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A Study in Naturally Occurring Organic Compound of Guaiacol by ab initio DFT Calculations, Molecular Structure, Chemical Shielding Anisotropy and Other Molecular Parameters

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ABSTRACT

The FT-Raman and FT-Infrared spectra of Guaiacol have been recorded in the regions $3500-100 \text{ cm}^{-1}$ and $4000-500 \text{ cm}^{-1}$ respectively. The observed frequencies were assigned to various modes of vibrations on the basis of normal coordinate calculations, assuming C1 point group symmetry. The assignment of fundamental vibrations agrees well with the calculated frequencies. Second order perturbation energies and electron density (ED) transfer from filled lone pairs of Lewis base to unfilled Lewis acid sites of Guaiacol are discussed on the basis of NBO analysis. The theoretically calculated harmonic frequencies are scaled by common scale factor. The observed and the calculated frequencies are found to be in good agreement. The thermodynamic functions were obtained for the range of temperature 100–1000 K. The polarizability, first hyperpolarizability, anisotropy polarizability invariant has been computed using quantum chemical calculations. The chemical parameters were calculated from the HOMO and LUMO values. The NMR chemical shielding anisotropy (CSA) parameters were also computed for the title molecule.

1. Introduction

Guaiacol is a naturally occurring organic compound with the formula C6H4(OH)(OCH3), first isolated by Otto Unverdorben in 1826 [1]. Although it is biosynthesized by a variety of organisms [2], this yellowish aromatic oil is usually derived fromguaiacum or wood creosote. Samples darken upon exposure to air and light. Guaiacol is present in wood smoke, resulting from pyrolysis of lignin [3]. The compound contributes to the flavor of many compounds, e.g., roasted coffee.

Guaiacol is a precursor to various flavorings, such as eugenol [4] and vanillin [5]. Its derivatives are used medicinally as an expectorant, antiseptic, and local anesthetic. It also can be used as an indicator in chemical reactions that produce oxygen. When oxygen binds to it, the complex turns yellowish brown and absorbs light maximally at about 470 nm.

In industry, Guaiacol is produced by methylation of catechol, e.g., using potash and dimethyl sulfate [6]: C6H4(OH)2+(CH3O)2SO2 \rightarrow C6H4(OH)(OCH3)+

HO(CH3O)SO2

Guaiacol can be prepared by diverse routes in the laboratory. 2-Aminoanisole, derived in two steps from anisole, can be hydrolyzed via its diazonium derivative. Guaiacol can be synthesized by the dimethylation of catechol followed by selective monodemethylation [7].

Related compounds

Guaiacol carbonate is known as duotal, the phosphate asphosphatol, the phosphite as guaiacophosphal (phosphotal is a mixture of the phosphites of creosote phenols). The valerianicester of Guaiacol is known as geosote, the benzoic as benzosol, the salicylic as Guaiacolsalol, while the glycerin ether is the drugguaifenesin.

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The related derivative, dimethoxybenzeneorveratrole, is also useful. In preparation of food by smoking, Guaiacol is the main chemical responsible for the smoky taste, whereas syringol is responsible for the smoky aroma.

Guaiacolan organic compound with a strong, characteristic smell. It is a monomethylether of pyrocatechol. Colorless crystals melting point, 28.4°C, boiling point, 205°C. Readily soluble in ethanol and chloroform and poorly soluble in petroleum ether, it dissolves iodine and sulfur. Ferricchloride gives an alcohol solution of Guaiacol a blue coloration verging on green. Guaiacol is present in the distillation products of guaiacum, in the high-boiling distillates of beech tar, and in the dry distillation products of wood of leaf-bearing and coniferous species.

Guaiacol is produced synthetically by partial methylation of pyrocatechol or by diazotization of O-anisidine and decomposition of the compound with water. It is used to synthesize vanillin and medicinal preparations.

Considering the above mentioned aspects and the resulting demand of Guaiacol has led to search for commercially attractive and flexible compounds and to investigate the entire properties. To the best of our knowledge, FTIR and FT-Raman vibrational studies on the fundamental modes and electronic property investigations by NBO analysis, frontier molecular orbital's (FMOs) and thermodynamic properties on Guaiacol are inadequate in the literature. This inadequacy observed in the literature motivated us to investigate on Guaiacol by experimental techniques and theoretical methods. Thus, a detailed investigation have been attempted using LSDA and HSEH1PBE /6-311++G (d, p) basis set to provide more satisfactory and valuable information on electronic structure, molecular orbital's and potential energy distribution.

The optimized geometry, FMO's and their energy gaps, molecular electrostatic potential contour (MESP), total density region and electro static potential contour (MESP) map have been constructed at LSDA/6-311++G(d,p) level, in order to understand the electronic properties, electrophilic and nucleophilic active centers of Guaiacol.

2. Experimental Details

The methyl Guaiacol in the liquid (Clear - Slightly pale yellow - reddish yellow) were purchased from Lancaster Chemical Company, UK which is of spectroscopicgrade and hence used for recording the spectra as such without any further purification to record FTIR and FT-Raman spectra. The FTIR compounds were recorded by KBr pellet method in the region 4000-400cm⁻¹ using BROKER IFS 66V spectrometer with a Globar source. Ge/KBr beam splitter and a MCT detector. The frequencies for all sharp bands are accurate to 2cm⁻¹. The FT-Raman spectra were also recorded in the range 3500-50-cm⁻¹ by the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source with 200mW power operating at 1064nm. A liquid nitrogen cooled-Ge detector was used. The spectral resolution is 2 cm⁻¹.

3. Computational Details

Quantum chemical calculation were used for Guaiacol to out the optimized geometry and vibrational carry wavenumbers with the 2009 version of the Gaussian suite [8] using the LSDA and HSEH1PBE methods [9, 10] supplemented with standard 6-311++G(d,p) basis sets. The stability of the optimized geometries was confirmed by wavenumber calculations, which gave positive values for all the obtained wavenumbers. The vibrational modes were assigned by means of visual inspection using GAUSSVIEW program [11]. A comparison is made between the theoretically calculated frequencies and the experimentally measured frequencies. In this investigation we observed that the calculated frequencies were slightly greater than the fundamental frequencies. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies are usually scaled for comparison. In this work the force field was scaled according to the SQM procedure [12], the Cartesian representation of the force constants were transferred to a non-redundant set of local symmetry coordinates, chosen in accordance to the recommendations of Pulay et al. [13].Calculation of the potential energy distribution (PED) and the prediction of IR intensities and Raman activities were done on a PC with the VEDA 4 program [14]. The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities (Si) calculated by Gaussian 09W and adjusted during scaling procedure with VEDA 4 program were converted to relative Raman intensity (Ii) using the following relation from the basic theory of Raman scattering [15, 16].

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}S_{i}}{v_{i}[1 - exp(-hcv_{i} / kT)]}$$

Here, v_0 is the exciting frequency (cm⁻¹), v_i is the vibrational wavenumber of the ith normal mode, h, c and k are universal constants, and f is the suitably chosen common scaling factor for all the peak intensities. Finally, the thermodynamic properties of the optimized structures were obtained theoretically from the harmonic vibrations.

