
12	A'	1518	—	1559	1518	41.495	8.422	bCH (52), νCC (30)
13	A'	1468	—	1516	1468	37.550	10.673	bCHsb (77)
14	A''	1461	—	1504	1461	14.058	12.183	bCHopb (83)
15	A'	1429	—	1486	1429	5.851	19.586	bCHipb (70), νCC (10), bCH (10)
16	A'	1416	—	1465	1416	14.835	9.149	νCC (39), bCH (35), bCHipb (18)
17	A'	1324	—	1391	1324	31.290	5.311	bCOH (27), νCO (22), bCCO (21), νCC (13)
18	A'	1307	—	1371	1307	8.068	1.444	νCCar (65), bCH (20)
19	A'	1301	—	1331	1301	40.408	7.073	bCH (43), νCC (33)
20	A'	1267	—	1304	1267	245.222	3.723	νCO (37), Rtrigd (20), νCC (16)
21	A'	1181	—	1221	1181	5.734	6.023	bCH (61), νCC (21)
22	A'	1172	—	1209	1172	5.690	5.161	bCHopr (61), bCH (13)
23	A'	—	1137	1189	1137	0.662	4.334	bCHipr (78), bCHopr (14)
24	A'	1131	—	1176	1131	190.946	42.508	bCH (35), νCC (21)
25	A'	1107	—	1139	1107	245.972	63.024	νCCfn (25), Rtrigd (23), bCH (16), νOC (13)
26	A'	—	1100	1114	1100	318.070	20.809	νCO (40), bCOH (22), bCCO (11)
27	A'	1028	—	1069	1028	0.786	11.056	νCC (58), bCH (16)
28	A'	—	1010	1026	1010	29.566	2.343	νOC (51), νCC (28)
29	A''	929	—	991	929	0.010	0.464	ωCH (89)
30	A''	854	—	966	854	1.379	1.924	ωCH (82), ttrigd (12)
31	A''	846	—	863	846	36.522	1.244	ωCH (39), ωCO (32), ttrigd (20)
32	A'	825	—	834	825	24.090	22.373	νCCar (32), Rsymd (27), νOC (22)
33	A''	774	—	830	774	0.365	4.928	ωCH (84)
34	A''	—	755	775	755	1.082	0.243	ttrigd (51), ωCC (15), ωCH (14), tCO (11)
35	A'	698	—	725	698	35.539	3.075	bCCO (44), νCO (25), bCOH (25)
36	A''	634	—	710	634	76.887	0.059	tCO (57), ωCH (20), ttrigd (12)
37	A'	617	—	647	617	0.592	6.441	Rsymd (81)
38	A'	550	—	603	550	14.566	0.968	Rsymd (32), νCCfn (13), νCO (11), bCCO (11), bCOC (10)
39	A''	545	—	601	545	27.876	4.847	ωCO (42), tOH (14), ωCH (11), ωCC (11)

TABLE 8: Continued.

Sl. no.	Symmetry species C_s	Observed wavenumbers cm^{-1}		Calculated wavenumbers B3LYP/6-31G** force field cm^{-1}		IR intensity	Raman activity	Characterization of normal modes with PED (%)
		FTIR	Raman	Unscaled	Scaled			
40	A'	525	—	511	525	12.735	1.849	bCCO (82)
41	A'	505	—	511	505	50.036	5.698	tOH (24), ttrigd (23), ω CO (19), ω CH (14)
42	A'	440	—	481	440	3.190	2.294	bCO (35), bCOC (29)
43	A''	—	375	427	375	0.415	0.023	tsym (60), ω CH (19), tsym (17)
44	A'	—	310	335	310	3.569	0.577	Rsymd (48), ν CCfn (25)
45	A''	—	285	304	285	4.416	0.596	ω CC (33), tsym (24), tCO (16)
46	A'	—	220	267	220	3.713	2.509	bCOC (29), bCO (17)
47	A''	—	165	226	165	0.047	0.429	tCH ₃ (85)
48	A'	—	111	165	111	0.211	0.159	bCC (80)
49	A''	—	98	132	98	2.323	0.292	Tasym (30), tCOC (30), ω CC (11), ω CH (10), tsym (10)
50	A''	—	70	78	70	1.302	1.199	tCO (95)
51	A''	—	60	65	60	0.898	0.216	tCOC (48), tCO (31), tCH ₃ (12)

R: ring; b: bending; deform: deformation; sym: symmetric; asy: asymmetric; ω : wagging; t: torsion; trig: trigonal; ν : stretching; ips: in-plane stretching; ipb: in-plane bending; ops: out-of-plane stretching; opb: out-of-plane bending; sb: symmetric bending; ipr: in-plane rocking; opr: out-of-plane rocking.
Only contributions larger than 10% are given.

