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Electronic [UV–Visible] and vibrational [FT-IR] investigation and NMR spectroscopic analysis of some halogen substituted chromone (6-Fluorochromone, 6-Chlorochromone, 6-Bromochromone)

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ABSTRACT

This work deals with the successful spectroscopic properties (infrared, Nuclear magnetic resonance and UV–Vis) and theoretical calculations of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, Cl and Br)] molecules, namely Chromone (Chr), 6-Fluorochromone (6-Flchr), 6-Chlorochromone (6-Clchr), 6-Bromochromone (6-Brchr). The analysis of the infrared, NMR and UV–Vis spectra of chromone and some halogen substituted chromone molecules, supported by DFT calculations, for the first time has afforded the opportunity to characterize unambiguously the main vibrational bands for these important molecules.

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1. Introduction

Chromone is a derivative of benzopyran with a substituted keto group on the pyran ring. Chromones are oxygen-containing heterocyclic compounds. Although the chromone core does not contain a nitrogen atom, chromone natural products are classified as alkaloids because nitrogenous moieties are usually attached to them [1]. In the FDA Orange Book, the chromone core is one of the top 100 most used ring systems for small molecule drugs listed [2].

Chromones exhibit important pharmacological activities, such as anti-inflammatory and anticancer due to their well-recognized antioxidant properties [3–5]. These compounds show the variety of pharmacological activities and the change in their structure offer a high degree of diversity that has been found useful for the search for novel therapeutic agents [6–8]. It is common and integral constituent of a variety of medicinal agents [6,9,10]. Chromone-based drugs exhibit anticancer, *anti*-HIV, antioxidant, anti-inflammatory, analgesic, antimicrobial, antimalarial, anti-diabetic, anticonvulsant, antiplatelet, gastroprotective, antihistaminic, antihypertensive, and insecticidal activity [11,12].

The chromone core is being a key element of pharmacophores of many biologically active molecules displaying diverse medicinal applications. The development of new chromone-based protective and potentially therapeutic agents is an important research area in Medicinal Chemistry. Since oxidative damage in numerous cell targets (DNA, lipids, and proteins) is known to be directly linked to a number of severe pathologies, in other words liver toxicity, cardiovascular and neurodegenerative disorders and cancer, the design of new antioxidant agents from natural sources has been the object of vigorous study in the last decade, with a view to establishing successful chemopreventive strategies as well as chemotherapeutic alternatives (e.g. combination therapy) [7].

Vibrational spectra of related Chromones were analyzed both by computational and experimental methods [13,14]. Chromone and two carboxylic derivatives chromone-2-carboxyl acid and chromone-3-carboxylic acid were investigated as to their conformational preferences by vibrational spectroscopy [6]. The present work reports a conformational study, by vibrational spectroscopy coupled to quantum mechanical calculations (at density functional theory and plane-wave levels), of chromone and two derivatives

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displaying a carboxyl moiety in different positions of the heterocyclic ring-chromone-2-carboxyl acid (2CA) and chromone-3-carboxylic acid (3CA). Most recently, Kupcewicz et al. [15] have reported novel bright-blue luminescent complex of Zn(II) with 7-amino-methylchromen-4-one using photophysical properties and DFT calculations. Moreover, UV absorption spectra of Chromones were recently subject of study, especially by the good agreement between experimental spectra and those obtained by theoretical calculations [16–18]. The crystal structure of Chromone [19], 6-Fluorochromone [19], 6-Chlorochromone [19] and 6-Bromochromone [20] was reported in earlier paper.

To the best of our knowledge, there is not any review summarizing the literature on the vibrational assignments of chromone ($C_9O_2H_6$) and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules. This manuscript aims to cover the work on the DFT study and spectroscopic characterization of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules. We reports the results of a systematic study of geometrical and electronic structure and vibrational spectra of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules based on their experimental Infrared, NMR and UV–Vis spectra and density functional theory (DFT) computations. ^1H and ^{13}C NMR chemical shift values of the chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules in the ground state were calculated using the DFT method.

2. Experimental and computational details

The vibrational, NMR and UV–Vis spectra and some electronic properties of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules was carried out with Gaussian 09 [21] program and Gauss View 3.0 [22] graphical interface. In all calculations such as geometry optimization, vibrational frequency and other molecular property calculations were performed by B3LYP [23–25] functional and 6-311G(d,p) basis set. The vibrational assignments were made on the basis of the potential energy distribution (PED) calculated with scaled quantum mechanics (SQM) program [26] based on DFT calculation. Only PED components $\geq$ 10% was evaluated to perform the final assignment. NMR analysis has been done by using Gauge Independent Atomic Orbital (GIAO) method. In addition, the UV–Vis spectra, frontier molecular orbital analysis and density of state analysis were performed.

Chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules was supplied from Sigma-Aldrich. The FT-IR spectra of Chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules was recorded in the ranged of 4000-550 cm^{-1} (the spectral resolution was 4 cm^{-1} and 32 scan) with Bruker Vertex 80 FT-IR spectrometer equipped with a diamond crystal ATR (attenuated total reflectance) accessory. UV–Vis absorption spectra of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules was performed Lambda 2S, Perkin Elmer UV–Vis spectrometer at RT in the range of 200–1100 nm. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer in DMSO.

2.1. Molecular geometry

Molecular structure and atomic numbering were presented in Fig. 1. The calculated structural parameters with the X-Ray data for optimized were provided in Table 1. The calculated data was compared with determined X-Ray data of Chromone [19], 6-Fluorochromone [19], 6-Chlorochromone [19], 6-Bromochromone [20] molecules.

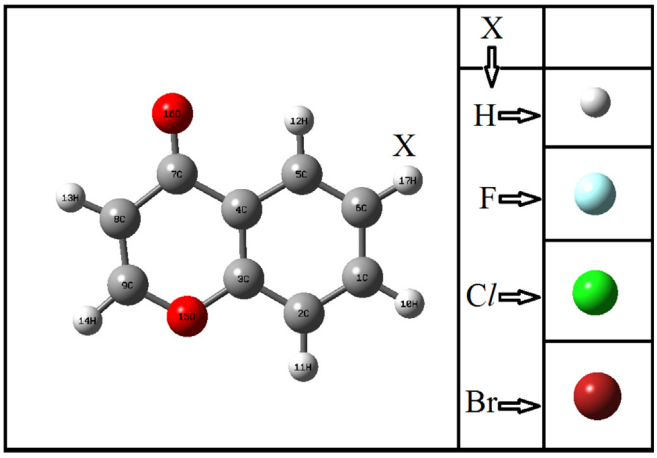


Fig. 1. Molecular structure and atomic numbering of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

2.2. Vibrational analysis

Chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules has 17 atoms, so it has 45 normal modes. Chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules has the Cs symmetry. All the 45 fundamental vibrations are active in both FT-IR and FT-Raman spectra. The experimental FT-IR frequencies with theoretical calculations for various modes of vibrations are assigned and presented in Tables 2–5. The computed frequencies in the harmonic approximation were scaled to closer reproduce experimental value [27]. In our present study, the scale factor of 0.9682 was used for B3LYP/6-311G(d,p) method. The experimental FT-IR of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules were shown in Fig. 2. When the experimental FT-IR spectra data of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules are compared with those of predicted spectral data, it is possible to notice that both spectral data overlap almost perfectly.