4. Result and discussion

4.1. Molecular structure description

Molecular symmetry can be used to predict many

Bond	Value (°)		Bond angle	Value (°	······································	Dihedral Angle	Value (°)		
Length	LSDA	HSEH		LSDA	HSEH1PBE		LSDA	HSEH	
Ū		1PBE						1PBE	
C1-C2	1.40	1.40	C2-C1-C6	118.91	119.15	C6-C1-C2-C3	-1.87	-1.18	
C1-C6	1.39	1.39	C2-C1-H7	122.54	121.74	C6-C1-C2-O12	176.74	178.23	
C1-H7	1.35	1.36	C6-C1-H7	118.45	119.01	H7-C1-C2-C3	-178.14	-177.40	
C2-C3	1.39	1.39	C1-C2-C3	119.57	119.61	H7-C1-C2-O12	0.47	2.01	
C2-O12	1.35	1.36	C1-C2-O12	118.04	117.80	C2-C1-C6-C5	0.78	0.48	
C3-C4	1.39	1.39	C3-C2-O12	122.38	122.58	C2-C1-C6-H17	-179.02	-178.97	
C3-O14	1.10	1.09	C2-C3-C4	120.91	120.67	H7-C1-C6-C5	177.20	176.81	
C4-C5	1.39	1.39	C2-C3-O14	118.75	119.15	H7-C1-C6-H17	-2.59	-2.64	
C4-H15	1.09	1.08	C4-C3-O14	120.34	120.17	С2-С1-Н7-С8	-56.05	-67.17	
C5-C6	1.39	1.39	C3-C4-C5	119.68	119.89	C6-C1-H7-C8	127.66	116.60	
C5-H16	1.09	1.08	C3-C4-H15	119.72	119.58	C1-C2-C3-C4	1.64	1.05	
C6-H17	1.09	1.08	C5-C4-H15	120.60	120.53	C1-C2-C3-O14	-179.69	-179.85	
H7-C8	1.41	1.42	C4-C5-C6	119.59	119.53	O12-C2-C3-C4	-176.91	-178.33	
C8-H9	1.10	1.09	C4-C5-H16	120.44	120.48	012-C2-C3-O14	1.76	0.77	
C8-H10	1.10	1.09	C6-C5-H16	119.96	119.99	С1-С2-О12-Н13	-178.08	-178.06	
C8-H11	1.11	1.10	C1-C6-C5	121.31	121.14	С3-С2-О12-Н13	0.49	1.33	
H9-O12	2.17	2.36	C1-C6-H17	117.02	117.56	C2-C3-C4-C5	-0.27	-0.20	
O12-H13	0.97	0.96	C5-C6-H17	121.67	121.30	C2-C3-C4-H15	179.48	179.58	
			C1-H7-C8	116.38	115.70	O14-C3-C4-C5	-178.92	-179.29	
			H7-C8-H9	111.69	111.48	O14-C3-C4-H15	0.83	0.49	
			H7-C8-H10	106.33	106.18	C3-C4-C5-C6	-0.84	-0.51	
			H7-C8-H11	110.36	110.49	C3-C4-C5-H16	179.66	179.67	
			H9-C8-H10	109.82	109.53	H15-C4-C5-C6	179.41	179.72	
			H9-C8-H11	109.49	109.78	H15-C4-C5-H16	-0.09	-0.11	
			H10-C8-H11	109.09	109.30	C4-C5-C6-C1	0.58	0.36	
			C2-O12-H13	108.95	109.15	C4-C5-C6-H17	-179.63	179.79	
						H16-C5-C6-C1	-179.92	-179.81	
						H16-C5-C6-H17	-0.13	-0.38	
						C1-H7-C8-H9	62.95	62.45	
						C1-H7-C8-H10	-177.27	-178.32	
						C1-H7-C8-H11	-59.10	-59.91	

Table 1. Optimized geometrical parameters of Guaiacolobtainedby LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d.p) level calculations

molecular properties, such as its dipole moment and its allowed spectroscopic transitions. The labeling of the atoms in Guaiacol is given in Fig. 1 and the global minimum energy obtained by LSDA and HSEH1PBE with the standard basis set 6-311++G (d, p) are found to be -379.8717 A.U. and -382.3601 A.U, respectively. The optimized geometrical parameters of the title compound calculated by LSDA and HSEH1PBE /6-311++G (d, p) are presented in Table 1.



Fig 1.Optimized molecular structure of Guaiacol. 4.2. Analysis of Vibrational spectra

The geometry of the molecules under investigation is considered by possessing C_1 point group symmetry and the optimized molecular structure is obtained from GAUSSAN 09W and GAUSSVIEW programs as shown in Fig. 1.The Guaiacol cotinate consists of 17 atomshence undergoes45 fundamentalmodes of vibrations of each compound are distributed into their educible representations under C1 symmetry as 31 in-planevibrations of A' species and 14 out of plane vibrations of A'' species.

i.e., $\Gamma_{vib} = 31 \text{ A}' + 14 \text{ A}''$

All vibrations are active in both IR and Raman. The title molecule contains fluorine atom and carbonyl group with benzene ring. The experimental and calculated FTIR and FT-Raman spectra of Guaiacol are given in Figs. 2 and 3, respectively.





Fig. 3. FT-Raman spectrum of Guaiacol.

4.2.1. CH3 group vibrations

The title compound possesses a single CH₃ group in fourth position of the ring in Table 2. The CH methyl group stretching vibrations are generallyobserved in the range $3000-2800 \text{ cm}^{-1}$ [17, 18]. For theassignments of CH₃ group frequencies one can expect nine fundamentals viz., namely the symmetrical stretching in CH₃(CH_{3sym.stretch}), asymmetrical stretching (CH_{3asym.stretch}), symmetrical (CH_{3sym.deform}) and asymmetrical (CH_{3asy.deform}) deformationmodes, in-plane rocking (CH_{3ipr}), out-of-plane rocking (CH_{3opr}), CH₃ wagging (CH_{3wag}.) and twisting (CH₃) modes. Methylgroups are generally referred as an electron donating substitutionin the aromatic ring system.

The recorded FT-IR and FT-Raman spectra of Guaiacol have strong and very weak intensity bands at 2962 and 2843 cm⁻¹and they are assigned to CH3 stretching vibrations of Guaiacol. The CH₃ss frequency is established at 2911 cm⁻¹ in the FT-Raman spectrum of Guaiacol. The methyl deformation modes mainly coupled with thein-plane bending vibrations and are also well established. The in-plane methyl deformation mode of Guaiacol is found at 1599 cm⁻¹in FT-IR spectrum. The band at 1468 cm⁻¹ in FT-IR is attributed to CH₃ out-of-plane deformation mode of Guaiacol. The bands obtained at 1261 and 1226 cm⁻¹ in FT-IR and FT-Raman spectra are assigned to CH₃ in-plane and out-of-plane rocking modes, respectively. The contributions for all these modes are about 85%. In the present study, they show good agreement with the calculated values.

4.2.2. C-H Vibration

Usually the bands in the range 3100-3000 cm⁻¹ are assigned to C-H stretching vibrations of aromatic compounds, which is the characteristic region for the ready identification of C-H stretching vibrations [19]. In this region, the bands are not affected appreciably by the nature of the substituent; the C-H stretching modes usually appear with strong Raman intensity and are highly polarized. Fundamental mode observed at 3072 and 3027 cm⁻¹ in FTIR and FT Raman, respectively, are assigned to the C-H stretching vibration of Guaiacol. The C-H in-plane bending vibrations are observed in the region 1350-950 cm⁻¹. The frequency of the C-H outof-plane bending modes depends mainly on the number of the adjacent hydrogen atoms on the ring and not very much affected by the nature of substituents. The C-H out-of-plane bending modes usually medium to strong intensity arises in the region 950-600 cm⁻¹ [20-22]. In this study, the C-H inplane bending vibration is assigned to 1098 cm⁻¹ in FTIR and 1042 cm⁻¹ in FT Raman. The C-H out-of-plane bending vibration is observed 913 cm⁻¹ in FTIR and 836 cm⁻¹ in FT-Raman. Above mentioned C-H in-plane and out-of-plane bending mode of the title compound is well agreed with reported data [23-25].