FIGURE 3: FT-Raman spectra of O-Anisic acid (a) observed and (b) calculated with B3LYP/6-31G**.

FIGURE 4: FTIR spectra of Anisic acid (a) observed and (b) calculated with B3LYP/6-31G**.

FIGURE 5: FT-Raman spectra of Anisic acid (a) observed and (b) calculated with B3LYP/6-31G**.

title molecules, all the hydrogen atoms have a net positive charge, in particular, the hydrogen atoms H(10) that have charge of 0.5047 and 0.5050, respectively. The presence of large amounts of negative charge on oxygen and net positive charge on H(10) atoms may suggest the presence of inter-molecular hydrogen bonding in the crystalline phase.

Highest occupied molecular orbital and lowest unoccupied molecular orbital are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in π -electron systems and also explains several types of reaction in conjugated system [32]. The conjugated molecules are

characterized by a small highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) separation, which is the result of a significant degree of inter-molecular charge transfer from the end-capping electron-donating groups to the efficient electron-acceptor groups through π conjugated path [33]. Both the highest occupied molecular orbital and lowest unoccupied molecular orbital are the main orbitals that take part in chemical stability [34]. Energy difference between HOMO and LUMO orbital is called energy gap that is an important stability for structures which are given in Table II. We performed an analysis of all the molecular orbitals involved, taking into consideration

TABLE 9: Atomic charges for optimized geometry of O-Anisic acid (OAA) and Anisic acid (AA) obtained by B3LYP/6-31G** density functional calculations.

Atoms ^a	Mulliken	
	OAA	AA
C ₁	0.0018	0.0373
C ₂	0.3297	-0.1002
C ₃	-0.1368	-0.1219
C ₄	-0.0836	0.3612
C ₅	-0.0943	-0.1394
C ₆	-0.1061	-0.1118
C ₇	0.5570	0.5445
O ₈	-0.4650	-0.4848
O ₉	-0.5104	-0.5064
H ₁₀	0.3198	0.3217
O ₁₁ (H ₁₁)	-0.4841	0.1203
C ₁₂ (H ₁₂)	-0.0837	0.1021
H ₁₃ (O ₁₃)	0.1064	-0.5111
H ₁₄ (C ₁₄)	0.1352	-0.0831
H ₁₅	0.1211	0.1099
H ₁₆	0.0913	0.1302
H ₁₇	0.0929	0.1246
H ₁₈	0.0886	0.0913
H ₁₉	0.1200	0.1155

^aThe atoms indicated in the parenthesis belong to AA.

TABLE 10: Natural atomic charges of O-Anisic acid (OAA) and Anisic acid (AA) calculations performed at the B3LYP/6-31G** level of theory.

Atoms ^a	OAA	AA
C ₁	-0.2176	-0.2053
C ₂	0.3724	-0.1746
C ₃	-0.3284	-0.2801
C ₄	-0.1952	0.3443
C ₅	-0.2720	-0.3289
C ₆	-0.1806	-0.1748
C ₇	0.8091	0.8139
O ₈	-0.5861	-0.6102
O ₉	-0.7295	-0.7217
H ₁₀	0.5047	0.5050
O ₁₁ (H ₁₁)	-0.4921	0.2634
C ₁₂ (H ₁₂)	-0.3307	0.2544
H ₁₃ (O ₁₃)	0.2070	-0.5119
H ₁₄ (C ₁₄)	0.2390	-0.3300
H ₁₅	0.2070	0.2090
H ₁₆	0.2443	0.2352
H ₁₇	0.2426	0.2090
H ₁₈	0.2439	0.2449
H ₁₉	0.2621	0.2585

^aThe atoms indicated in the parenthesis belong to AA.
For numbering of atoms refer to Figures 1(a) and 1(b).

that orbital 40 is the HOMO and orbital 41 is the LUMO for OAA and AA, respectively.