In the aromatic compounds, there are three types of vibrations between carbon and hydrogen atoms. One of them is the C–H stretching vibrations, which are appearing in the range of 3300-3000 cm^{-1} [28,29]. Other vibrations are the bending vibrations, which are C–H in-plane bending and out-of-plane bending vibrations. These are detected at 1450-1000 cm^{-1} region and 1000-750 cm^{-1} region, respectively [30–32].

In the present investigation of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules, the C–H stretching vibrations of the $C_9O_2H_6$ (Chromone) molecule predicted six bands at 3030-3075 cm^{-1} region by means of DFT calculation. All of them are in-plane vibrations (A′). Two of them were experimentally observed at the similar region. 3049 cm^{-1} and 3085 cm^{-1} peaks were detected in the FT-IR spectrum and assigned to the C–H stretching vibrations of the Chr molecule. Machado et al. [7] reported that FT-IR and FT-Raman spectra of Chromone molecule were given at the earlier work. In that study, the C–H stretching vibrations were reported at 3070/3069 cm^{-1}, 3085/3086 cm^{-1} and 3096/3097 cm^{-1} by FT-IR/FT-Raman spectra. Authors couldn't only be detected the 3096 cm^{-1} pattern. Other C–H stretching vibrations measured the FT-IR spectra. In our experimental study, FT-IR spectral data are good agreed well with those of Machado et al. [7]. The C–H stretching vibrations of 6-Fluorochromone molecule were detected at 3080 cm^{-1}, 3065 cm^{-1} and 3033 cm^{-1} by FT-IR spectra. Those of 6-

Table 1
Optimized geometric parameters of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules at DFT levels [Bond length in (Å), Bond angles in (°) and Dihedral angles (°)].

Bond length	Theo.	X-Ray[a]	Theo.	X-Ray[a]	Theo.	X-Ray[a]	Theo.	X-Ray[b]
C_1–C_2	1.385	1.376	1.384	1.381	1.383	1.377	1.384	1.367
C_1–C_6	1.402	1.399	1.396	1.388	1.401	1.397	1.401	1.389
C_1–H_{10}	1.084	0.977	1.082	0.980	1.082	0.949	1.082	1.095
C_2–C_3	1.396	1.396	1.396	1.397	1.396	1.398	1.396	1.408
C_2–H_{11}	1.082	0.956	1.082	0.952	1.082	0.949	1.082	0.837
C_3–C_4	1.399	1.391	1.399	1.397	1.398	1.394	1.398	1.386
C_3–O_{15}	1.373	1.372	1.372	1.378	1.371	1.373	1.370	1.371
C_4–C_5	1.402	1.400	1.401	1.403	1.401	1.405	1.402	1.404
C_4–C_7	1.483	1.476	1.485	1.473	1.485	1.477	1.485	1.471
C_5–C_6	1.383	1.380	1.376	1.376	1.380	1.379	1.380	1.379
C_5–H_{12}	1.083	0.957	1.082	1.064	1.082	1.950	1.082	0.913
C_6-X_{17}	1.083	0.983	1.349	1.357	1.756	1.743	1.915	1.906
C_7–C_8	1.462	1.445	1.461	1.450	1.461	1.451	1.462	1.455
C_7–O_{16}	1.222	1.232	1.221	1.232	1.221	1.232	1.221	1.238
C_8–C_9	1.343	1.334	1.344	1.342	1.343	1.339	1.343	1.324
C_8–H_{13}	1.081	0.957	1.081	1.026	1.081	0.950	1.081	1.066
C_9–H_{14}	1.082	0.932	1.082	0.906	1.082	0.951	1.082	0.819
C_9–O_{15}	1.352	1.354	1.351	1.357	1.352	1.360	1.352	1.364
Bond angles								
C_2–C_1–C_6	120.6	120.7	119.2	118.8	119.7	119.7	119.7	120.2
C_2–C_1–H_{10}	119.4	118.6	121.3	123.7	120.4	120.1	120.1	127.0
C_6–C_1–H_{10}	119.9	120.6	119.3	117.3	119.8	120.1	120.1	112.7
C_1–C_2–C_3	118.8	118.7	119.1	118.7	119.2	118.9	119.2	118.2
C_1–C_2–H_{11}	122.0	121.5	121.5	125.2	121.4	120.5	121.3	125.4
C_3–C_2–H_{11}	119.1	119.7	119.3	115.9	119.3	120.5	119.3	114.7
C_2–C_3–C_4	121.5	121.6	121.4	122.1	121.3	121.7	121.3	122.2
C_2–C_3–O_{15}	116.6	116.0	116.7	116.0	116.7	115.7	116.7	115.2
C_4–C_3–O_{15}	121.8	122.2	121.8	121.8	121.8	122.5	121.9	122.4
C_3–C_4–C_5	118.4	118.4	118.5	118.6	118.9	118.7	118.9	118.3
C_3–C_4–C_7	120.3	119.8	120.3	120.1	120.3	119.8	120.3	120.4
C_5–C_4–C_7	121.2	121.6	120.6	121.1	120.6	121.8	120.6	121.2
C_4–C_5–C_6	120.6	120.3	119.0	118.6	119.5	119.0	119.6	119.0
C_4–C_5–H_{12}	117.3	118.4	119.1	122.0	118.2	120.4	117.9	111.3
C_6–C_5–H_{12}	121.9	121.2	121.7	119.7	122.1	120.4	122.4	127.9
C_1–C_6–C_5	119.8	120.0	122.1	123.3	121.2	121.7	121.1	121.8
C_1–C_6-X_{17}	119.8	119.9	118.2	117.9	118.9	117.9	118.9	118.2
C_5–C_6-X_{17}	120.2	120.0	119.6	118.6	119.8	120.3	119.8	119.8
C_4–C_7–C_8	113.3	113.8	113.2	114.0	113.1	113.7	113.1	113.3
C_4–C_7–O_{16}	122.9	122.6	122.7	122.2	122.8	121.8	122.8	122.2
C_8–C_7–O_{16}	123.6	123.5	124.0	123.7	123.9	124.3	123.9	124.4
C_7–C_8–C_9	121.3	121.6	121.3	121.4	121.3	121.7	121.3	121.6
C_7–C_8–H_{13}	118.6	118.9	118.5	120.4	118.5	119.1	118.6	123.7
C_9–C_8–H_{13}	120.0	119.4	120.0	118.1	120.0	119.1	120.0	114.3
C_8–C_9–H_{14}	124.5	126.0	124.5	128.9	124.6	117.7	124.6	121.8
C_8–C_9–O_{15}	124.6	124.4	124.6	124.2	124.6	124.3	124.6	124.7
H_{14}–C_9–O_{15}	110.7	109.4	110.7	106.8	110.7	117.8	110.7	113.2
C_3–O_{15}–C_9	118.5	117.9	118.4	118.3	118.4	117.7	118.5	117.4
Dihedral angles								
C_6–C_1–C_2–C_3	0.0	−1.12	0.0	0.74	0.0	0.42	0.0	1.56
C_6–C_1–C_2–H_{11}	180.0	179.8	180.0	177.9	180.0	179.5	180.0	166.6
H_{10}–C_1–C_2–C_3	180.0	178.2	180.0	176.7	180.0	179.5	180.0	179.9
H_{10}–C_1–C_2–H_{11}	0.0	−0.74	0.0	4.52	0.0	0.41	0.0	14.85
C_2–C_1–C_6–C_5	0.0	0.81	0.0	0.45	0.0	0.21	0.0	0.91
C_2–C_1–C_6-X_{17}	180.0	178.7	180.0	179.5	180.0	179.4	180.0	179.6
H_{10}–C_1–C_6–C_5	180.0	178.5	180.0	177.2	180.0	179.7	180.0	179.6
H_{10}–C_1–C_6-X_{17}	0.0	1.91	0.0	2.71	0.0	0.60	0.0	1.66
C_1–C_2–C_3–C_4	0.0	0.40	0.0	0.61	0.0	0.16	0.0	0.60
C_1–C_2–C_3–O_{15}	180.0	178.9	180.0	179.3	180.0	179.8	180.0	178.9
H_{11}–C_2–C_3–C_4	180.0	179.4	180.0	178.2	180.0	179.8	180.0	167.26
H_{11}–C_2–C_3–O_{15}	0.0	0.08	0.0	1.83	0.0	0.11	0.0	12.33
C_2–C_3–C_4–C_5	0.0	0.62	0.0	0.15	0.0	0.31	0.0	1.04
C_2–C_3–C_4–C_7	180.0	177.9	180.0	179.2	180.0	178.4	180.0	178.6
O_{15}–C_3–C_4–C_5	180.0	179.9	180.0	179.8	180.0	179.6	180.0	179.40
O_{15}–C_3–C_4–C_7	0.0	1.29	0.0	0.81	0.0	1.56	0.0	0.87
C_2–C_3–O_{15}–C_9	180.0	177.1	180.0	179.5	180.0	178.4	180.0	178.33
C_4–C_3–O_{15}–C_9	0.0	−2.19	0.0	0.47	0.0	1.57	0.0	1.26
C_3–C_4–C_5–C_6	0.0	−0.93	0.0	0.17	0.0	0.52	0.0	1.70
C_3–C_4–C_5–H_{12}	180.0	178.7	180.0	176.3	180.0	179.5	180.0	168.3
C_7–C_4–C_5–C_6	180.0	177.6	180.0	179.5	180.0	178.2	180.0	178.03
C_7–C_4–C_5–H_{12}	0.0	−2.66	0.0	3.01	0.0	1.72	0.0	1.41
C_3–C_4–C_7–C_8	0.0	0.51	0.0	0.66	0.0	0.75	0.0	0.19
C_3–C_4–C_7–O_{16}	180.0	179.3	180.0	178.5	180.0	178.3	180.0	178.6
C_5–C_4–C_7–C_8	180.0	178.0	180.0	179.9	180.0	179.5	180.0	179.5