4.2.3. C–C vibration

The carbon–carbon stretching modes of the pyridine ring appear in the region $1650-1200 \text{ cm}^{-1}$ are determined not so much by the nature of the substituent but by the form of substitution around the ring [26, 27]. In Guaiacol C–C stretching bands in the infrared spectrum appeared at 161641cm⁻¹ (s), 1523 cm^{-1} (m). The bands observed at 1630 cm^{-1} (w), 1367 cm^{-1} (w) and 1303 cm^{-1} (w) in FT– Raman spectrum are assigned to the ring carbon–carbon stretching vibrations. All other observed C-C-C in-plane and out of plane bending vibrations of the compounds are completely assigned and are presented in Table 2. The C-C-C in-plane bending vibrations of Guaiacol are observed in FT–IR spectrum at 760 cm⁻¹ (medium-to-strong) and 558 cm⁻¹

*P. Dinesh / Elixir Org. Chem. 120 (2018) 51264-51277*Table 2. Detailed assignment of fundamental vibrations of Guaiacolby normal mode analysis based on scaled quantum Mechanical force field.

No.	Observed	frequency (cm ⁻¹)	Calculated frequency (cm ⁻¹)							Characterization of normal			
	FT-IR	FT-Raman	LSDA/6-311++G(d,p)					HSEH1PBE/6-311++G(d,p)					modes with PED(%)
			Unscaled	Scaled	IR	Raman	Raman	Unscaled	Scaled	IR	Raman	Raman	
					Activity	Activity	Intensity			Activity	Activity	Intensity	
1	3328	-	3220	3226	65.63	143.53	152.9	3284	3228	70.79	106.22	96.85	CH (99)
2	3058	3072	3132	3068	2.85	263.75	503.3	3221	3069	7.21	233.35	406.54	CH (99)
3	-	3027	3121	3042	3.43	62.08	119.8	3210	3043	10.83	59.69	105.21	CH (99)
4	2968	2949	3112	2998	1.50	77.99	152.0	3198	2999	2.65	77.16	137.61	CH _{3ips} (99)
5	2911	2934	3074	2946	8.17	114.72	232.4	3168	2947	12.50	89.51	164.58	$CH_{3ss}(99)$
6	-	2849	3073	2898	9.90	105.88	214.8	3157	2899	19.94	106.40	197.99	CH _{3ops} (99)
7	2843	-	3021	2853	18.99	60.52	129.7	3114	2857	26.34	53.97	105.00	C=O (93)
8	1641	-	1645	1654	70.34	180.94	421.9	1685	1656	66.82	143.49	304.00	CC (84), bCN (13)
9	-	1630	1636	1642	20.95	25.46	306.4	1668	1644	18.44	25.81	295.56	CC (85), bCH (12)
10	-	1599	1627	1609	25.97	8.21	100.2	1661	1610	18.31	9.16	105.98	CH3 _{ipb} (89)
11	1523	-	1520	1531	189.75	5.05	73.2	1555	1533	146.17	3.78	51.71	bCH (65), Rtrigd(19)
12	-	1471	1460	1482	26.93	2.56	41.1	1507	1483	12.47	8.17	121.12	CH3 _{sb} (96)
13	1468	-	1439	1453	19.72	8.24	137.0	1498	1454	23.91	2.86	43.09	CH3 _{opb} (96)
14	-	1454	1410	1532	10.55	10.35	181.0	1484	1534	14.51	9.56	147.26	CN (79), bCC (19)
15	1446	-	1409	1428	3.32	1.63	28.5	1468	1430	2.96	2.57	40.62	<i>b</i> OH (80), <i>b</i> CO (17)
16	1367	-	1403	1392	15.82	5.47	96.9	1384	1395	20.35	2.35	43.00	CC(81), Rasymd(15)
17	-	1303	1302	1312	216.72	32.07	680.4	1327	1313	201.06	19.18	388.91	CC(70), CO(17),CH(13)
18	1261	1264	1265	1260	23.56	2.04	46.5	1307	1263	44.80	18.78	394.89	CH _{3ipr} (78)
19	1226		1254	1242	44.26	0.76	17.6	1276	1245	81.76	0.87	19.40	CH _{3opr} (77)
20	1208	1167	1163	1198	24.07	3.32	92.5	1210	1199	31.91	3.54	89.54	CC(77), CC(21)
21	1177	-	1137	1153	37.16	5.68	166.9	1187	1154	43.43	3.59	95.30	CC(74), Rsymd(17)
22	-	1153	1132	1146	1.91	1.63	48.4	1175	1148	7.05	2.91	78.90	<i>b</i> C=O(73), <i>b</i> CC(13)
23	1110	-	1126	1123	24.00	5.08	152.7	1174	1128	5.35	3.63	98.86	CN(60),CC(25),Rtrigd(15)
24	-	1098	1087	1095	58.34	0.31	10.2	1119	1098	57.30	0.38	11.54	<i>b</i> CC(72), CO(13)
25	1042	-	1058	1042	53.83	3.23	112.4	1072	1044	42.69	17.10	576.90	<i>b</i> CH(85), CC(12)
26	1027	1040	1039	1038	2.96	20.10	729.0	1059	1039	27.41	12.08	419.44	CO(82)
27	-	913	922	912	0.44	0.04	2.0	972	916	0.20	0.03	1.42	<i>b</i> C=O(73), <i>b</i> CC(13)
28	908	902	888	898	4.04	0.17	9.0	939	899	2.94	0.11	4.98	<i>b</i> CH(63), CC(23)
29	834	836	843	830	23.45	2.69	157.6	861	833	21.56	1.56	86.95	<i>b</i> CO(72), <i>b</i> CC(13)
30	-	760	809	758	0.63	0.61	39.0	850	755	4.39	0.76	43.65	<i>b</i> CH(65), <i>Rtrigd</i> (19)
31	758	-	754	745	12.02	22.76	1715.7	771	746	25.18	17.48	1251.19	<i>b</i> CC(63), <i>b</i> CO(17)
32	-	730	720	728	82.82	0.42	34.8	756	729	66.39	3.51	262.90	Rsymd(69), Rasymd(21)
33	-	585	719	682	0.48	1.66	139.3	747	687	2.57	5.44	418.68	<i>b</i> CC(65), R <i>trigd</i> (19)
34	558	-	586	576	3.83	1.89	247.5	602	578	2.34	1.94	240.31	<i>b</i> CC(55), <i>w</i> CC(23)
35	532	535	568	539	0.69	6.64	932.9	580	540	1.08	6.44	863.29	<i>b</i> CL(60), <i>Rtrigd</i> ((19)
36	-	473	551	468	6.37	2.24	336.9	560	469	7.64	2.33	337.64	wCC(57), <i>t</i> R <i>sym</i> (25)
37	437	-	469	442	6.62	0.59	125.5	490	444	8.63	0.69	132.83	wCC(53), wCO(29)
38	-	356	431	365	6.10	0.47	118.6	442	367	6.69	0.52	126.46	wCC(55), tRasym(23)
39	-	310	360	335	64.57	1.93	716.6	360	334	6.29	1.47	547.10	<i>t</i> R <i>trig</i> (53), <i>w</i> Cl(27)
40	-	293	339	302	35.69	1.46	616.0	322	306	72.35	1.53	719.97	wCl(53), wCO(23)
41	-	-	286	298	6.13	0.72	435.0	299	299	26.28	0.72	395.53	wCO(51),wCC(23)
42	-	-	262	260	4.22	0.69	497.8	241	263	4.82	1.02	875.15	CH ₃ twist(61)
43	-	-	178	182	3.14	1.20	1937.8	168	185	2.02	0.67	1214.73	<i>t</i> Rasym(60), wCO(21)
44	-	-	131	130	1.84	2.86	8637.1	136	133	2.24	2.61	7302.54	<i>tRsym</i> (51), <i>tRasym</i> (21)
45	-	-	74	76	65.63	1.58	15341.9	80	78	4.21	1.60	13043.49	wCO(52), tRing(19)

