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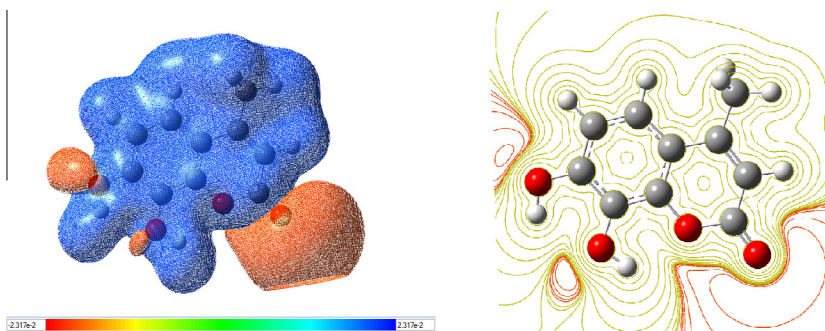
Infrared, Raman and NMR spectra, conformational stability and vibrational assignment of 7,8-Dihydroxy-4-Methylcoumarin [☆]

Yusuf Erdogdu ^{a,*}, Semran Saglam ^b^a Department of Physics, Ahi Evran University, 40040 Kirsehir, Turkey^b Department of Physics, Gazi University, 06100 Ankara, Turkey

HIGHLIGHTS

- FT-IR, FT-Raman and FT-NMR spectra of 7,8-Dihydroxy-4-Methylcoumarin molecule are recorded and analyzed.
- Theoretical approach to spectra based on DFT (B3LYP) method with cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets.
- The observed and calculated FT-IR, FT-Raman and NMR experimental data are in close agreement.
- The most stable conformer has been predicted.
- All calculations are calculated theoretically using Gaussian 09 and Spartan 10 software.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a combined some (infrared, Raman and NMR) spectroscopic and quantum chemistry study on 7,8-Dihydroxy-4-Methylcoumarin molecule (78D4MC). The Raman and IR spectra of 78D4MC molecule were recorded and analyzed in the region $3500\text{--}50\text{ cm}^{-1}$ and $4000\text{--}400\text{ cm}^{-1}$, respectively. Potential energy scans were performed at the MMFF level of theory. All possible conformers, which are results at the MMFF level theory, were re-computed at the B3LYP functional with cc-pVDZ basis set. The optimized geometrical parameters, harmonic vibrational wavenumbers and NMR chemical shifts of the most stable conformer were calculated at the B3LYP/6-311G(d,p), cc-pVTZ and cc-pVQZ level in the proximity of the isolated molecule. DFT calculations were combined with Pulay's scaled quantum mechanics force field (SQMFF) methodology in order to fit the theoretical wavenumbers to the experimental ones.

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Introduction

Coumarins are a class of O-heterocyclic natural products widely distributed in high plants, but also found in fungi and bacteria, being structurally characterized by the presence of the

2H-benzopyran-2-one nucleus [1–3]. Coumarin dyes are widely employed in the chemical industry, medicine, engineering and physics, with widely different applications such as for providing fragrance or for generating laser light in the green–blue spectral region [4–6]. Coumarins and their derivatives, natural or synthetic, have diverse toxicities. The constituents of the benzopyrone ring can serve, for example, as fungicide, antibacterial and anti-HIV agents [7] and can possess antithrombotic properties, reducing total cholesterol and triglycerides and causing hypotension in vivo, among effects [8]. One of the more than 1300 coumarins

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* Corresponding author. Tel.: +90 3862528050; fax: +90 3862528054.

E-mail address: yusuferdogdu@gmail.com (Y. Erdogdu).

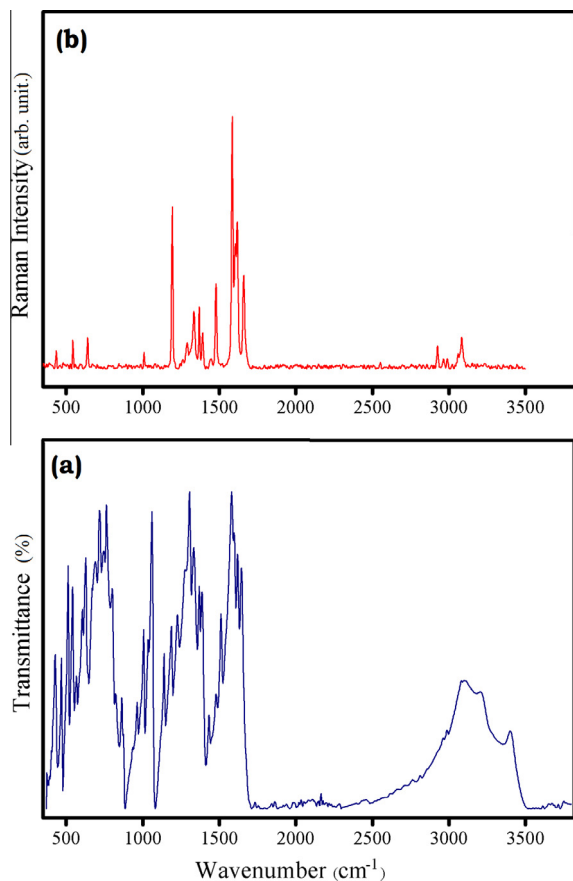


Fig. 1. FT-IR (a) and FT-Raman (b) spectra of 78D4MC.

already identified is seselin, a naturally occurring angular pyranocoumarin that exhibits some important biological properties, such as anticancer [9] and antifungal [10].

To the best of our knowledge, no geometrical structure and detailed vibrational analysis data for 78D4MC molecule were yet published. With this study, we intend to gain a deeper insight into the structure, vibrational (FT-IR and FT-Raman) and Nuclear Magnetic Resonance spectra of this biologically active molecule. FT-IR, FT-Raman and NMR spectroscopic study of the 78D4MC molecule in the spectral range 4000–400 cm^{-1} (FT-IR) and 3500–50 cm^{-1} (FT-Raman) were recorded. In addition, Density Functional Theory (DFT) calculations were performed for an isolated molecule. The results were used to assign the observed wavenumbers to the vibrational modes. Good agreement between the predicted values and observed wavenumbers was obtained.