Table 1 (*continued*)

Bond length	Theo.	X-Ray[a]	Theo.	X-Ray[a]	Theo.	X-Ray[a]	Theo.	X-Ray[b]
$C_5–C_4–C_7–O_{16}$	0.0	0.78	0.0	0.81	0.0	0.45	0.0	1.03
$C_4–C_5–C_6–C_1$	0.0	0.23	0.0	0.02	0.0	0.27	0.0	0.77
$C_4–C_5–C_6–X_{17}$	180.0	179.7	180.0	179.9	180.0	178.9	180.0	177.9
$H_{12}–C_5–C_6–C_1$	180.0	179.44	180.0	176.5	180.0	179.7	180.0	164.9
$H_{12}–C_5–C_6–X_{17}$	0.0	0.10	0.0	3.46	0.0	1.08	0.0	13.8
$C_4–C_7–C_8–C_9$	0.0	−1.43	0.0	0.24	0.0	0.05	0.0	0.86
$C_4–C_7–C_8–H_{13}$	180.0	178.0	180.0	177.0	180.0	179.9	180.0	175.2
$O_{16}–C_7–C_8–C_9$	180.0	179.7	180.0	178.9	180.0	178.9	180.0	179.3
$O_{16}–C_7–C_8–H_{13}$	0.0	−0.73	0.0	2.73	0.0	1.04	0.0	6.26
$C_7–C_8–C_9–H_{14}$	180.0	179.6	180.0	177.4	180.0	179.8	180.0	175.1
$C_7–C_8–C_9–O_{15}$	0.0	0.61	0.0	0.08	0.0	0.1	0.0	0.52
$H_{13}–C_8–C_9–H_{14}$	0.0	0.09	0.0	4.16	0.0	0.15	0.0	0.27
$H_{13}–C_8–C_9–O_{15}$	180.0	178.9	180.0	178.4	180.0	179.8	180.0	175.4
$C_8–C_9–O_{15}–C_3$	0.0	1.25	0.0	0.02	0.0	0.84	0.0	0.57
$H_{14}–C_9–O_{15}–C_3$	180.0	177.9	180.0	177.8	180.0	179.1	180.0	176.5

[a] Taken from Ref. [19].
[b] Taken from Ref. [20].

Table 2
Experimental and predicted vibrational wave number for chromone molecule at B3LYP/6-311G(d,p).