Abbreviations:-b-bending; g-out-of-plane bending; t-torsion; R-ring;; asym-assymetic; sym-symmetric; vs-very strong; s-strong; ms-medium strong; m-medium; w-weak; vw-very-weak.

(weak) and a strong band at 730 cm⁻¹ identified in FT–Raman spectrum. The C-C-C out-of-plane bending vibrations of the title compounds are well identified in the recorded spectra, within their characteristic region.

4.2.4. C–O vibrations:

Generally, the C–O vibrations occur in the region 1260–1000 cm⁻¹[28]. In the present study, the C–O stretching vibrations are assigned at 1153, 913 cm⁻¹in FT-Raman spectrum of Guaiacol. According to the literature [29], the C–O vibration is pushed to the lower region by the influence of other vibrations, because of the proximity in Guaiacol C–O in plane bending vibration is found at 836 cm⁻¹in FT-Raman spectrum.

4.2.5. Ring Vibrations

In case of Guaiacol, the carbon atoms coupled together in the hexagonal chain of ring possesses two C–C stretching vibrations at 908, 758 and 913, 760 cm⁻¹in FT-IR and FT-Raman. The in-plane and out-of-plane bending vibrations of the benzene ring are generally observed below 1002cm⁻¹ [30] and these modes are not pure but they contributes drastically from other vibrations and are substituent-sensitive. In the title molecule, the ring in-plane and out-of plane bending modes are affected to a great extent by the substituents and produce bands below 558cm⁻¹. From PED results, the bands present at 356 and 293 cm⁻¹in FT-Raman are assigned to C ring. The scaled theoretical wave numbers corresponding to all the ring vibrations are found to have a good correlation with their available experimental observations.

5. HOMO-LUMO analysis

In the first hyper polarizability value, there is an inverse relationship between first hyper polarizability and HOMO–LUMO gap, allowing the molecular orbital's to overlap to have a proper electronic communication conjugation, which is a marker of the intra-molecular charge transfer from the electron donating group through the p-conjugation system to the electron accepting group [31,32]. Many organic molecules, containing conjugated p-electrons characterized by large values of molecular first hyper polarizabilities were analyzed by means of vibrational spectroscopy [33, 34].

In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. But the intra molecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman intensity strong at the same time. The most important orbitals in a molecule are the frontier molecular orbitals, called HOMO and LUMO. These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [35]. The frontier molecular orbitals play an important role in the electric and optical properties [36]. 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 intra-molecular charge transfer from the end-capping electron-donor groups to the efficient electronacceptor groups through p-conjugated path [37].

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by LSDA and HSEH1PBE /6-311++G (d, p) method is shown below. The energy gap between HOMO and LUMO is shown in Table 3 which shows that charge transfer may be taking place from Guaiacolatom in Fig. 4.The energy difference between HOMO and LUMO orbital which is called as energy gap is a critical parameter in determining molecular electrical transport properties in DOS Spectrum analysis Fig. 5, because it is a measure electron conductivity calculated -7.5558 eV and -2.0700 eV for Guaiacol, respectively.



Fig 4. The Frontier Molecular Orbital's for Guaiacol.



Fig 5. Density of States (DOS) diagram for Guaiacol.

Based on density functional descriptors global chemical reactivity descriptors of compounds such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [38-42, 26].

Pauling introduced the concept of electronegativity as the power of an atom in a compound to attract electrons to it. Hardness (η), chemical potential (μ) and electronegativity (χ) and softness are defined follows.

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{\nu(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{\nu(r)}$$
$$\mu = \left(\frac{\partial E}{\partial N} \right)_{\nu(r)}$$
$$\chi = -\mu = -\left(\frac{\partial E}{\partial N} \right)_{\nu(r)}$$

Where, *E* and v(r) are electronic energy and external potential of an N-electron system respectively. Softness is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness.

$$\eta$$
 Using Koop man's theorem

closed-shell compounds $\eta,\,\mu$ and χ can be defined as

for

$$\eta = \frac{(1-A)}{2}$$
$$\mu = \frac{-(1+A)}{2}$$
$$\chi = \frac{(1+A)}{2}$$

Where, A and I are the ionization potential and electron affinity of the compounds respectively. Electron affinity refers to the capability of aligned to accept precisely one electron from a donor. However, in many kinds of bonding viz., covalent hydrogen bonding, and partial charge transfer takes place. Recently Parr et al. [38] have defined a new descriptor to quantify the global electrophilic power of the compound as electrophilicity index (ω) , which defines a quantitative classification of the global electrophilic nature of a compound. Parr et al. [38] have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows

 $\omega = \frac{\mu^2}{2\eta}$

The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [26, 43, 44]. The calculated value of electrophilicity index describes the biological activity of Guaiacol. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table 3.

6. Natural bond orbital (NBO) analysis

The NBO calculations were performed using NBO 3.1 program as implemented in the Gaussian 09W package at the LSDA and HSEH1PBE /6-311++G (d, p) level in order to understand various second-order interactions between the filled orbital's of one subsystem and vacant orbital's of another subsystem, which is the measure of the delocalization or hyper conjugation.

By the use of the second-order bond-antibond (donoracceptor) NBO energetic analysis, insight in the most important delocalization schemes was obtained. The change in electron density (ED) of $(\sigma \square \square \pi \square)$ antibonding orbital's and E(2) energies have been calculated by natural bond orbital (NBO) analysis [45] using DFT method to give clear evidence of stabilization originating from various molecular interactions. NBO analysis has been performed on Guaiacol in order to elucidate intra-molecular hydrogen bonding, intracharge transfer (ICT) interactions molecular and delocalization of p-electrons of the benzene ring. The hyperconjugative interaction energy was deduced from the second-order perturbation approach [46]. For each donor (i) and acceptor (j), the stabilization energy E2 associated with the delocalization $i \rightarrow j$ is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_i - \varepsilon_j}$$

Where q_i is the donor orbital occupancy, \Box_i and \Box_i are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. The most important interactions between Lewis and non-Lewis orbital's with oxygen lone pairs are the second order perturbation energy values, E(2), corresponding to these interactions, and the overlap integral of each orbital pair. The second order perturbation theory analysis of Fock matrix in NBO basis of Guaiacol (Table 4-5) also indicates intra-molecular interactions due to the orbital overlap of

 $\pi(C_1 - C_2)$ and $\pi^*(C_1 - C_6)$, resulting in high electron density (approx. 0.069e) of anti-bonding π orbitals (C-C). The intra-molecular charge transfer from O atom of the CO-CH3 group to the C-C bond. The orbital overlap between π $(C_3 - C_4)$ and $\pi^*(C_5 - C_6)$ results in intra-molecular charge transfer causing stabilization of the system. The charge transfer from $\sigma(C_5 - C_6)$ to $\sigma^*(C_1 - C_2)$ amounts to the stabilization of 28.89 kcal/mol. The magnitude of charge transfer from the lone pairs of O_{12} to antibonding $\boldsymbol{\sigma}(C_1 - C_2)$ and $\sigma^*(C_3 - C_4)$, σ orbitals amount to stabilization of 15.91 and 19.66 kcal/mol, respectively.