Experimental

The FT-IR spectrum of 78D4MC molecule which was recorded in the region 4000–400 cm^{-1} on IFS 66 V spectrophotometer using KBr pellet technique is shown in Fig. 1. The spectral resolution is $\pm 2 \text{ cm}^{-1}$. As shown in Fig. 1 is the FT-Raman spectrum of 78D4MC molecule, which has been recorded with Bruker FRA 106/S in the region 50–3500 cm^{-1} using 1064 nm line of Nd:YAG laser as excitation. The spectra were recorded with scanning speed of 30 $\text{cm}^{-1} \text{ min}^{-1}$ of spectral width 2 cm^{-1} . The frequencies of all sharp bands were accurate to $\pm 1 \text{ cm}^{-1}$. The ^{13}C NMR spectra were taken in chloroform solutions and all signals were referenced to TMS on a Bruker Superconducting FT-NMR Spectrometer.

Computational procedure

All calculations were performed at Density Functional Theory [11,12] using Gaussian 09 program [13], invoking gradient

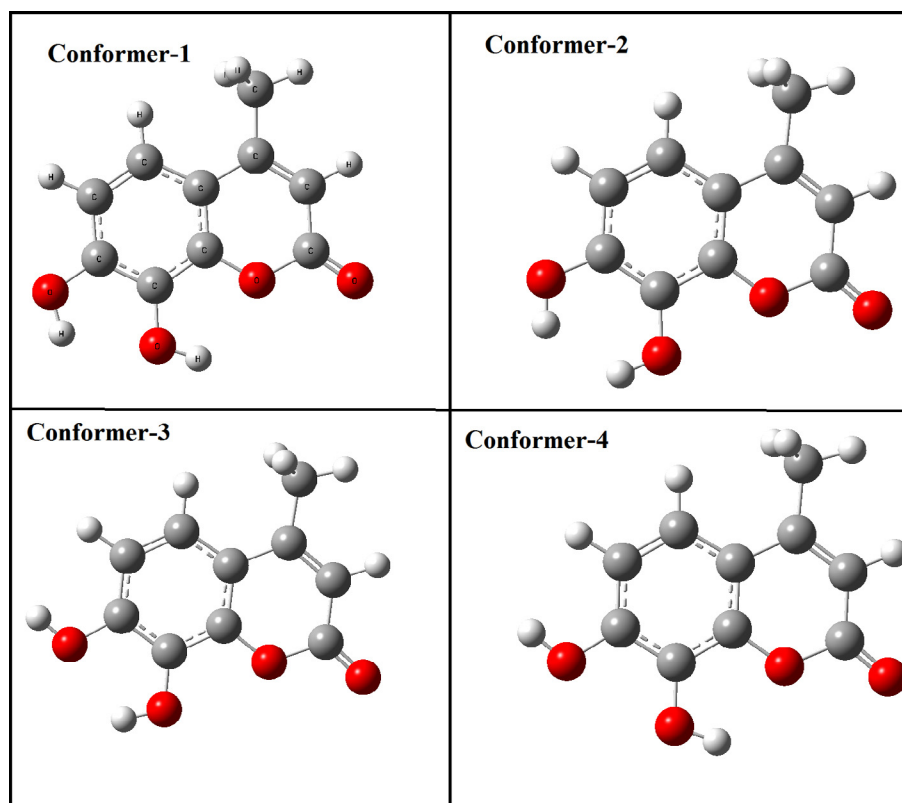


Fig. 2. All conformers and its geometry of 78D4MC.

Table 1

Energetic of the four conformers of 7,8-Dihydroxy-4-Methylcoumarin calculated at the B3LYP/cc-pVDZ level.

Conformers	E (Hartree)	ΔE (kcal/mol)
Conformer-1	−686.98627867	0.000
Conformer-2	−686.96652936	0.155
Conformer-3	−686.97781310	5.078
Conformer-4	−686.97903643	5.268

geometry optimization [14]. Geometry optimization, harmonic vibrational spectra and NMR spectra were calculated B3LYP method [15–18]. Later, based on the SQMFF procedure [19], the harmonic force fields for the more stable conformer were evaluated at the same theory level. The theoretical vibrational spectra of 78D4MC molecule were interpreted by means of Total Energy Distribution (TED) using the SQM program [20]. Only TED

components $\geq 10\%$ was considered to perform the final assignment. It should be noted that Gaussian 09 program does not calculate the Raman intensities. The Raman activities were transformed into Raman intensities by using Raint program [21].

Results and discussion

Conformational analysis and geometry optimization

In order to determine the possible conformations of 78D4MC molecule, potential energy scans were performed using the Spartan 10 [22] program at the MMFF level of theory. The scans were performed minimizing the potential energy in all geometrical parameters, which involved varying the dihedral angles at a step of 10° in the range of 0– 360° rotation around the bond and some atoms. Candidate conformational geometries of 78D4MC molecule were re-optimized by B3LYP/cc-pVDZ level of theory. Since

Table 2

Optimized geometric parameters of 7,8-Dihydroxy-4-Methylcoumarin.