		Freq.[a]	I_{IR}[b]	New Exp.	Exp[c].	PED[d]
ν_1	A″	114	1.73		113[e]	$\tau_{CCCO}(31)+\tau_{CCCC}(31)+\tau_{CCCH}(14)+\tau_{CCOC}(11)$
ν_2	A″	154	0.32		-/169	$\tau_{CCCC}(37)+\tau_{CCCH}(22)+\tau_{CCOC}(19)+\tau_{CCCO}(18)$
ν_3	A″	235	0.00		-/249	$\tau_{CCCO}(34)+\tau_{CCCC}(33)+\tau_{CCCH}(19)$
ν_4	A′	281	1.48		-/289	$\delta_{CCC}(38)+\delta_{CCO}(27)+\delta_{CCH}(13)+\nu_{CC}(12)$
ν_5	A″	395	1.31		404/410	$\tau_{CCCC}(29)+\tau_{CCCH}(27)+\tau_{CCCO}(19)+\tau_{CCOC}(15)$
ν_6	A″	456	0.13		461/454	$\tau_{CCCC}(29)+\tau_{CCCH}(29)+\tau_{CCCO}(23)+\tau_{OCCH}(10)$
ν_7	A′	456	1.42			$\delta_{CCC}(37)+\delta_{CCO}(20)+\delta_{CCH}(18)+\nu_{CC}(10)$
ν_8	A′	480	0.08		470/470	$\delta_{CCC}(30)+\delta_{CCO}(24)+\nu_{CC}(19)+\delta_{CCH}(15)$
ν_9	A′	518	3.24		491/491	$\delta_{CCO}(35)+\delta_{CCH}(21)+\delta_{CCC}(20)+\nu_{CC}(10)$
ν_{10}	A″	530	0.50		527/527	$\tau_{CCCH}(27)+\tau_{CCCC}(25)+\tau_{CCCO}(23)+\tau_{CCOC}(11)$
ν_{11}	A′	563	1.37	572	573/576	$\delta_{CCC}(34)+\delta_{CCH}(25)+\delta_{CCO}(17)+\nu_{CC}(15)$
ν_{12}	A″	670	1.55	676	680/683	$\tau_{CCCC}(36)+\tau_{CCCH}(22)+\tau_{CCCO}(13)$
ν_{13}	A′	702	0.25		716/718	$\nu_{CC}(28)+\delta_{CCC}(28)+\delta_{CCH}(25)$
ν_{14}	A″	753	8.26	752	758/759	$\gamma_{CCH}(51)+\tau_{CCCC}(23)+\tau_{CCCO}(10)$
ν_{15}	A″	765	15.0	773	776/774	$\gamma_{CCH}(57)+\tau_{CCCC}(14)$
ν_{16}	A′	789	1.95	799	801/802	$\delta_{CCC}(35)+\delta_{CCH}(28)+\nu_{CC}(13)+\delta_{CCO}(10)$
ν_{17}	A″	827	8.13	835	835/833	$\gamma_{CCH}(69)+\tau_{OCCC}(10)+\tau_{CCCC}(12)$
ν_{18}	A′	844	5.42			$\delta_{CCO}(26)+\delta_{CCC}(25)+\delta_{CCH}(25)+\nu_{CC}(10)+\nu_{CO}(10)$
ν_{19}	A″	865	1.55	862	864/863	$\gamma_{CCH}(67)+\tau_{CCCC}(14)$
ν_{20}	A″	942	0.01			$\gamma_{CCH}(68)+\tau_{CCCH}(11)$
ν_{21}	A″	953	0.29	958	957/958	$\gamma_{CCH}(73)+\tau_{CCCC}(12)$
ν_{22}	A″	978	0.02		984/983	$\gamma_{CCH}(77)+\tau_{CCCC}(13)$
ν_{23}	A′	993	5.55	1008	1011/1012	$\delta_{CCH}(32)+\nu_{CC}(30)+\nu_{CO}(11)+\delta_{CCO}(10)$
ν_{24}	A′	1021	4.48	1031	1036/1034	$\delta_{CCH}(47)+\nu_{CC}(23)+\delta_{CCC}(10)+\delta_{CCO}(10)$
ν_{25}	A′	1064	0.21	1078	1077/-	$\delta_{CCH}(32)+\delta_{CCC}(31)+\nu_{CC}(11)+\delta_{CCO}(10)$
ν_{26}	A′	1108	7.20			$\delta_{CCH}(60)+\nu_{CC}(20)$
ν_{27}	A′	1134	0.42	1122	1127/1128	$\delta_{CCH}(63)+\nu_{CC}(18)$
ν_{28}	A′	1172	2.07	1186	1191/1195	$\delta_{CCH}(51)+\nu_{CC}(18)+\delta_{CCC}(11)+\nu_{CO}(10)$
ν_{29}	A′	1215	2.52			$\delta_{CCH}(47)+\nu_{CC}(21)+\delta_{CCO}(13)+\nu_{CO}(10)$
ν_{30}	A′	1238	9.40	1232	1235/1239	$\delta_{CCH}(53)+\delta_{CCC}(10)+\nu_{CC}(10)$
ν_{31}	A′	1296	34.2	1251	1256/1255	$\delta_{CCH}(38)+\nu_{CC}(25)+\delta_{CCC}(10)$
ν_{32}	A′	1324	20.5	1315	1317/1318	$\nu_{CC}(40)+\delta_{CCH}(28)+\delta_{CCC}(10)$
ν_{33}	A′	1377	13.7	1340	1346/1346	$\delta_{CCH}(53)+\nu_{CC}(17)+\delta_{OCH}(13)$
ν_{34}	A′	1446	28.2	1400	1405/1406	$\delta_{CCH}(49)+\nu_{CC}(21)+\delta_{CCC}(14)$
ν_{35}	A′	1454	0.44	1456	1462/1462	$\delta_{CCH}(52)+\nu_{CO}(15)+\nu_{CC}(11)$
ν_{36}	A′	1557	2.92	1563	1566/1567	$\nu_{CC}(34)+\delta_{CCH}(33)+\delta_{CCC}(14)$
ν_{37}	A′	1599	8.50			$\delta_{CCH}(37)+\nu_{CO}(26)+\delta_{CCC}(13)+\nu_{CC}(11)$
ν_{38}	A′	1606	20.1	1614	1616/1616	$\nu_{CC}(30)+\delta_{CCH}(29)+\delta_{CCO}(11)+\delta_{CCC}(10)$
ν_{39}	A′	1681	100	1635	1652/1670	$\nu_{CO}(26)+\nu_{CC}(18)+\delta_{CCH}(18)+\delta_{CCC}(23)$
ν_{40}	A′	3072	1.02	3049	3070/3069	$\nu_{CH}(80)$
ν_{41}	A′	3085	2.40	3085	3085/3086	$\nu_{CH}(80)$
ν_{42}	A′	3096	1.25			$\nu_{CH}(82)$
ν_{43}	A′	3100	1.35			$\nu_{CH}(84)$
ν_{44}	A′	3101	1.70		3096/3097	$\nu_{CH}(83)$
ν_{45}	A′	3118	1.64			$\nu_{CH}(82)$

ν: Stretching, δ: In-plane bending, γ: Out-of-plane bending, τ: Torsion.
[a] Obtained from the wave number calculated at B3LYP/6-311G(d,p) using scaling factors 0.9682 [27].
[b] Relative absorption intensities normalized with highest peak absorption equal to 100.
[c] Observed vibrational spectral data from the FT-IR and FT-Raman of chromone [7].
[d] Total energy distribution calculated B3LYP/6-311G(d,p) level, PED less than 10% are not shown.
[e] Taken from INS spectra of chromone [7].