Table 3. HOMO-LUMO energy and other related properties of Guaiacolbased on LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d.p) method.

Parameters	LSDA/		HSEH1PBE/		
	6-311++G	+(d , p)	6-311++G	(d,p)	
	A.U	eV	A.U	eV	
HOMO-5	-0.3406	-9.2682	-0.3644	-9.9158	
HOMO-4	-0.3333	-9.0695	-0.3484	-9.4804	
HOMO-3	-0.3144	-8.5553	-0.3326	-9.0505	
HOMO-2	-0.2711	-7.3770	-0.2817	-7.6654	
HOMO -1	-0.2427	-6.6042	-0.2464	-6.7048	
НОМО	-0.2194	-5.9702	-0.2224	-6.0518	
LUMO - HOMO (Energy gap)	-0.1451	-3.9483	-0.1992	-5.4205	
LUMO	-0.0653	-1.7769	-0.0232	-0.6313	
LUMO+1	-0.0533	-1.4504	-0.0168	-0.4571	
LUMO+2	-0.0446	-1.2136	-0.0107	-0.2912	
LUMO+3	-0.0201	-0.5469	+0.0008	0.0217	
LUMO+4	-0.0134	-0.3646	+0.0060	0.1632	
LUMO+5	+0.0024	0.0653	+0.0212	0.5769	
Global Hardness (η)	-0.07705	-2.0966	-0.0996	-2.7102	
Electronegativity (χ)	-0.14235	-3.8735	-0.1228	-3.3415	
Global softness (s)	-12.9786	-353.1658	-10.0402	-273.2078	
Chemical potential (µ)	0.14235	3.8735	0.1228	3.3415	
Global Electrophilicity (ω)	-0.1315	-3.5782	-0.0757	-2.0599	
Dipole moment (µ)	2.1818Del	bye	2.1550 De	bye	
Mean polarizability(α)	-50.5148x	10 ⁻³⁰ esu	-50.1835 >	k 10 ⁻³⁰ esu	
Anisotropy of the polarizability ($\Delta \alpha$)	142.7492x	x 10 ⁻³⁰ esu	152.4155	x 10 ⁻³⁰ esu	
First hyperpolarizability(β)	8.942x 10	⁻³⁰ esu	8.795 x 10 ⁻³⁰ esu		
Optimized global minimum Energy	-419.8383	(Hartrees)	-421.6524	(Hartrees)	
RMS	0.0000064	10 (a.u.)	0.00001179(a.u.)		

7. Molecular Electrostatic Potentials (MEP)

Molecular electrostatic potential used extensively for interpreting potentials have been and predicting the reactive behavior of a wide variety of chemical system in both electrophilic and nucleophilic reactions, the study of biological recognition processes and hydrogen bonding interactions [47]. V(r), at a given point r(x, y,z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and positive test charge (a proton)located at *r*. Unlike many of the other quantities used at present and earlier as indices of reactivity, V(r) is a real physical property that can be determined experimentally by diffraction or by computational methods. For the systems studied the MEP values were calculated as described previously, using the following equation [48]:

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr'$$

Where, the summation runs over all the nuclei A in the molecule and polarization and reorganization effects are neglected. Z_A is the charge of the nucleus A, located at R_A and q(r0) is the electron density function of the molecule.

To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, the MEP at the LSDA and HSEH1PBE /6-311++G (d, p) optimized geometry was calculated In the present study, the electrostatic potential (ESP), electron density (ED) and the molecular electrostatic potential (MEP) map figures for Guaiacol are shown in Fig. [6-10]. The ED plots for title molecule show a uniform distribution. However, it can be seen from the ESP figures, that while the negative ESP is localized more over the oxygen atom and fluorine atoms and is reflected as a yellowish blob, the positive ESP is localized on the rest of the molecule. This result is expected, because ESP correlates with electro negativity and partial charges.

 Table 4. Second order perturbation theory of fock matrix in NBO basis using LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d,p) basis set for Guaiacol.

Donor NBO (i)	Acceptor NBO (j)	E(2) j K/mol	$ \mathbf{E}(\mathbf{j}) - \mathbf{E}(\mathbf{i}) \mathbf{a.u.} $	F(i, j) a.u.
LSDA/6-311++0	G(d , p)			
π(C1 - C2)	π*(C1 - C6)	3.65	1.16	0.058
π(C1 - C2)	π*(C2 - C3)	3.98	1.15	0.06
σ(C1 - C2)	σ*(C3 - C4)	14.26	0.24	0.053
σ(C1 - C2)	σ*(C5 - C6)	13.38	0.25	0.052
π(C1 - C6)	π*(C1 - C2)	3.92	1.13	0.059
π(C1 - C6)	π*(C2 - O12)	4.24	0.84	0.053
π(C2 - C3)	π*(C1 - C2)	4.21	1.13	0.062
π(C2 - C3)	π*(C1 - O7)	3.63	0.88	0.05
π(C3 - C4)	π*(C2 - O12)	4.48	0.83	0.055
σ(C3 - C4)	σ*(C1 - C2)	14.99	0.22	0.053
σ(C3 - C4)	σ*(C5 - C6)	13.83	0.23	0.051
π(C3 - H14)	π*(C1 - C2)	3.88	0.96	0.055
π(C3 - H14)	π*(C4 - C5)	3.25	0.99	0.051
π(C4 - H15)	π*(C2 - C3)	3.36	0.95	0.051
π(C4 - H15)	π*(C5 - C6)	3.47	0.97	0.052
π(C5 - C6)	π*(C1 - O7)	4.29	0.85	0.054
σ(C5 - C6)	σ*(C1 - C2)	15.91	0.22	0.054
σ(C5 - C6)	σ*(C3 - C4)	14.77	0.22	0.052
π(C5 - H16)	π*(C1 - C6)	3.35	0.96	0.051
π(C5 - H16)	π*(C3 - C4)	3.57	0.97	0.053
π(C6 - H17)	π*(C1 - C2)	3.98	0.95	0.055
HSEHPBE/6-311	++G(d,p)		•	
π(C1 - C2)	π*(C1 - C6)	3.55	1.29	0.06
π(C1 - C2)	π*(C2 - C3)	3.7	1.28	0.062
σ(C1 - C2)	σ*(C3 - C4)	18.19	0.29	0.065
σ(C1 - C2)	σ*(C5 - C6)	17.58	0.29	0.064
π(C1 - C6)	π*(C1 - C2)	3.81	1.26	0.062
π(C1 - C6)	π*(C2 - O12)	4.27	0.98	0.058
π(C2 - C3)	π*(C1 - C2)	4.01	1.26	0.064
π(C2 - C3)	π*(C1 - O7)	3.79	1	0.055
π(C3 - C4)	π*(C2 - O12)	4.55	0.97	0.059
σ(C3 - C4)	σ*(C1 - C2)	19.1	0.26	0.065
σ(C3 - C4)	σ*(C5 - C6)	18.12	0.27	0.064
π(C3 - H14)	π*(C4 - C5)	3.45	1.1	0.055
π(C4 - H15)	π*(C2 - C3)	3.47	1.07	0.054
π(C4 - H15)	π*(C5 - C6)	3.64	1.09	0.056
π(C5 - C6)	π*(C1 - O7)	4.49	0.98	0.059
π(C5 - C6)	π*(C1 - C2)	19.66	0.26	0.066
σ(C5 - C6)	σ*(C3 - C4)	18.32	0.27	0.064
σ(C5 - H16)	σ*(C1 - C6)	3.52	1.08	0.055
π(C5 - H16)	π*(C3 - C4)	3.66	1.09	0.056
π(C6 - H17)	π*(C1 - C2)	4.14	1.07	0.06
$\pi(C6 - H17)$	$\pi^{*}(C4 - C5)$	3.51	1.09	0.055