Bond lengths (Angstrom)	Bond angles (Degree)		Dihedral angles (Degree)				
	Theoretical	X-ray ^a	Theoretical	X-ray ^a			
C ₁ –C ₂	1.401	1.393	C ₂ –C ₁ –C ₆	119.6	120.9	C ₆ –C ₁ –C ₂ –C ₃	0.001
C ₁ –C ₆	1.403	1.395	C ₂ –C ₁ –O ₁₆	120.2	116.0	C ₆ –C ₁ –C ₂ –O ₁₅	179.9
C ₁ –O ₁₆	1.356	1.369	C ₆ –C ₁ –O ₁₆	120.1	123.1	O ₁₆ –C ₁ –C ₂ –C ₃	180.0
C ₂ –C ₃	1.395	1.390	C ₁ –C ₂ –C ₃	119.5	117.5	O ₁₆ –C ₁ –C ₂ –O ₁₅	−0.002
C ₂ –O ₁₅	1.368	1.357	C ₁ –C ₂ –O ₁₅	117.7	123.2	C ₂ –C ₁ –C ₆ –C ₅	0.005
C ₃ –C ₄	1.408	1.402	C ₃ –C ₂ –O ₁₅	122.7	119.3	C ₂ –C ₁ –C ₆ –H ₉	179.9
C ₃ –O ₁₄	1.367	1.380	C ₂ –C ₃ –C ₄	121.7	122.7	O ₁₆ –C ₁ –C ₆ –C ₅	−179.9
C ₄ –C ₅	1.411	1.386	C ₂ –C ₃ –O ₁₄	115.0	115.4	O ₁₆ –C ₁ –C ₆ –H ₉	−0.005
C ₄ –C ₇	1.453	1.451	C ₄ –C ₃ –O ₁₄	123.1	121.8	C ₂ –C ₁ –O ₁₆ –H ₂₁	0.001
C ₅ –C ₆	1.390	1.357	C ₃ –C ₄ –C ₅	117.6	116.6	C ₆ –C ₁ –O ₁₆ –H ₂₁	−179.9
C ₅ –H ₈	1.090		C ₃ –C ₄ –C ₇	117.0	117.8	C ₁ –C ₂ –C ₃ –C ₄	−0.001
C ₆ –H ₉	1.090		C ₅ –C ₄ –C ₇	125.2	125.5	C ₁ –C ₂ –C ₃ –O ₁₄	179.9
C ₇ –C ₁₀	1.363	1.346	C ₄ –C ₅ –C ₆	121.1	122.8	O ₁₅ –C ₂ –C ₃ –C ₄	−179.9
C ₇ –C ₁₇	1.503	1.496	C ₄ –C ₅ –H ₈	119.6		O ₁₅ –C ₂ –C ₃ –O ₁₄	−0.003
C ₁₀ –C ₁₁	1.454	1.431	C ₆ –C ₅ –H ₈	119.2		C ₁ –C ₂ –O ₁₅ –H ₂₂	180.0
C ₁₀ –H ₁₂	1.090		C ₁ –C ₆ –C ₅	120.3	119.4	C ₃ –C ₂ –O ₁₅ –H ₂₂	−0.001
C ₁₁ –O ₁₃	1.205	1.230	C ₁ –C ₆ –H ₉	118.2		C ₂ –C ₃ –C ₄ –C ₅	−0.000
C ₁₁ –O ₁₄	1.408	1.358	C ₅ –C ₆ –H ₉	121.4		C ₂ –C ₃ –C ₄ –C ₇	−179.9
O ₁₅ –H ₂₂	0.972		C ₄ –C ₇ –C ₁₀	118.9	118.5	O ₁₄ –C ₃ –C ₄ –C ₅	−179.9
O ₁₆ –H ₂₁	0.972		C ₄ –C ₇ –C ₁₇	120.0	119.9	O ₁₄ –C ₃ –C ₄ –C ₇	0.012
C ₁₇ –H ₁₈	1.102		C ₁₀ –C ₇ –C ₁₇	121.0	121.6	C ₂ –C ₃ –O ₁₄ –C ₁₁	180.0
C ₁₇ –H ₁₉	1.102		C ₇ –C ₁₀ –C ₁₁	123.7	122.6	C ₄ –C ₃ –O ₁₄ –C ₁₁	0.012
C ₁₇ –H ₂₀	1.098		C ₇ –C ₁₀ –H ₁₂	121.6		C ₃ –C ₄ –C ₅ –C ₆	0.001
			C ₁₁ –C ₁₀ –H ₁₂	114.6		C ₃ –C ₄ –C ₅ –H ₈	−179.9
			C ₁₀ –C ₁₁ –O ₁₃	127.2	125.5	C ₇ –C ₄ –C ₅ –C ₆	179.9
			C ₁₀ –C ₁₁ –O ₁₄	115.5	118.7	C ₇ –C ₄ –C ₅ –H ₈	−0.006
			O ₁₃ –C ₁₁ –O ₁₄	117.1	115.8	C ₃ –C ₄ –C ₇ –C ₁₀	−0.007
			C ₃ –O ₁₄ –C ₁₁	121.4	120.6	C ₃ –C ₄ –C ₇ –C ₁₇	−180.0
			C ₂ –O ₁₅ –H ₂₂	107.7		C ₅ –C ₄ –C ₇ –C ₁₀	−179.9
			C ₁ –O ₁₆ –H ₂₁	107.4		C ₅ –C ₄ –C ₇ –C ₁₇	−0.004
			C ₇ –C ₁₇ –H ₁₈	110.9		C ₄ –C ₅ –C ₆ –C ₁	−0.002
			C ₇ –C ₁₇ –H ₁₉	110.9		C ₄ –C ₅ –C ₆ –H ₉	179.9
			C ₇ –C ₁₇ –H ₂₀	111.2		H ₈ –C ₅ –C ₆ –C ₁	179.9
			H ₁₈ –C ₁₇ –H ₁₉	106.8		H ₈ –C ₅ –C ₆ –H ₉	−0.001
			H ₁₈ –C ₁₇ –H ₂₀	108.3		C ₄ –C ₇ –C ₁₀ –C ₁₁	−0.024
			H ₁₉ –C ₁₇ –H ₂₀	108.3		C ₄ –C ₇ –C ₁₀ –H ₁₂	179.9
						C ₁₇ –C ₇ –C ₁₀ –C ₁₁	−180.0
						C ₁₇ –C ₇ –C ₁₀ –H ₁₂	−0.018
						C ₄ –C ₇ –C ₁₇ –H ₁₈	−59.32
						C ₄ –C ₇ –C ₁₇ –H ₁₉	59.31
						C ₄ –C ₇ –C ₁₇ –H ₂₀	179.9
						C ₁₀ –C ₇ –C ₁₇ –H ₁₈	120.6
						C ₁₀ –C ₇ –C ₁₇ –H ₁₉	−120.6
						C ₁₀ –C ₇ –C ₁₇ –H ₂₀	−0.007
						C ₇ –C ₁₀ –C ₁₁ –O ₁₃	179.9
						C ₇ –C ₁₀ –C ₁₁ –O ₁₄	0.048
						H ₁₂ –C ₁₀ –C ₁₁ –O ₁₃	−0.089
						H ₁₂ –C ₁₀ –C ₁₁ –O ₁₄	180.0
						C ₁₀ –C ₁₁ –O ₁₄ –C ₃	−0.041
						O ₁₃ –C ₁₁ –O ₁₄ –C ₃	−179.9

^a X-ray data taken from Ref. [23].

Table 3
Calculated and observed wavenumbers (cm^{-1}) of 7,8-Dihydroxy-4-Methylcoumarin.