Chlorochromone and 6-Bromochromone molecules were measured at 3041, 3068, 3097 cm^{-1} and 3036, 3067, 3094 cm^{-1} by FT-IR.

FT-IR spectrum of the Chromone molecule showed the ten bands between 1000 cm^{-1} - 1456 cm^{-1} region, which were assigned to the in-plane bending vibrations by using PED calculation. These peaks are 1008 cm^{-1}, 1031 cm^{-1}, 1078 cm^{-1}, 1122 cm^{-1}, 1186 cm^{-1}, 1232 cm^{-1}, 1251 cm^{-1}, 1340 cm^{-1}, 1400 cm^{-1} and 1456 cm^{-1} by FT-IR spectrum of Chromone molecule. In the present work, the spectral data of in-plane CH bending of Chromone molecule vibrations were similar to that reported by Macchado et al. [7]. Ip C–H bending peaks were occurred at 1022-1457 cm^{-1} region for 6-Flourochromone, at 1019-1436 cm^{-1} region for 6-Chlourochromone; at 1020-1459 cm^{-1} region for 6-Bromochromone by FT-IR spectra. Ip C–H bending experimental vibrations of Chromone molecule agrees well with those of 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

In the present work, the bands at 752 cm^{-1}, 773 cm^{-1}, 835 cm^{-1}, 862 cm^{-1} and 958 cm^{-1} attributed to the out-of-plane CH bending vibration of chromone molecule by FT-IR spectrum. Out-of-plane CH bending vibrations of the 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules occurred at 823 cm^{-1}, 860 cm^{-1}, 914 cm^{-1} and 965 cm^{-1} for 6-Flchr; 813 cm^{-1}, 898 cm^{-1}, and 953 cm^{-1} for 6-*Cl*chr; at 812 cm^{-1}, 835 cm^{-1}, 896 cm^{-1} and 954 cm^{-1} for 6-Brchr by FT-IR spectra.

In the FT-IR spectra, one very strong band observed at 1635 cm^{-1} (Chr), 1637 cm^{-1} (6-Flchr), 1632 cm^{-1} (6-*Cl*chr) and 1633 cm^{-1} (6-Brchr). These vibrations assigned to the C=O stretching vibrations by use PED results. In the PED results, the C=O vibrations were predicted to the mixed with CC stretching and CCC, CCH bending vibrations. The C=O vibrations has a much higher relative infrared intensity for all molecules. Three bands at 1654 cm^{-1}, 1563 cm^{-1} and 1315 cm^{-1} in FT-IR spectrum was assigned to the CC stretching vibrations of the Chromone. Machado et al. [7] reported that the C–C stretching vibration of Chromone molecule observed at 1616 cm^{-1}, 1566 cm^{-1}, 1317 cm^{-1} in the FT-IR spectrum. Our experimental results agree well with those of

Table 3
Experimental and predicted vibrational wave number for 6-Fluorochromone molecule at B3LYP/6-311G(d,p).

		Freq.[a]	I_{IR}[b]	Exp. IR	PED[c] (%)
ν_1	A″	96	0.72		$\tau_{CCCC}(31)+\tau_{CCCO}(28)+\tau_{CCCH}(10)$
ν_2	A″	152	0.08		$\tau_{CCCC}(35)+\tau_{CCOH}(17)+\tau_{CCCO}(15)+\tau_{CCCH}(14)$
ν_3	A″	180	1.12		$\tau_{CCCC}(25)+\tau_{CCCO}(25)+\tau_{CCOC}(12)+\tau_{CCCH}(12)$
ν_4	A′	229	0.58		$\delta_{CCC}(27)+\delta_{CCO}(20)+\nu_{CC}(17)+\delta_{CCF}(13)+\tau_{CCCH}(10)$
ν_5	A″	331	0.85		$\tau_{CCCO}(29)+\tau_{CCCC}(18)+\tau_{CCCF}(12)+\tau_{CCCH}(10)$
ν_6	A′	385	2.00		$\delta_{CCC}(34)+\delta_{CCF}(20)+\delta_{CCH}(16)+\delta_{CCO}(13)+\nu_{CC}(10)$
ν_7	A′	409	0.39		$\delta_{CCC}(38)+\delta_{CCH}(19)+\delta_{CCO}(14)+\nu_{CC}(11)$
ν_8	A″	415	0.82		τ_{CCCC} (32)$+\tau_{CCCH}(20)+\tau_{CCCO}(16)+\tau_{CCOC}(13)$
ν_9	A″	485	0.23		$\tau_{CCCO}(23)+\tau_{CCCC}(20)+\tau_{CCCH}(18)+\tau_{CCOC}(14)$
ν_{10}	A′	505	0.34		$\tau_{CCCC}(35)+\tau_{CCCO}(18)+\tau_{CCCH}(17)+\tau_{CCOC}(10)$
ν_{11}	A′	512	0.47		$\delta_{CCC}(20)+\nu_{CC}(18)+\delta_{CCH}(16)+\delta_{CCF}(13)$
ν_{12}	A′	544	4.82		$\delta_{CCC}(30)+\delta_{CCH}(21)+\delta_{CCO}(21)+\nu_{CC}(17)$
ν_{13}	A″	546	2.35		$\tau_{CCCC}(30)+\tau_{CCCH}(30)+\tau_{CCCO}(15)$
ν_{14}	A″	671	0.02	619	$\tau_{CCCC}(38)+\gamma_{CCH}(21)+\tau_{CCCO}(16)$
ν_{15}	A′	692	7.91	699	$\delta_{CCC}(26)+\delta_{CCH}(24)+\delta_{CCO}(11)+\nu_{CC}(10)$
ν_{16}	A′	716	2.87	730	$\nu_{CC}(26)+\delta_{CCC}(21)+\delta_{CCH}(19)+\delta_{CCO}(10)$
ν_{17}	A″	751	1.00	758	$\tau_{CCCC}(32)+\gamma_{CCH}(28)+\tau_{CCCO}(15)+\tau_{HCOC}(11)$
ν_{18}	A″	811	2.85		$\gamma_{CCH}(45)+\tau_{HCCO}(19)+\tau_{HCCF}(10)$
ν_{19}	A″	831	24.4	823	$\gamma_{CCH}(27)+\tau_{HCCO}(21)+\tau_{CCCC}(16)+\tau_{CCCO}(12)$
ν_{20}	A′	847	6.76		$\delta_{CCC}(22)+\delta_{CCH}(20)+\delta_{CCO}(20)+\nu_{CC}(11)$
ν_{21}	A″	887	2.98	860	$\gamma_{CCH}(62)+\tau_{HCCF}(17)$
ν_{22}	A′	906	6.12	891	$\nu_{CC}(27)+\delta_{CCH}(24)+\delta_{CCC}(20)$
ν_{23}	A″	932	0.29	914	$\gamma_{CCH}(58)+\tau_{HCCF}(12)$
ν_{24}	A″	942	0.03	965	$\gamma_{CCH}(57)+\tau_{HCCO}(21)$
ν_{25}	A′	1009	8.68	1022	$\delta_{CCH}(37)+\nu_{CC}(20)+\delta_{CCO}(13)+\nu_{CO}(12)+\delta_{CCC}(11)$
ν_{26}	A′	1042	0.99	1063	$\delta_{CCH}(40)+\delta_{CCC}(26)+\nu_{CC}(16)$
ν_{27}	A′	1101	6.14	1129	$\delta_{CCH}(60)+\nu_{CC}(17)$
ν_{28}	A′	1142	6.57	1167	$\delta_{CCH}(34)+\delta_{CCC}(20)+\nu_{CC}(13)$
ν_{29}	A′	1193	5.58	1198	δ_{CCH} (43)$+\nu_{CC}(20)+\nu_{CO}(10)$
ν_{30}	A′	1214	0.52		$\delta_{CCH}(51)+\nu_{CC}(15)+\delta_{CCC}(10)$
ν_{31}	A′	1239	10.3	1252	$\delta_{CCH}(29)+\nu_{CC}(25)+\nu_{CF}(13)+\delta_{CCC}(13)$
ν_{32}	A′	1282	60.3		$\delta_{CCH}(32)+\nu_{CC}(20)+\delta_{CCC}(14)+\nu_{CO}$ (12)
ν_{33}	A′	1324	4.40	1310	$\nu_{CC}(47)+\delta_{CCH}(17)$
ν_{34}	A′	1372	4.82	1342	$\delta_{CCH}(48)+\nu_{CC}(16)+\delta_{HCO}(13)$
ν_{35}	A′	1423	24.5	1393	$\delta_{CCH}(30)+\nu_{CC}(29)+\delta_{CCC}(13)+\delta_{CCO}(11)$
ν_{36}	A′	1460	65.6	1457	$\delta_{CCH}(43)+\nu_{CC}(23)$
ν_{37}	A′	1564	10.1	1570	$\nu_{CC}(34)+\delta_{CCH}(26)+\delta_{CCC}(15)+\nu_{CO}(10)$
ν_{38}	A′	1603	3.98		$\nu_{CC}(29)+\delta_{CCH}(28)+\nu_{CO}(10)+\delta_{CCC}(12)$
ν_{39}	A′	1609	14.0	1613	$\nu_{CC}(30)+\delta_{CCH}(27)+\delta_{CCC}(15)$
ν_{40}	A′	1682	100	1637	$\nu_{CO}(26)+\delta_{CCC}(23)+\nu_{CC}(18)+\delta_{CCH}(17)$
ν_{41}	A′	3095	0.45	3033	$\nu_{CH}(78)$
ν_{42}	A′	3102	0.36	3065	$\nu_{CH}(81)$
ν_{43}	A′	3107	0.20	3080	$\nu_{CH}(82)$
ν_{44}	A′	3110	1.74		$\nu_{CH}(75)$
ν_{45}	A′	3119	1.41		$\nu_{CH}(82)$