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P. Dinesh / Elixir Org. Chem. 120 (2018) 51264-51277 Table 5. The angular properties of natural hybrid orbital's (NHO) of Guaiacolusing LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d,p) basis set.

NBO	LSDA/6-311++G(d,p)					NBO	HSEH1PBE/6-311++G(d,p)										
	Line of Centres Hybrid 1			Hybrid	Hybrid 2			Line of Centres		Hybrid	1		Hybrid	12			
	Theta	Phi	Theta	Phi	Dev	Theta	Phi	Dev		Theta	Phi	Theta	Phi	Dev	Theta	Phi	Dev
σ(C1 - C2)	87.4	83.6	86.5	88	4.4	91.9	259	4.7	σ(C1 - C2)	87.4	83.6	86.7	87.8	4.2	92	259.3	4.4
π □(C1 - C2)	87.4	83.6	173.9	22.8	89.7	174.2	19.2	89.9	π(C1 - C2)	87.4	83.6	174	21.3	89.8	174.2	18.6	89.8
σ(C1 - C6)	87.3	323.4	87.3	322.4	1				σ(C1 - O7)	95.3	203.5	94.7	201.1	2.5			
σ(C1 - O7)	95.3	203.5	94.6	201	2.6				σ(C2 - C3)	84.7	23.5	84.4	25.3	1.8			
σ(C2 - C3)	84.7	23.5	84.4	25.7	2.2				σ(C2 - O12)	92.7	143.4	93.5	142.4	1.3			
σ(C2 - O12)	92.7	143.4	93.6	142.4	1.3				σ(C3 - C4)	87.3	323.4				92.9	144.5	1.1
σ(C3 - C4)	87.3	323.4				93.1	145	1.7	π(C3 - C4)	87.3	323.4	174.9	24.9	90.3	5.3	201.9	89.9
π(C3 - C4)	87.3	323.4	175	25.8	90.4	5.3	201.3	89.9	σ(C3 - H14)	87.4	83.6	87.6	84.9	1.3			
σ(C3 - H14)	87.4	83.6	87.8	85.2	1.6				σ(C5 - C6)	95.3	203.5	95.9	202.4	1.2	85.3	24.6	1.3
σ(C4 - C5)	92.6	263.6	92.6	262.2	1.4				π(C5 - C6)	95.3	203.5	5.7	203.3	89.7	5	201.4	89.7
σ(C5 - C6)	95.3	203.5	96	202.5	1.2	85.5	24.5	1.2	σ(O7 - C8)	64	138.2				114.7	321.7	3.4
π(C5 - C6)	95.3	203.5	5.7	203.4	89.6	5	200.9	89.7	σ(C8 - H9)	116	88.8	117.2	87.1	1.9			
σ(O7 - C8)	64	138.2				114.9	320.8	2.5	σ(C8 - H10)	95.3	203.5	95.4	206.3	2.8			
σ(C8 - H9)	116	88.8	118	87.5	2.3				σ(C8 - H11)	14.1	23.7	15.5	17	2.2			
σ(C8 - H10)	95.3	203.5	95.4	206.3	2.8				σ(C1 - C2)	87.4	83.6	174	21.3	89.8	174.2	18.6	89.8
σ(C8 - H11)	14.1	23.7	15.8	14.7	2.8				σ(C3 - C4)	87.3	323.4	174.9	24.9	90.3	5.3	201.9	89.9
π *(C1 - C2)	87.4	83.6	173.9	22.8	89.7	174.2	19.2	89.9	π *(C5 - C6)	95.3	203.5	5.7	203.3	89.7	5	201.4	89.7
π *(C3 - C4)	87.3	323.4	175	25.8	90.4	5.3	201.3	89.9	π *(C1 - C2)	87.4	83.6	86.7	87.8	4.2	92	259.3	4.4
π *(C5 - C6)	95.3	203.5	5.7	203.4	89.6	5	200.9	89.7	π *(C1 - C2)	87.4	83.6	174	21.3	89.8	174.2	18.6	89.8

In the majority of the MEPs, while the maximum negative region which preferred site for electrophilic attack indications as red color, the maximum positive region which preferred site for nucleophilic attack symptoms as blue color. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading and is very useful in research of molecular structure with its physiochemical property relationship. The resulting surface simultaneously displays molecular size and shape and electrostatic potential value. In the present study, 3D plots of molecular electrostatic potential (MEP) of Guaiacol has been draw in Fig. [11, 12]. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red <orange < yellow < green < blue. The negative (red1 and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Fig. 6.



Fig 6. Molecular electrostatic potential for Guaiacol.



Fig 7. Electrostatic potential surface for Guaiacol.



Fig 8.The total alpha density surface for Guaiacol.



Fig 9.The total electron density surface for Guaiacol.



Fig 10. The total alpha density surface for Guaiacol.



Fig 11. Electron density contour surface for Guaiacol.



Fig 12. Electrostatic Potential MEP for Guaiacol. 8. Thermodynamic properties

On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity $(C_{p,m}^o)$, enthalpy changes (ΔH_m^o) and entropy (S_m^o) for the title molecule at the method of LSDA and HSEH1PBE /6-311++G (d, p) were obtained from the theoretical harmonic frequencies and listed in Table 6. From Table 6, it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increases with temperature expect Gibb's free energy. The correlation equations between heat capacity, entropy, enthalpy changes in Fig. 13



fig 13. Correlation graph of thermodynamic parameters for Guaiacol.

All the thermodynamic data supply helpful information for the further study on the Guaiacol. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamic theoretical harmonic frequencies and listed in Table 7.

Table 7. Theoretically computed zero point vibrational energy (kcal mol⁻¹), rotational constant (GHz),

rotational temperature (kelvin), thermal energy (kcal mol⁻¹), molar capacity at constant volume (calmol⁻¹ kelvin⁻¹), entropy (cal mol⁻¹ kelvin⁻¹), vibrational temperature (kelvin) of Guaiacol by LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d,p) method.