Theoretical (B3LYP)						Experimental			
Mode		6-311G(d,p)			cc-pVTZ	cc-pVQZ			
No.	Sym.	Freq ^a	I _{IR} ^b	I _{Raman} ^b	Freq ^a	Freq ^a	FT-IR	FT-Raman	% TED ^c
V ₁	A''	78	0	4	79	78			$\tau_{\text{cccc}}(27\%) + \tau_{\text{occc}}(12\%) + \tau_{\text{cocc}}(15\%) + \tau_{\text{coco}}(11\%)$
V ₂	A''	100	0	12	100	101			$\tau_{\text{cccc}}(46\%) + \tau_{\text{ccco}}(15\%) + \tau_{\text{cocc}}(12\%)$
V ₃	A''	153	0	5	155	156			$\tau_{\text{cccc}}(27\%) + \tau_{\text{occc}}(25\%) + \tau_{\text{Hccc}}(21\%)$
V ₄	A''	172	0	1	174	175			$\tau_{\text{cccc}}(11\%) + \tau_{\text{occc}}(22\%) + \tau_{\text{cocc}}(12\%) + \tau_{\text{occo}}(10\%)$
V ₅	A''	200	0	11	202	203			$\delta_{\text{ccc}}(34\%) + \delta_{\text{occ}}(37\%)$
V ₆	A'	204	1	11	205	206			$\tau_{\text{Hccc}}(62\%) + \tau_{\text{cccc}}(13\%)$
V ₇	A'	278	1	6	279	281			$\delta_{\text{occ}}(55\%) + \delta_{\text{ccc}}(26\%)$
V ₈	A''	285	0	4	287	287			$\tau_{\text{cccc}}(30\%) + \tau_{\text{occc}}(26\%)$
V ₉	A'	302	0	9	302	304			$\delta_{\text{occ}}(38\%) + \delta_{\text{ccc}}(33\%)$
V ₁₀	A''	313	2	2	315	316			$\tau_{\text{ccco}}(50\%) + \tau_{\text{Hccc}}(20\%)$
V ₁₁	A''	377	26	16	374	384	391		$\tau_{\text{Hccc}}(92\%)$
V ₁₂	A'	398	0	36	398	400	401		$\nu_{\text{oc}}(11\%) + \delta_{\text{ccc}}(26\%) + \delta_{\text{occ}}(17\%) + \delta_{\text{oco}}(12\%)$
V ₁₃	A'	414	0	49	415	417	427	432	$\nu_{\text{cc}}(13\%) + \delta_{\text{ccc}}(18\%) + \delta_{\text{occ}}(24\%) + \delta_{\text{coc}}(16\%)$
V ₁₄	A''	449	6	6	449	452			$\delta_{\text{ccc}}(49\%) + \delta_{\text{occ}}(25\%)$
V ₁₅	A'	458	2	5	458	460	468		$\tau_{\text{Hccc}}(93\%)$
V ₁₆	A''	500	1	8	509	510			$\tau_{\text{cccc}}(36\%) + \tau_{\text{occc}}(10\%) + \tau_{\text{Hccc}}(11\%)$
V ₁₇	A'	518	1	39	518	520	512		$\nu_{\text{cc}}(31\%) + \delta_{\text{ccc}}(19\%) + \delta_{\text{occ}}(21\%)$
V ₁₈	A''	552	0	2	562	564	566	543	$\tau_{\text{cccc}}(29\%) + \tau_{\text{ccch}}(15\%) + \tau_{\text{ccco}}(11\%) + \tau_{\text{occo}}(13\%)$
V ₁₉	A'	592	1	5	592	595	605		$\delta_{\text{ccc}}(33\%) + \delta_{\text{occ}}(24\%) + \delta_{\text{oco}}(18\%)$
V ₂₀	A''	610	0	1	618	621			$\nu_{\text{cc}}(25\%) + \nu_{\text{oc}}(13\%) + \delta_{\text{ccc}}(10\%) + \delta_{\text{cco}}(30\%)$
V ₂₁	A'	618	6	61	624	627	627	638	$\tau_{\text{cccc}}(16\%) + \tau_{\text{Hccc}}(18\%) + \tau_{\text{occc}}(15\%) + \tau_{\text{occo}}(10\%)$
V ₂₂	A''	668	0	0	693	696	690		$\nu_{\text{cc}}(24\%) + \delta_{\text{ccc}}(23\%) + \delta_{\text{occ}}(11\%)$
V ₂₃	A'	693	0	1	699	702	717		$\tau_{\text{Hccc}}(13\%) + \tau_{\text{occc}}(18\%) + \tau_{\text{cocc}}(10\%) + \tau_{\text{occh}}(16\%)$
V ₂₄	A''	709	2	4	741	747	745		$\tau_{\text{cccc}}(44\%) + \tau_{\text{cocc}}(10\%) + \tau_{\text{occo}}(11\%)$
V ₂₅	A'	780	0	9	781	785	761		$\nu_{\text{cc}}(27\%) + \nu_{\text{oc}}(19\%) + \delta_{\text{ccc}}(10\%) + \delta_{\text{oco}}(10\%) + \delta_{\text{cco}}(10\%)$
V ₂₆	A''	784	3	0	795	798	800		$\tau_{\text{Hccc}}(62\%) + \tau_{\text{Hcco}}(19\%)$
V ₂₇	A'	805	4	12	808	813	822		$\nu_{\text{cc}}(16\%) + \nu_{\text{oc}}(45\%)$
V ₂₈	A''	845	5	2	853	855	862		$\tau_{\text{Hccc}}(37\%) + \tau_{\text{occh}}(44\%)$
V ₂₉	A''	902	0	0	918	922			$\tau_{\text{Hccc}}(42\%) + \tau_{\text{Hcch}}(43\%) + \tau_{\text{Hcco}}(10\%)$
V ₃₀	A'	926	6	5	926	930	933		$\nu_{\text{cc}}(32\%) + \nu_{\text{oc}}(22\%) + \delta_{\text{ccc}}(10\%)$
V ₃₁	A'	989	3	30	988	992			$\delta_{\text{Hcc}}(49\%) + \tau_{\text{Hccc}}(16\%)$
V ₃₂	A''	1025	0	1	1028	1032	1006	1006	$\delta_{\text{Hcc}}(58\%) + \tau_{\text{Hccc}}(40\%)$
V ₃₃	A'	1027	15	16	1028	1032	1034		$\nu_{\text{cc}}(11\%) + \nu_{\text{oc}}(50\%) + \delta_{\text{Hcc}}(14\%)$
V ₃₄	A'	1097	8	47	1099	1103			$\nu_{\text{cc}}(38\%) + \delta_{\text{Hcc}}(40\%)$
V ₃₅	A'	1121	7	40	1122	1127	1140		$\nu_{\text{cc}}(35\%) + \nu_{\text{oc}}(11\%) + \delta_{\text{Hcc}}(17\%) + \delta_{\text{hoc}}(10\%)$
V ₃₆	A'	1167	15	9	1164	1167			$\nu_{\text{cc}}(21\%) + \nu_{\text{oc}}(14\%) + \delta_{\text{Hcc}}(28\%) + \delta_{\text{hoc}}(21\%)$
V ₃₇	A'	1187	13	13	1184	1188	1188	1194	$\nu_{\text{cc}}(21\%) + \delta_{\text{Hcc}}(26\%) + \delta_{\text{hoc}}(25\%)$
V ₃₈	A'	1221	23	18	1216	1219			$\nu_{\text{cc}}(15\%) + \delta_{\text{Hcc}}(52\%)$
V ₃₉	A'	1224	2	3	1225	1230	1226		$\nu_{\text{cc}}(18\%) + \nu_{\text{oc}}(22\%) + \delta_{\text{hoc}}(28\%)$
V ₄₀	A'	1269	38	12	1263	1265	1273	1290	$\nu_{\text{cc}}(10\%) + \nu_{\text{oc}}(45\%) + \delta_{\text{hoc}}(19\%)$
V ₄₁	A'	1333	14	1	1333	1338	1332	1336	$\delta_{\text{Hcc}}(40\%) + \delta_{\text{hoc}}(17\%)$
V ₄₂	A'	1361	3	70	1358	1361	1367	1369	$\delta_{\text{Hcc}}(37\%) + \delta_{\text{Hcch}}(41\%)$
V ₄₃	A'	1367	1	3	1363	1368	1386	1390	$\nu_{\text{cc}}(57\%) + \delta_{\text{hoc}}(11\%)$
V ₄₄	A'	1382	6	29	1378	1382			$\nu_{\text{cc}}(45\%) + \delta_{\text{hoc}}(24\%)$
V ₄₅	A'	1434	23	34	1431	1434			$\delta_{\text{Hcc}}(14\%) + \delta_{\text{Hcch}}(58\%) + \tau_{\text{Hccc}}(19\%)$
V ₄₆	A''	1435	2	9	1431	1437	1432	1446	$\delta_{\text{Hcch}}(62\%) + \tau_{\text{Hccc}}(24\%)$
V ₄₇	A'	1445	5	20	1441	1447	1479	1480	$\nu_{\text{cc}}(50\%) + \nu_{\text{oc}}(13\%) + \delta_{\text{Hcc}}(10\%)$
V ₄₈	A'	1502	4	8	1500	1505	1510		$\nu_{\text{cc}}(39\%) + \nu_{\text{oc}}(16\%) + \delta_{\text{Hcc}}(21\%)$
V ₄₉	A'	1568	16	91	1564	1568	1580	1586	$\nu_{\text{cc}}(63\%)$
V ₅₀	A'	1605	31	100	1601	1605	1618	1617	$\nu_{\text{cc}}(61\%)$
V ₅₁	A'	1610	12	28	1605	1608	1644	1660	$\nu_{\text{cc}}(67\%)$
V ₅₂	A'	1766	100	52	1750	1748	1732		$\nu_{\text{oc}}(84\%)$
V ₅₃	A'	2931	1	27	2927	2937	2962	2925	$\nu_{\text{HC}}(99\%)$
V ₅₄	A''	2980	2	11	2973	2984	2986	2986	$\nu_{\text{HC}}(100\%)$
V ₅₅	A'	3020	3	11	3013	3024			$\nu_{\text{HC}}(100\%)$
V ₅₆	A'	3088	0	9	3083	3093	3079	3084	$\nu_{\text{HC}}(99\%)$
V ₅₇	A'	3099	0	15	3093	3103			$\nu_{\text{HC}}(99\%)$
V ₅₈	A'	3102	1	22	3096	3107			$\nu_{\text{HC}}(100\%)$
V ₅₉	A'	3654	20	10	3635	3656			$\nu_{\text{HO}}(100\%)$
V ₆₀	A'	3658	12	3	3638	3658			$\nu_{\text{HO}}(100\%)$