ν: Stretching, δ: In-plane bending, γ: Out-of-plane bending, τ: Torsion.
[a] Obtained from the wave number calculated at B3LYP/6-311G(d,p) using scaling factors 0.9682 [27].
[b] Relative absorption intensities normalized with highest peak absorption equal to 100.
[c] Total energy distribution calculated B3LYP/6-311G(d,p) level, PED less than 10% are not shown.

Table 4
Experimental and predicted vibrational wave number for 6-Chlorochromone molecule at B3LYP/6-311G(d,p).

		Freq.[a]	I_{IR}[b]	Exp. IR	PED[c] (%)
ν_1	A″	83	0.62		$\tau_{CCCC}(33)+\tau_{CCCO}(24)+\tau_{CCCH}$ (11)
ν_2	A″	149	0.02		$\tau_{CCCC}(32)+\tau_{CCCO}(23)+\tau_{CCCH}$ (14)
ν_3	A″	162	1.17		$\tau_{CCCC}(28)+\tau_{CCCO}(18)+\tau_{CCOC}(16)+\tau_{CCCC}(12)$
ν_4	A′	181	0.36		$\delta_{CCC}(23)+\delta_{CCCl}(25)+\delta_{CCO}(20)+\nu_{CC}(17)$
ν_5	A″	304	0.03		$\tau_{CCCO}(31)+\tau_{CCCC}(16)+\tau_{CCCC}(12)$
ν_6	A′	335	1.61		$\delta_{CCC}(29)+\delta_{CCCl}(17)+\delta_{CCO}(15)+\delta_{CCH}(15)$
ν_7	A′	342	0.21		$\delta_{CCC}(26)+\delta_{CCH}(16)+\delta_{CCO}(12)+\nu_{CCl}(11)+\nu_{CC}(11)$
ν_8	A″	406	1.85		$\tau_{CCCC}(28)+\tau_{CCCH}(21)+\tau_{CCCO}(16)+\tau_{CCOC}(14)$
ν_9	A″	475	0.89		$\tau_{CCCC}(26)+\tau_{CCCO}(21)+\tau_{CCCH}(18)+\tau_{CCOC}$ (12)
ν_{10}	A′	492	0.50		$\delta_{CCC}(26)+\delta_{CCO}(22)+\delta_{CCH}(15)+\nu_{CC}(11)+\delta_{COC}$ (10)
ν_{11}	A′	500	0.01		$\delta_{CCC}(24)+\delta_{CCO}(21)+\nu_{CC}(20)+\delta_{CCH}(16)$
ν_{12}	A″	534	3.14		$\tau_{CCCC}(28)+\tau_{CCCO}(20)+\tau_{CCCO}(19)$
ν_{13}	A′	537	8.24	569	$\delta_{CCC}(30)+\delta_{CCO}(26)+\delta_{CCH}(15)+\nu_{CC}(14)+\nu_{CC}$ (11)+
ν_{14}	A′	618	8.82	628	$\delta_{CCC}(34)+\delta_{CCH}(22)+\nu_{CCl}(11)+\nu_{CC}(10)$
ν_{15}	A″	672	0.12	667	$\tau_{CCCC}(43)+\tau_{CCCH}(24)+\tau_{CCCO}(11)$
ν_{16}	A′	713	0.59	734	$\delta_{CCC}(28)+\nu_{CC}(23)+\delta_{CCH}(19)$
ν_{17}	A″	755	0.69		$\gamma_{CCH}(57)+\tau_{CCCO}(15)+\tau_{CCOC}(10)$
ν_{18}	A″	810	4.78	813	$\gamma_{CCH}(42)+\tau_{HCCO}(18)+\tau_{CCCC}(16)$
ν_{19}	A″	830	20.9		$\gamma_{HCC}(44)+\tau_{CCCC}(17)+\tau_{CCCO}(13)$
ν_{20}	A′	832	8.97	837	$\delta_{CCC}(26)+\delta_{CCH}(20)+\nu_{CC}(13)+\nu_{C\text{-}Cl}(10)$
ν_{21}	A′	847	3.69	867	$\delta_{CCC}(24)+\delta_{CCH}(20)+\delta_{CCO}(15)\nu_{CC}(12)+\nu_{CO}(10)$
ν_{22}	A″	909	1.04	898	$\gamma_{CCH}(58)+\tau_{HCCCl}(16)$
ν_{23}	A″	943	0.09		γ_{CCH} (48)+$\tau_{CCCC}(21)$
ν_{24}	A″	944	0.22	953	$\gamma_{CCH}(54)+\tau_{HCCO}(13)$
ν_{25}	A′	1004	10.7	1019	$\delta_{CCH}(29)+\nu_{CC}(20)+\nu_{CO}(14)+\delta_{CCO}(14)$
ν_{26}	A′	1046	0.91	1058	$\delta_{CCH}(44)+\nu_{CC}(21)+\delta_{CCC}(20)$
ν_{27}	A′	1076	10.8	1097	$\delta_{CCH}(30)+\delta_{CCC}(28)+\nu_{CC}(15)$
ν_{28}	A′	1117	3.57	1135	$\delta_{CCH}(54)+\nu_{CC}(22)$
ν_{29}	A′	1170	1.65	1185	$\delta_{CCH}(37)+\nu_{CC}(23)+\nu_{CO}(10)$
ν_{30}	A′	1208	3.14		$\delta_{CCH}(35)+\nu_{CC}(24)+\delta_{CCC}(11)+\delta_{CCO}(11)$
ν_{31}	A′	1225	0.92	1229	$\delta_{CCH}(57)+\nu_{CC}(13)$
ν_{32}	A′	1282	70.3		$\delta_{CCH}(32)+\nu_{CC}(21)+\delta_{CCC}(11)+\delta_{CCO}(10)$
ν_{33}	A′	1310	6.86	1301	$\nu_{CC}(48)+\delta_{CCH}(16)$
ν_{34}	A′	1370	2.57	1328	$\delta_{CCH}(50)+\nu_{CC}(14)+\delta_{HCO}(12)$
ν_{35}	A′	1409	31.6	1385	$\nu_{CC}(26)+\delta_{CCH}(21)+\delta_{CCO}(11)$