PARAMETER	LSDA	HSEH1PBE
Zero point vibrational energy	83.69665	86.19150
Rotational constant	2.95886	2.87997
	1.50678	1.50207
	1.04148	1.03815
Rotational temperatures	0.14200	0.13822
	0.07231	0.07209
	0.04998	0.04982
Energy		
Total	88.964	91.386
Translation	0.889	0.889
Rotational	0.889	0.889
Vibrational	87.187	89.608
Molar capacity at constant volu	ume	
Total	31.935	31.135
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	25.974	25.174
Entropy		
Total	89.029	88.661
Translational	40.361	40.361
Rotational	28.628	28.661
Vibrational	20.041	19.639

9. Chemical Shielding Anisotropy (CSA) parameters

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the structure determination of large molecules. The NMR technique is based on the sensitively of magnetic properties, typically isotropic chemical shielding (ICS), to the chemical environment of the nuclei. The full NMR shielding tensor in Fig. 14 is nonsymmetrical and of rank 2, containing nine independent quantities are used to predict the CSA parameters defined by Czinkiet al. [49] as follows. The isotropic chemical shielding, α_{iso} one of the scalar invariants of the tensor, is given by 1/3 of the trace of (α).

$$\alpha_{iso} = (1/3)Tr\sigma = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3 = (\sigma_1 + \sigma_2 + \sigma_3)/3$$

In NMR spectroscopy the concept of anisotropy was advanced from the theory of axially symmetric tensors, where two principal components have the same value. The anisotropy (Δ) is the difference of the two distinct components in this generalization,

$$\Delta = \sigma_3 - (\sigma_1 + \sigma_2)/2 = 3(\sigma_3 - \sigma_{iso})/2$$

The asymmetry (η) was intended to show the deviation from the axially symmetric tensor,

 $\eta = (\sigma_2 - \sigma_1) / (\sigma_3 - \sigma_{iso})$

In the case of an axially symmetric tensor, $\eta = 0$ The CSA parameters, span (Ω) and skew (k) of the shielding tensor are in Fig. 15,

$$\Omega = \sigma_3 - \sigma_1 (\Omega \ge 0)$$

and

$$k = 3(\sigma_2 - \sigma_{iso}) / \Omega = (2\sigma_2 - \sigma_1 - \sigma_3) / \Omega(-1 \le k \le +1)$$

where the principal components (Eigen values of σ^s) are
labeled according to $(-1 \le k \le +1)$.

The symmetric Eigen values are obtained from the following relations,

$$\sigma_{1} = \sigma_{iso} - \Omega(k+3)/6$$

$$\sigma_{2} = \sigma_{iso} + \Omega k/3$$

$$\sigma_{3} = \sigma_{iso} - \Omega(k-3)/6$$

The CSA parameters (ρ) and (τ) describe the magnitude and orientation of the anisotropy, respectively

$$(\rho) = sqrt([(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2]/2)$$

and
$$(3\tau) = k\pi + (-1)^{(k+1)} \arcsin (\text{mod } e(\sigma))$$

$$(k = 0, \pm 1, \pm 2, \pm 3)$$

The CSA parameters (ρ) and (τ) are also expressed in terms of span (Ω) and skew (k) are as follows

$$(\rho,\tau) = \left(\left(\frac{\Omega}{2}\sqrt{3+k^2}\right), \arcsin\left\lfloor\frac{k(9-k^2)}{(3+k^2)^{\frac{3}{2}}}\right\rfloor \right)$$

Using the above said relations the complete nuclear magnetic resonance(NMR) chemical-shielding tensors, r, have been computed at density functional theory (DFT) and HF, within the gauge-including atomic orbital (GIAO) formalism, for both structure of the molecule Guaiacol. The CSA parameters of the carbon nitrogen and hydrogen atoms of the molecule both in monomer and dimer are calculated in DFT method with the level of LSDA and HSEH1PBE /6-311++G (d, p) and presented in Table 8.



Fig 14.The NMR Spin-Spin shielding surfaces for Guaiacol.



Fig 15. The NMR shielding surfaces for Guaiacol. 10. Magnetic susceptibility

Atoms, molecules, free radicals or ions which contain one or more unpaired electron will possess permanent magnetic dipole moment, which arises from the residual spin and angular momentum of the unpaired electrons. All substances having permanent magnetic moment display paramagnetic behavior in nature.

Atom	σ 1(ppm)	σ 2(ppm)	σ 3(ppm)	σ _{iso (} ppm)	σ _{aniso (} ppm)	η	Ω(ppm)	k	ρ(ppm)	mode(σ)	τ(rad)
	LSDA										
					C ¹³		1				
C1	-33.217	-12.265	97.332	17.284	120.073	0.262	130.549	-0.679	121.436	0.900	0.374
C2	-45.848	22.711	93.473	23.446	105.042	0.979	139.321	-0.016	120.661	0.027	0.009
C3	-33.345	51.885	151.031	56.523	141.761	0.902	184.376	-0.075	159.825	0.130	0.044
C4	-53.867	40.729	172.725	53.196	179.293	0.791	226.591	-0.165	197.123	0.281	0.095
C5	-56.820	37.274	171.922	50.792	181.695	0.777	228.741	-0.177	199.131	0.301	0.102
C6	-30.388	37.842	162.356	56.603	158.629	0.645	192.744	-0.292	169.277	0.480	0.167
C8	85.829	94.900	181.196	120.642	90.831	0.150	95.367	-0.810	91.170	0.967	0.437
					H ¹				-		
H9	11.335	20.938	32.216	21.496	16.080	0.896	20.881	-0.080	18.103	0.138	0.046
H10	24.487	26.797	33.305	28.196	7.663	0.452	8.818	-0.476	7.919	0.721	0.268
H11	24.307	26.811	33.931	28.350	8.372	0.449	9.624	-0.480	8.648	0.725	0.270
H13	20.399	25.505	36.516	27.473	13.564	0.565	16.117	-0.366	14.267	0.585	0.208
H14	22.082	23.226	28.744	24.684	6.091	0.282	6.663	-0.656	6.171	0.885	0.362
H15	21.641	24.135	27.510	24.429	4.622	0.810	5.869	-0.150	5.102	0.256	0.086
H16	21.617	23.934	27.360	24.303	4.585	0.758	5.744	-0.193	5.005	0.327	0.111
H17	21.493	23.210	27.928	24.210	5.576	0.462	6.435	-0.466	5.771	0.710	0.263
					HSEH1PBE						
	_				C ¹³	_					
C1	-30.203	4.121	109.083	27.667	122.124	0.422	139.286	-0.507	125.689	0.754	0.285
C2	-41.849	30.136	105.533	31.273	111.390	0.969	147.382	-0.023	127.648	0.040	0.013
C3	-31.142	51.612	161.049	60.506	150.814	0.823	192.192	-0.139	166.977	0.238	0.080
C4	-51.149	45.210	178.786	57.616	181.755	0.795	229.934	-0.162	199.997	0.276	0.093
C5	-51.320	44.209	178.020	56.969	181.575	0.789	229.340	-0.167	199.534	0.284	0.096
C6	-24.392	47.603	168.264	63.825	156.658	0.689	192.655	-0.253	168.609	0.421	0.145
C8	118.344	229.276	323.862	223.828	150.052	1.109	205.518	0.080	178.171	-0.137	-0.046
					H^{1}						
H9	11.846	21.527	32.868	22.080	16.181	0.897	21.021	-0.079	18.224	0.136	0.046
H10	24.906	27.263	34.201	28.790	8.116	0.436	9.295	-0.493	8.369	0.739	0.277
H11	25.010	27.335	34.521	28.955	8.349	0.418	9.511	-0.511	8.588	0.759	0.287
H13	19.611	25.182	37.400	27.397	15.003	0.557	17.789	-0.374	15.760	0.595	0.212
H14	21.590	23.595	28.745	24.643	6.153	0.489	7.155	-0.440	6.393	0.678	0.249
H15	21.632	24.493	27.625	24.583	4.563	0.940	5.993	-0.045	5.192	0.079	0.026
H16	21.614	24.488	27.539	24.547	4.488	0.960	5.925	-0.030	5.132	0.052	0.017
H17	21.500	23.827	28.319	24.549	5.655	0.617	6.818	-0.318	6.003	0.518	0.181

Table 8. NMR –Chemical Shielding Anisotropy parameters of Guaiacol based on LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d,p) method.