^a Obtained from the wave numbers calculated at 0.967 for 6-311G(d,p), 0.965 for cc-pVTZ, 0.969 for cc-pVQZ. ν : stretching, δ : in-plane bending, γ : out-of plane bending, τ : torsion.

^b Relative absorption intensities and Relative Raman intensities normalized with highest peak absorption equal to 100.

^c Total energy distribution calculated B3LYP/6-311G(d,p) level of theory. Only contributions 10% are listed.

conformer-1 was determined to be the most stable as shown in Fig. 2, its properties were further specified using B3LYP method with 6-311G(d,p), cc-pVTZ and cc-pVQZ basis sets. Other conformations were not considered because of their high energy. For

comparison, ground state energies and relative energies of all conformers were listed in Table 1.

The optimized geometrical parameters (bond lengths, bond angles and dihedral angles) of the conformer 1 were given in Table 2.

The calculated geometrical parameters are compared with X-ray data [23].

Vibrational analysis

The molecule 78D4MC molecule consist of 22 atoms, hence one have 60 normal modes of vibrations. A complete vibrational analysis of the 60 fundamental vibrational modes of 78D4MC molecule has been done using B3LYP level with 6-311G(d,p), cc-pVTZ and cc-pVQZ basis sets. 78D4MC molecule belongs to C_s point group symmetry. The 60 fundamental vibrations of the molecule can be distributed as 40 in-plane vibrations of A' species and 20 out-of-plane vibrations of A'' species, i.e., $\Gamma_{\text{vib}} = 40A' + 20A''$. The calculated vibrational wavenumbers, observed at FT-IR and FT-Raman peaks and the calculated TED for each normal mode were listed in Table 3. The assignments in Table 3 were given as per the internal coordinate system suggested by Pulay et al. The experimental FT-IR spectra in 4000–400 cm^{-1} region and corresponding Raman spectra in 3500–100 cm^{-1} region is shown in Fig. 1. A close agreement between the scaled and experimental frequencies of the infrared and Raman bands can be noticed by comparing Fig. 1 and Table 3. Correlation plots between calculated and observed wavenumbers are shown in Fig. 3.