ν_{36}	A′	1444	43.4	1436	$\delta_{CCH}(50)+\nu_{CC}(22)+\delta_{CCC}(11)$
ν_{37}	A′	1550	4.48	1559	$\nu_{CC}(34)+\delta_{CCH}(27)+\delta_{CCC}(18)$
ν_{38}	A′	1591	7.58		$\nu_{CC}(35)+\delta_{CCH}(28)+\delta_{CCC}(17)$
ν_{39}	A′	1603	13.6	1607	$\nu_{CC}(29)+\delta_{CCH}(24)+\nu_{CO}(10)+\delta_{CCC}(10)+\delta_{HCO}(10)$
ν_{40}	A′	1683	100	1632	$\nu_{CO}(35)+\nu_{CC}(19)+\delta_{CCH}(18)+\delta_{CCC}(13)$
ν_{41}	A′	3094	0.20	3041	$\nu_{CH}(78)$
ν_{42}	A′	3103	0.38	3068	$\nu_{CH}(81)$
ν_{43}	A′	3108	0.13	3097	$\nu_{CH}(82)$
ν_{44}	A′	3110	1.57		$\nu_{CH}(46)$
ν_{45}	A′	3120	1.48		$\nu_{CH}(82)$

ν: Stretching, δ: In-plane bending, γ: Out-of-plane bending, τ: Torsion.
[a] Obtained from the wave number calculated at B3LYP/6-311G(d,p) using scaling factors 0.9682 [27].
[b] Relative absorption intensities normalized with highest peak absorption equal to 100.
[c] Total energy distribution calculated B3LYP/6-311G(d,p) level, PED less than 10% are not shown.

Machado et al. [7]. Those of 6-halogen substituted chromone derivatives were at 1613/1607/1601 cm^{-1} for 6-Flchr/6-*Cl*chr/6-Brchr, 1570/1559/1556 cm^{-1} for 6-Flchr/6-*Cl*chr/6-Brchr and 1310/1301/1326 cm^{-1} for 6-Flchr/6-*Cl*chr/6-Brchr. In the PED results, all of the C—C stretching vibration was predicted to mix with CCC and CCO bending vibrations.

The C—Br stretching mode appears at 480-200 cm^{-1} wavenumber regions as reported by Varsayani [33]. The stretching vibration associated with C—Br bond was represented as mode no 5. C—Br stretching vibration was appeared at 260 cm^{-1} by DFT. This vibration couldn't be measured by FT-IR spectrum. PED contribution of this vibration was calculated at 30% with CCC (20%), CCH (14%) bending and CC (14%) stretching vibrations. Generally C—*Cl* absorption was obtained in the region 850-550 cm^{-1} [34,35]. The C—Cl stretching vibrations were detected at 628 and 837 cm^{-1} by FT-IR spectrum. But, PED contributions of C—*Cl* stretching vibrations were smaller than those of CCC, CCH bending vibrations. While the PED contribution of the C—*Cl* stretching vibrations were predicted at about 10%, those of the CCC, CCH bending vibrations were calculated at about 30% and 20%. The C—F stretching vibration is observed in the region 1250-1350 cm^{-1} [36,37]. In the present work, 1252 cm^{-1} peak was measured in the FT-IR spectrum and assigned to the C—F stretching vibration. The same PED contribution trend of the C—*Cl* stretching vibration was calculated those of C—F stretching vibration. PED contribution of the C—F stretching vibration was appeared about 10% with about 30% for CCH bending vibration, about 20% for C—C stretching vibration and about 10% for CCC bending vibration.

2.3. NMR spectra

Using optimized geometry of the chromone and the 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules, theoretical ^1H NMR and ^{13}C NMR chemical shifts were computed through GIAO method by using B3LYP/6-311G(d,p) level. The experimental and calculated chemical shifts for ^1H and ^{13}C nuclei are compared in Table 6 and Fig. 3. The experimental and theoretical ^1H and ^{13}C NMR spectra were observed in a DMSO-d_6 solvent.

Table 5
Experimental and predicted vibrational wave number for 6-Bromochromone molecule at B3LYP/6-311G(d,p).