 σ 1, σ 2, σ 3 - Eigen values of the symmetrized shielding tensor η- asymmetry Ω-span k- skew σ_{iso} - isotropic shielding tensor, σ aniso - Shielding Anisotropy ρ- magnitude of anisotropy, τ- orientation if anisotropy





When a paramagnetic substance is placed in a magnetic field, they will align themselves in the direction of the field and thus produces positive magnetic susceptibility, which depends on the temperature; since thermal agitation will oppose the alignment of the magnetic dipoles.





The effectiveness of the field diminishes with increase in temperature. The magnetic susceptibility (χ_m) of the molecules for various temperatures are predicted with knowledge of unpaired electron [50] and presented in Table 9. The graphical representation of (χ_m) with 1/T (temperature⁻¹) is shown in Fig. [16-18]. The effective magnetic moment is found to be a constant, which is 1.6900 x10⁻⁵ (BM) and the Curie constant is obtained from the magnetic moment (μ_m) and is found to be 3.0700x10⁻⁵.



Fig 18. The magnetic C / (T-theta) for Guaiacol. 11. Natural Charges

The total atomic charges of Guaiacol molecule are obtained by Mulliken population analysis with LSDA and HSEH1PBE /6-311++G (d, p) basis set are listed in Table 10. From the results, it is clear that the substitution in Guaiacol leads to the redistribution of electron density. The σ electron with drawing character of the Cl₇ atom in Guaiacol is demonstrated by the decrease in electron density on C₃ atom. In Guaiacol the C₈ atom is more acidic due to more positive charge. The Mulliken atomic charges of the methyl group hydrogen atoms are lesser than hydrogen atom. The graphical representation of atomic charges of the atoms obtained by LSDA for Guaiacol is shown in Fig. [19, 20].



Fig 19. The Mulliken charges distribution for Guaiacol.

Since the charge distribution on the molecule has an important influence on the vibrational spectra, the net charge distribution of Guaiacol was calculated by the natural population analysis (NPA) method with LSDA and HSEH1PBE /6-311++G (d, p) basis sets and the charges are listed in Table 10.

The corresponding NPA plot is shown in Fig. 20. The atomic charges of Guaiacol calculated by NPA analysis using LSDA and HSEH1PBE /6-311++G (d, p) basis sets are presented in Table 10. Among the carbon atoms C_2 and C_3 have positive charge while C_1 , C_4 and C_5 have negative charge.



Fig 20. Mulliken atomic charge and Natural Population Analysis Plot for Guaiacol. Table 10. Natural atomic charge distribution of Guaiacol on LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d,p)

methods.												
Atoms	Atomic Cha	Atomic Charges										
	LSDA/6-31	1++G(d,p)	HSEH1PBE/6-311++G(d,p)									
	Mulliken	NPA	Mulliken	NPA								
C1	-0.4977	0.2556	-0.4227	0.2610								
C2	0.0939	0.2267	-0.0166	0.2413								
C3	0.0661	-0.2762	0.0719	-0.2549								
C4	-0.2190	-0.2342	-0.2721	-0.2190								
C5	-0.2179	-0.2270	-0.2446	-0.2154								
C6	-0.1147	-0.2505	0.0676	-0.2452								
07	-0.0731	-0.5197	-0.1193	-0.5716								
C8	-0.4653	-0.3127	-0.4053	-0.2396								
H9	0.2001	0.2367	0.1840	0.2245								
H10	0.1945	0.2027	0.1759	0.1795								
H11	0.1815	0.1861	0.1553	0.1642								
012	-0.2183	-0.7102	-0.2369	-0.7261								
H13	0.2852	0.4908	0.2723	0.4978								
H14	0.1475	0.2290	0.1612	0.2286								
H15	0.2043	0.2284	0.1991	0.2214								
H16	0.2067	0.2292	0.2016	0.2214								
H17	0.2264	0.2455	0.2286	0.2323								

12. Conclusion

A complete structural, thermodynamic, vibrational and electronic investigations along with FT-IR and FT-Raman spectroscopes and were performed on Guaiacol order to identify its structural and spectroscopic properties. A complete vibrational analysis of Guaiacol was performed using the basis of *ab initio* DFT calculation based on LSDA and HSEH1PBE level with the standard basis sets 6- 311++G (d, p). Comparison between the calculated and experimental structural parameters indicated that LSDA and HSEH1PBE was in good agreement with experimental observations. Complete vibrational analysis of Guaiacol has been investigated by FT-IR and FT-Raman spectroscopy.

Table 9. Magnetic susceptibility of Guaiacolby LSDA/6311++G(d,p) and HSEH1PBE/6311++G(d,p).

Temperature	LS	DA/6-311++G(d,p)		HSEH1PBE/6-311++G(d,p)			
	Magnetic susceptibility	1/Susceptibility	1/Temperature	Magnetic susceptibility	1/Susceptibility	1/Temperature	
50	1.23E-06	8.14E+05	2.00E-02	1.69E-06	5.91E+05	2.00E-02	
100	6.14E-07	1.63E+06	1.00E-02	8.46E-07	1.18E+06	1.00E-02	
150	4.10E-07	2.44E+06	6.67E-03	5.64E-07	1.77E+06	6.67E-03	
200	3.07E-07	3.25E+06	5.00E-03	4.23E-07	2.36E+06	5.00E-03	
250	2.46E-07	4.07E+06	4.00E-03	3.38E-07	2.96E+06	4.00E-03	
273	2.25E-07	4.44E+06	3.66E-03	3.10E-07	3.23E+06	3.66E-03	
298.15	2.06E-07	4.85E+06	3.35E-03	2.84E-07	3.52E+06	3.35E-03	
300	2.05E-07	4.88E+06	3.33E-03	2.82E-07	3.55E+06	3.33E-03	
350	1.76E-07	5.70E+06	2.86E-03	2.42E-07	4.14E+06	2.86E-03	
400	1.54E-07	6.51E+06	2.50E-03	2.11E-07	4.73E+06	2.50E-03	
450	1.37E-07	7.32E+06	2.22E-03	1.88E-07	5.32E+06	2.22E-03	
500	1.23E-07	8.14E+06	2.00E-03	1.69E-07	5.91E+06	2.00E-03	

The intermolecular hydrogen bond in dimer structure was also analyzed. The effects of hydrogen bond due to dimerization were discussed with the natural atomic hybridization. The role of nitro and carboxylic group in the vibrational frequencies of the title compound has been studied. . NBO analysis has also been performed on Guaiacol molecule, in order to elucidate intermolecular hvdrogen bonding, intermolecular charge transfer. rehybridization and delocalization of electron density. Thermodynamic parameters were calculated theoretically for the range 100-1000 K. The electric dipole moments and the first order hyperpolarizability of the compound have been calculated by DFT method. Quantum chemical parameters such as HOMO, LUMO, other molecular studies and NMRchemical shielding anisotropy (CSA) parameters of Guaiacol have been computed.

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