The Infrared spectrum of 78D4MC molecule displays four peaks within the 2900–3100 cm^{-1} region. Within 2900–3200 cm^{-1} region, CH stretching vibrations were determined in the previous

studies [24–30]. In this region, there are three CH_3 stretching vibrations of the methyl group. The methyl group belongs to one symmetric CH_3 and two asymmetric CH_3 stretching vibrations. Of these, the highest peak (2986 cm^{-1}) was observed for the asymmetric stretching vibrations in the FT-IR spectra. This peak was predicted at 2980 cm^{-1} (6-311G(d,p)), 2973 cm^{-1} (cc-pVTZ) and 2984 (cc-pVQZ) using the DFT calculations. The other asymmetric stretching vibration could not be detected by means of either FT-IR or FT-Raman spectra. The symmetric CH_3 vibration the methyl group experimentally observed at 2962 cm^{-1} (FT-IR) and 2925 cm^{-1} (FT-Raman). This vibration was predicted at 2931 cm^{-1} (6-311G(d,p)) using theoretical calculations.

Vibrations of the methyl group in 78D4MC molecule should be described by 12 normal modes [31]. But, we evaluate some bending vibrations as following text. 1432 cm^{-1} (FT-IR), 1446 cm^{-1} (FT-Raman) and 1435 cm^{-1} (B3LYP/6-311G(d,p)) peak was assigned to the CH_3 scissoring vibrations (modes no: 46). Other scissoring vibration was predicted 1434 cm^{-1} . But, the IR and Raman counterpart of this vibration could not be measured. A CH_3 wagging vibration was observed at 1367 cm^{-1} (FT-IR), 1369 cm^{-1} (FT-Raman). Twisting vibration was observed at 1006 cm^{-1} (FT-IR, FT-Raman). The same mode was theoretically calculated at 1025 cm^{-1} using B3LYP/6-311G(d,p) level of theory.

The coumarin ring of 78D4MC molecule has three CH stretching vibrations. We observed only one CH stretching vibration in the

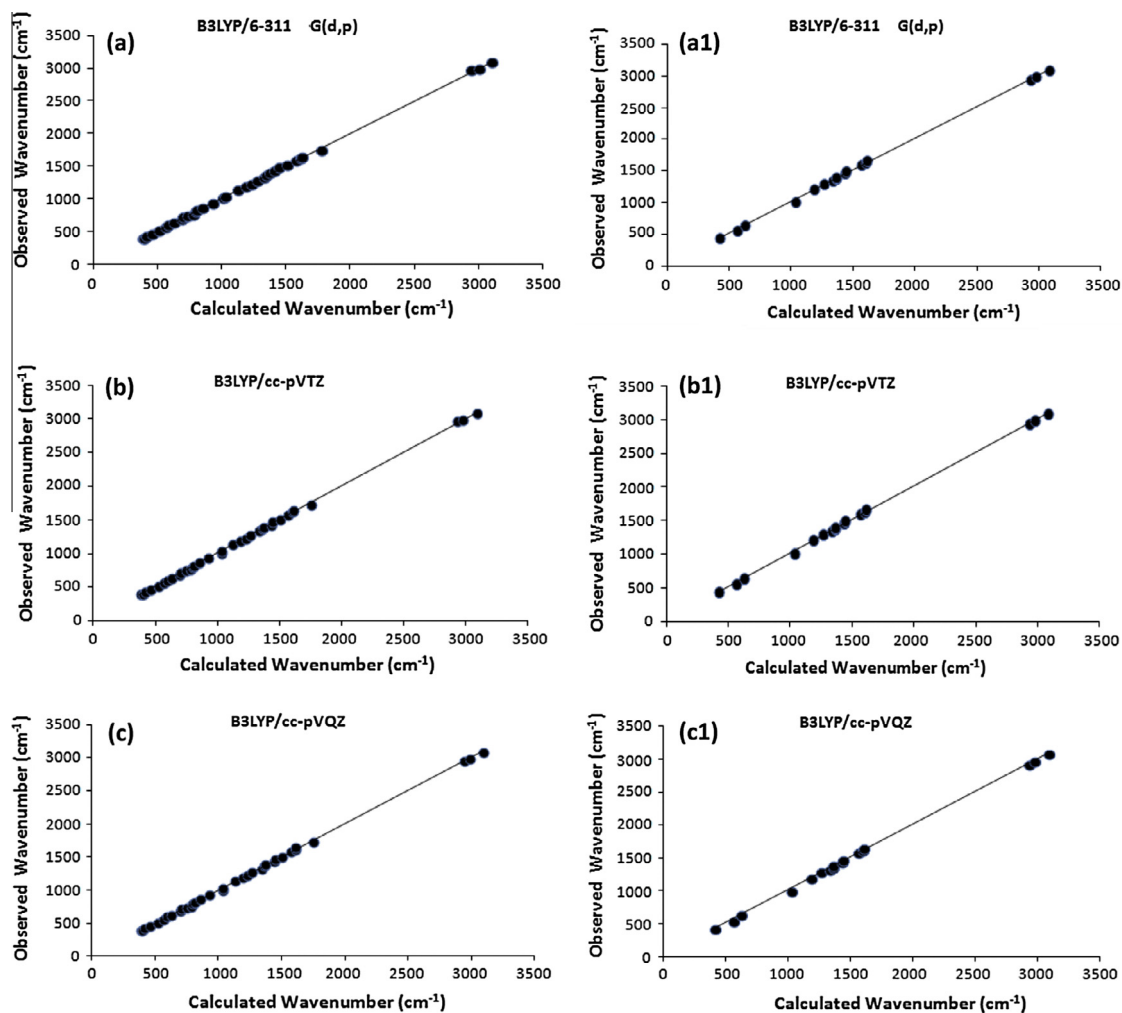


Fig. 3. Correlation plot between calculated and experimental wavenumbers [a, b and c plots are infrared spectral data. a1, b1 and c1 are Raman spectral data].

Table 4

The observed and predicted ^1H and ^{13}C NMR isotropic chemical shifts of 78D4MC (with respect to TMS, all values in ppm).