Many organic molecules that contain conjugated π electrons are characterized as hyperpolarisabilities and are analyzed by means of vibrational spectroscopy. The analysis

TABLE 11: Calculated quantum chemical parameters of O-Anisic acid (OAA) and Anisic acid (AA) derivatives.

Parameters	OAA	AA
E_{HOMO}	-0.227	-0.231
E_{LUMO}	-0.041	-0.036
ΔE	0.186	0.195
χ	0.134	0.133
H	0.093	0.097
Σ	10.752	10.256

TABLE 12: Calculated ^{13}C NMR chemical shifts (ppm) of O-Anisic acid (OAA) and Anisic acid (AA).

Carbon ^a	Exp		B3LYP/6-31G**	
	OAA	AA	OAA	AA
C ₁	117.82	123.15	104.47	126.20
C ₂	158.48	131.46	146.96	139.36
C ₃	112.04	113.84	96.81	122.72
C ₄	135.17	162.97	119.26	171.25
C ₅	121.91	113.84	104.47	110.47
C ₆	133.47	131.46	120.19	137.51
C ₇	166.34	167.14	146.09	171.74
C ₁₂ (C ₁₄)	56.74	55.44	43.22	55.49

^aThe atoms indicated in the parenthesis belong to AA.

TABLE 13: Experimental and calculated ^1H NMR chemical shifts (ppm) of O-Anisic acid (OAA) and Anisic acid (AA).

Proton ^a	Exp		B3LYP/6-31G**	
	OAA	AA	OAA	AA
H ₁₀	10.30	13	11	11
H ₁₃ , H ₁₄ , H ₁₅ (H ₁₁)	4.066	7.914	3.932	8.405
H ₁₆ (H ₁₂)	7.08	7.027	6.831	7.147
H ₁₇ (H ₁₅ , H ₁₆ , H ₁₇)	7.56	3.836	7.570	3.824
H ₁₈	7.10	7.027	7.069	6.673
H ₁₉	8.13	7.914	3.932	8.217

^aThe atoms indicated in the parenthesis belong to AA.

of the wave function indicates that the electron absorption corresponds to the transition from the ground state to the first excited state and is mainly described by the one-electron excitation from the HOMO to the LUMO. The HOMO, of π nature (i.e., aromatic ring), is delocalized over the whole C-C bond. By contrast, the LUMO is located over the aromatic ring. Consequently, the HOMO-LUMO transition implies an electron density transfer to COOH and OCH₃ group from the aromatic ring.

The theoretical basis for the new quantities lies in the density functional formalism [35]. Since molecular orbital (MO) theory is by far the most widely used by chemists, it is important to place χ and η in a MO framework. It has already been shown [36] that the MO theory of the chemical bond contains the values of χ and η for the bonding fragments. Hard molecules have a large HOMO-LUMO gap, and soft molecules have a small HOMO-LUMO gap. A small

FIGURE 6: Contour surfaces of frontier molecular orbitals of O-Anisic acid.

FIGURE 7: Contour surfaces of frontier molecular orbitals of Anisic acid.

HOMO-LUMO gap automatically means small excitation energies to the manifold of excited states. Therefore, soft molecules, with a small gap, will be more polarizable than hard molecules. High polarizability was the most characteristic property attributed to soft acids and bases. Energy gaps should be small for best bonding, or both molecules should be soft.

In the present study, the title compound AA is dynamically more stable due to the large energy gap. OAA is a soft molecule due to small energy gap. The Contour surfaces of the frontier molecular orbitals are sketched in Figures 6 and 7.

5.1. NMR Spectra. DFT methods treat the electronic energy as a function of the electron density of all electrons simultaneously and thus include electron correlation effect [37]. In this study, molecular structure of the OAA and AA was optimized by using B3LYP method in conjunction with 6-31G**. ^{13}C and ^1H chemical shift calculations of the title compounds have been made by using GIAO method and same basis set. The isotropic shielding values were used to calculate the isotropic chemical shifts δ with respect to tetramethylsilane (TMS). The isotropic chemical shifts are frequently used as an aid in identification of reactive ionic species. The B3LYP method allows calculating the shielding

FIGURE 8: Plot of the calculated versus the experimental ^{13}C NMR and ^1H NMR chemical shifts (ppm) for O-Anisic acid.

constants with the proper accuracy, and the GIAO method is one of the most common approaches for calculating nuclear magnetic shielding tensors.