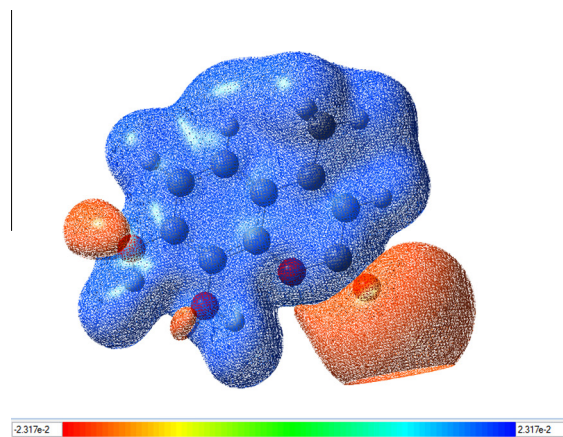
Atom numbering	Theoretical (B3LYP)			Experimental
	6-311G(d,p)	cc-pVTZ	cc-pVQZ	
C ₇	163.2	165.0	171.5	161.4
C ₁₁	161.7	164.9	170.7	155.2
C ₁	154.0	154.8	160.5	142.0
C ₃	148.0	149.9	154.6	136.9
C ₂	136.2	136.7	141.9	129.0
C ₅	121.0	121.8	127.0	109.7
C ₄	117.6	119.2	124.5	108.3
C ₆	115.1	115.2	120.3	104.9
C ₁₀	113.6	113.4	118.5	104.9
C ₁₇	21.44	21.59	24.43	14.89
H ₁₈	2.70	3.11	3.20	2.40
H ₁₉	2.70	3.11	3.20	2.40
H ₂₀	2.31	2.71	2.81	2.40
H ₂₂	5.52	6.27	6.55	6.21
H ₂₁	5.61	6.35	6.58	6.21
H ₁₂	6.13	6.54	6.69	6.80
H ₉	7.15	7.51	7.64	7.10
H ₈	7.39	7.86	7.97	7.10

^a ^1H NMR data taken from Ref. [38].

coumarin ring. The Infrared line at 3079 cm^{-1} , which has a Raman counterpart at 3084 cm^{-1} can be attributed to the CH stretching mode in the coumarin ring.

The Carbon=Oxygen (C=O) bands of the coumarin and its derivative are the most characteristic bands in the vibration spectrum. The C=O stretching vibrations are generally found in the region $1780\text{--}1700\text{ cm}^{-1}$. In this work, $\nu(\text{C=O})$ vibration of 78D4MC molecule was experimentally measured at 1732 cm^{-1} (FT-IR) as a weak band. Our calculation, this peak was calculated at 1766 cm^{-1} as very strong intensity. The intensity difference between observed and calculated vibration may come from the environment of the molecule. It is clear that the experimental results possess powder form, while theoretical calculations belong to gaseous phase.

In this region, other characteristic peak is the Carbon–Carbon (CC) bond stretching vibrations. CC stretching vibrations were measured smaller than C=O vibrations. In the FT-IR spectra, 1479 cm^{-1} , 1510 cm^{-1} , 1580 cm^{-1} , 1618 cm^{-1} and 1644 cm^{-1} peaks were determined as CC stretching vibrations. The Raman counterparts of them observed at 1480 cm^{-1} , 1586 cm^{-1} , 1617 cm^{-1} and 1660 cm^{-1} . According to the TED results, these are not pure modes. These mode include the in plane CH bending and C=O stretching vibrations in Table 3.



NMR spectra

Recently, Gauge Invariant Atomic Orbital's (GIAO) NMR DFT calculations have become popular [32–34]. These calculations can successfully determine the chemical shift for small molecules [32–35]. In the previous studies, it is reported that there are excellent agreement between experimental NMR spectra and theoretical ones, which are obtained GIAO's approach using Density Functional Theory (DFT-B3LYP) calculations [35–37]. In the present work, the ^1H and ^{13}C NMR chemical shifts of the most stable conformer of 78D4MC molecule were calculated using GIAO approximation in DMSO solution at IEF-PCM model.

The computed chemical shifts as well as measured NMR values were shown in Table 4. The range of the ^{13}C NMR chemical shifts for a typical organic molecule usually is $>100\text{ ppm}$ [38]. As expected, the ^{13}C NMR spectrum of 78D4MC molecule consists of ten resonance signals. Two of them were theoretically determined at 115.1 ppm (C₆) and 113.6 ppm (C₁₀) using the B3LYP/6-311G(d,p) level. These chemical shifts were measured at 104.9 ppm in the experimental NMR spectra. The chemical shifts experimentally measured at 161.4 ppm (C₇) and theoretically predicted at 163.2 ppm. C₁₇, belongs to carbon atom of the methyl group chemical shift was theoretically predicted at 21.44 ppm and experimentally observed at 14.89 ppm. The methyl groups are generally denoted as electron donating groups, so they will be more shielded. The experimental chemical shifts of protons attached to methyl group are shifted towards higher magnetic field.

Hussein was reported that spectroscopic properties and interaction with bovine serum albumin of 7,8-Dihydroxy-4-Methylcoumarin was investigated by some spectroscopic techniques [39]. ^1H NMR data taken from that manuscript. H₁₈, H₁₉ and H₂₀ chemical shifts were determined at 2.40 ppm. The protons on the methyl groups are equivalent. So, these protons produce one signal. It noted that the experimental chemical shifts of hydrogen atoms, which bonded hydroxyl group, were measured at 6.21 ppm by Hussein [39]. The chemical shifts of H₉ and H₈, which are equivalent protons, were experimentally measured at 7.10 ppm. As seen in Table 4, there is a good agreement between the predicted and observed chemical shifts were obtained.

Molecular electrostatic potential (MEP)

Molecular electrostatic potential (MEP) is created by the nuclei and the electrons. The MEP map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the molecule can have intermolecular

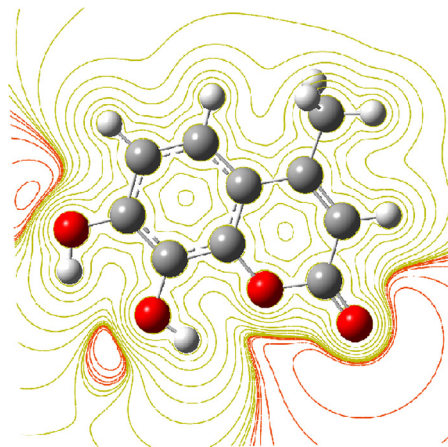


Fig. 4. Molecular potential maps of 78D4MC.

interactions. In other words, MEP have been used for understanding and predicting sites for electrophilic attack and nucleophilic reactions, the reactive behavior of a wide variety of chemical systems, the study of biological recognition processes and hydrogen bonding interactions [40–45]. MEP mapping is also very useful in the investigation of the molecular structure with its physiochemical property relationship [46–50]. To predict reactive sites for 78D4MC molecule, the calculated 3D MEP contour map was calculated at the B3LYP/cc-pVDZ as shown in Fig. 4.

HOMO–LUMO energies

The energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 78D4MC molecule were calculated using DFT method at B3LYP/cc-pVDZ level of theory. The frontier molecular orbitals (HOMO and LUMO) were shown in Fig. 5.

The analysis of frontier molecular orbital's showed that the HOMO is localized on the all molecule without methyl group, whereas LUMO is localized on all part of molecule. The computed HOMO–LUMO energy gap of 78D4MC molecule was predicted at 4.326 eV. By using HOMO and LUMO energy values for a molecule, the electron affinity (E_A), ionization potential (I_P) and chemical hardness (η), electronegativity (χ) and some properties of the molecule can be calculated using Koopman's theorem.

$$I_P \approx -E_{\text{HOMO}}$$

$$E_A \approx -E_{\text{LUMO}}$$

$$\eta = \left[\frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \right] \text{ or } \eta = (I_P - E_A)/2$$

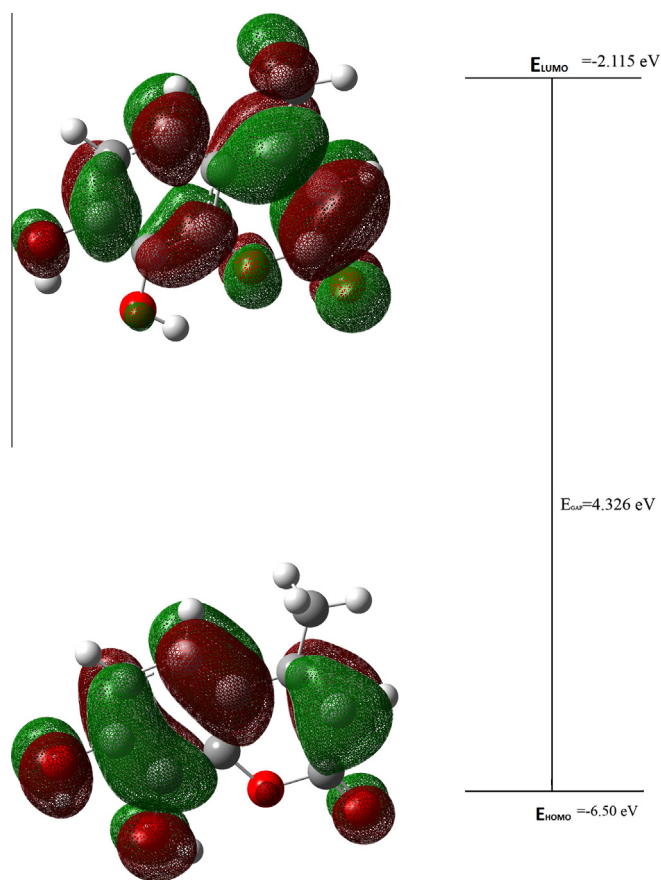


Fig. 5. HOMO LUMO plot of 78D4MC.

Table 5

Calculated some properties values of 78D4MC in its ground state.

	Conformer-1	Conformer-2	Conformer-3	Conformer-4
E_{HOMO} (eV)	−6.442	−6.500	−6.433	−6.372
E_{LUMO} (eV)	−2.115	−1.960	−1.950	−2.097
E_{CAP} (eV)	4.326	4.540	4.483	4.275
I_P (eV)	6.442	6.500	6.433	6.372
E_A (eV)	2.115	1.960	1.950	2.097
η (eV)	2.163	2.270	2.241	2.137
χ (eV)	4.278	4.230	4.191	4.234
<i>Dipole moment (D)</i>				
μ_{total}	3.615	5.334	7.977	6.374
μ_x	0.667	3.407	4.097	−1.476
μ_y	3.553	4.103	6.845	6.201
μ_z	−0.001	0.000	0.002	−0.000

$$\chi = \left[\frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \right] \text{ or } \chi = (I_P + E_A)/2$$

The ionization potential and electron affinity of the most stable conformer in gas phase were predicted at 6.442, 2.115 eV, respectively. The calculated results were presented in Table 5. Considering the chemical hardness, large chemical hardness expresses a hard molecule and small chemical hardness gap means a soft molecule. One can also relate the stability of molecule to hardness, which means that the molecule with least chemical hardness means it is more reactive [51,52].

Conclusions

A systematic study has been performed on the structural and spectral characteristics of 78D4MC molecule using experimental spectroscopic methods and quantum chemical calculations. FT-IR and FT-Raman spectra of 78D4MC molecule were experimentally recorded and analyzed. The conformational analysis results indicated that 78D4MC has four conformers. According to the optimized energy, Conformer-1 is obtained as the most stable structural form. The molecular geometry and vibrational wavenumbers of the most stable conformer have been calculated using DFT/B3LYP level with 6-311G(d,p), cc-pVTZ and cc-pVQZ basis sets. Potential energy distribution of normal modes was done using Scaled Quantum Mechanics (SQM) method by using Parallel Quantum Mechanic solutions program. A ^{13}C NMR spectrum of 78D4MC molecule was experimentally recorded. The chemical shifts were calculated from ^{13}C and ^1H NMR spectra in DMSO and calculated by GIAO method. MEP contour has been plotted in order to predict sites and relative reactivity toward electrophilic attack. The HOMO and LUMO analysis can be used to determine the charge transfer within the molecule. The calculated values of hardness, electronegativity, ionization potential and electron affinity were 2.163, 4.278, 6.442 and 2.115, respectively. Geometric parameters, FT-IR, FT-Raman and NMR data have been compared with experimental values and shown to have a good agreement with each other.

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