Theoretical and experimental chemical shifts of OAA and AA in ^1H and ^{13}C NMR spectra are gathered in Tables 12 and 13. The range of the ^{13}C NMR chemical shifts for a typical organic molecules usually is >100 ppm [38, 39] and the accuracy ensures reliable interpretation of spectroscopic parameters. In the present study, the ^{13}C NMR chemical shifts in the ring are >100 ppm, as they would be expected. The ^{13}C chemical shifts carbonyl carbons vary from 150 to 220 ppm. This depends on the decrease in electron donating or shielding ability of the attached atoms [40]. The $\text{C}=\text{O}$ groups of carboxylic acids and derivatives are in the range of 150–185 ppm [29].

Hydrogens bonded to an aromatic ring are strongly deshielded and absorb downfield. When the π -electrons enter the magnetic field, they circulate around the ring to generate a ring current. This produces a small induced magnetic field that reinforces the applied field outside the ring, resulting in aromatic protons being deshielded [41]. A related effect is observed for carboxylic acids. For these compounds, circulation of electrons in the double bonds produces induced magnetic field. These are responsible for the high chemical shift values of acid protons (H10). Carboxylic acids as stable hydrogen-bonded dimers in nonpolar solvents even at high dilution. The carboxylic proton therefore absorbs in a characteristically narrow range, 13.2 to 10.0 and is affected only slightly by concentration [29].

In a methyl group, a proton is covalently bonded to carbon, oxygen, or other atoms by a sigma bond. When placed in a strong magnetic field, the electrons of the sigma bond circulate to generate a small magnetic field which opposes the applied field. A nearby electronegative atom withdraws electron density from the neighbourhood of the proton, so that a smaller applied field is needed to cause the spin state of the proton to flip. The signal for a deshielded

TABLE 14: Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies ($\text{cal mol}^{-1} \text{K}^{-1}$), nuclear repulsion energy (Hartrees), and dipole moment (Debye) for OAA and AA.

Parameters	B3LYP/6-31G**	
	OAA	AA
Zero-point energy	93.06056	93.14966
	1.39942	3.44405
Rotational constants	1.14384	0.56752
	0.63193	0.48875
Entropy		
Total	99.243	97.126
Translational	40.967	40.967
Rotational	30.142	30.199
Vibrational	28.134	25.960
Dipole moment	2.4181	3.5822
Nuclear repulsion energy	592.968293	573.992628

proton (1 surrounded by less electron density) is observed to be more downfield than the signals for protons that are not deshielded by electronegative atoms [40]. The chemical shift value of C7 (OAA and AA) has bigger value than the other carbons due to the electronegative property of oxygen atom.

The linear correlations between calculated and experimental data of ^{13}C NMR and ^1H NMR spectra are determined as 0.9, and 1.0 for OAA and 0.9, and 0.9 for AA, respectively. There is an excellent linear relationship between experimental and computed results which are shown in Figures 8 and 9.

6. Thermodynamic Properties

Several calculated thermodynamical parameters are presented in Table 14 for OAA and AA, respectively. Scale factors have been recommended [42] for an accurate prediction in

FIGURE 9: Plot of the calculated versus the experimental ^{13}C NMR and ^1H NMR chemical shifts (ppm) for Anisic acid.

determining the zero-point vibration energies (ZPVE) and the entropy $S_{\text{vib}}(T)$. The total energies and the change in the total entropy at room temperature using B3LYP/6-31G** method are presented.

7. Conclusion

Attempts have been made in the present work for the molecular parameters and frequency assignments for the compounds OAA and AA from the FTIR and FT-Raman spectra. The equilibrium geometries and harmonic and anharmonic frequencies for the title compounds were determined and analyzed at DFT level of theory utilizing 6-31G** basis set. The assignments of most of the fundamentals of the title compounds provided in this work are quite comparable. The excellent agreement of the calculated and observed vibrational spectra reveals the advantages of a smaller basis set for quantum chemical calculations. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The experimental and theoretical investigation of the title compounds have been performed successfully by using ^1H and ^{13}C NMR. The various modes of vibrations were unambiguously assigned on the basis of the result of the PED output obtained from normal coordinate analysis. These studies confirm the presence of COOH and OCH_3 group. Dimeric molecules are held together by hydrogen bridges between carbonyl groups. The obtained data and simulations both show the way to the characterization of the molecules and help in spectra studies in the future.

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