		Freq.[a]	I_{IR}[b]	Exp. IR	PED[c] (%)
ν_1	A″	75	0.65		$\tau_{CCCO}(25)+\tau_{HCCBr}(10)+\tau_{CCCC}(30)+\gamma_{CCH}(10)$
ν_2	A″	145	0.21		$\tau_{CCCC}(33)+\tau_{CCCO}(22)+\gamma_{CCH}(12)$
ν_3	A′	146	0.30		$\delta_{CCBr}(29)+\delta_{CCC}(21)+\delta_{CCO}(18)+\nu_{CC}(16)$
ν_4	A″	158	0.96		$\tau_{OCCC}(37)+\tau_{CCCC}(27)+\gamma_{CCH}(13)$
ν_5	A′	260	0.56		$\nu_{CBr}(30)+\delta_{CCC}(20)+\delta_{CCH}(14)+\nu_{CC}(14)$
ν_6	A″	295	0.00		$\tau_{CCCO}(32)+\tau_{CCCC}(16)+\tau_{CCCBr}(11)+\tau_{HCCBr}(10)$
ν_7	A′	322	1.11		$\delta_{CCC}(35)+\delta_{CCO}(20)+\delta_{CCBr}(17)+\delta_{CCH}(16)$
ν_8	A″	403	1.88		$\tau_{CCCC}(28)+\gamma_{CCH}(23)+\tau_{CCCO}(15)+\tau_{CCOC}(13)$
ν_9	A″	472	1.04		$\tau_{CCCC}(26)+\tau_{OCCC}(21)+\gamma_{CCH}(20)+\tau_{CCOC}(10)$
ν_{10}	A′	484	0.98		$\delta_{CCO}(26)+\delta_{CCC}(25)+\delta_{CCH}(14)+\nu_{CC}(11)$
ν_{11}	A′	496	0.01		$\delta_{CCC}(25)+\delta_{CCO}(22)+\nu_{CC}(20)+\delta_{CCH}(14)$
ν_{12}	A″	529	2.32		$\tau_{CCCH}(28)+\tau_{CCCC}(26)+\tau_{CCCO}(20)$
ν_{13}	A′	533	9.07		$\delta_{CCC}(30)+\delta_{CCO}(25)+\delta_{CCH}(14)+\nu_{CC}(13)$
ν_{14}	A′	595	5.03	603	$\delta_{CCC}(35)+\delta_{CCH}(18)+\nu_{CBr}(10)+\delta_{CCO}(10)$
ν_{15}	A″	669	0.01	681	$\tau_{CCCC}(42)+\gamma_{CCH}(22)+\tau_{OCCC}(10)$
ν_{16}	A′	712	0.35	726	$\nu_{CC}(25)+\delta_{CCC}(29)+\delta_{CCH}(18)$
ν_{17}	A″	755	0.90		$\tau_{CCCC}(30)+\gamma_{CCCH}(27)+\tau_{OCCH}(11)+\tau_{OCCC}(14)$
ν_{18}	A″	809	5.40	812	$\gamma_{CCH}(60)+\tau_{HCCBr}(10)+\tau_{CCCC}(13)$
ν_{19}	A′	818	6.04		$\delta_{CCH}(22)+\delta_{CCC}(29)+\nu_{CC}(15)$
ν_{20}	A″	830	20.46	835	$\gamma_{CCH}(46)+\tau_{CCCC}(24)+\tau_{OCCC}(12)$
ν_{21}	A′	846	4.61	863	$\delta_{CCC}(26)+\delta_{CCO}(24)+\delta_{CCH}(19)$
ν_{22}	A″	911	0.98	896	$\gamma_{CCH}(58)+\tau_{HCCBr}(16)$
ν_{23}	A″	943	0.05		$\gamma_{CCH}(54)+\gamma_{OCH}(12)$
ν_{24}	A″	945	0.31	954	$\gamma_{CCH}(55)+\gamma_{OCH}(12)$
ν_{25}	A′	1003	10.6	1020	$\delta_{CCH}(30)+\nu_{CC}(29)+\delta_{CCO}(15)+\nu_{CO}(13)$
ν_{26}	A′	1045	1.23	1056	$\delta_{CCH}(40)+\nu_{CC}(24)+\delta_{CCC}(16)$
ν_{27}	A′	1067	7.53	1083	$\delta_{CCC}(30)+\delta_{CCH}(25)+\nu_{CC}(13)$
ν_{28}	A′	1118	4.72	1134	$\delta_{CCH}(54)+\nu_{CC}(21)$
ν_{29}	A′	1170	1.73	1184	$\delta_{CCH}(40)+\nu_{CC}(24)+\delta_{CCC}(10)$
ν_{30}	A′	1207	2.98		$\delta_{CCH}(35)+\delta_{CCO}(11)+\delta_{CCC}(10)+\nu_{CC}(24)$
ν_{31}	A′	1227	1.12	1231	$\delta_{CCH}(54)+\nu_{CC}(13)$
ν_{32}	A′	1281	73.2	1298	$\delta_{CCH}(32)+\nu_{CC}(21)+\nu_{CO}(10)+\delta_{CCC}(10)$
ν_{33}	A′	1308	8.66	1326	$\nu_{CC}(49)+\delta_{CCH}(15)+\delta_{COC}(10)+\delta_{CCO}(10)$
ν_{34}	A′	1369	1.71		$\delta_{CCH}(49)+\nu_{CC}(11)+\delta_{OCH}(11)$
ν_{35}	A′	1406	33.8	1384	$\delta_{CCH}(32)+\nu_{CC}(25)+\delta_{CCC}(10)+\delta_{CCO}(10)$
ν_{36}	A′	1442	40.6	1459	$\delta_{CCH}(51)+\nu_{CC}(20)+\delta_{CCC}(10)$
ν_{37}	A′	1547	4.29	1556	$\nu_{CC}(33)+\delta_{CCH}(25)+\delta_{CCC}(15)$
ν_{38}	A′	1586	7.98		$\nu_{CC}(36)+\delta_{CCH}(27)+\delta_{CCC}(17)$
ν_{39}	A′	1603	13.5	1601	$\nu_{CC}(29)+\delta_{CCH}(24)+\nu_{CO}(10)+\delta_{OCH}(10)$
ν_{40}	A′	1683	100	1633	$\nu_{CO}(25)+\nu_{CC}(23)+\delta_{CCC}(18)+\delta_{CCH}(16)$
ν_{41}	A′	3094	0.17	3036	$\nu_{CH}(77)$
ν_{42}	A′	3103	0.40	3067	$\nu_{CH}(80)$
ν_{43}	A′	3108	0.11	3094	$\nu_{CH}(82)$
ν_{44}	A′	3109	1.65		$\nu_{CH}(79)$
ν_{45}	A′	3121	1.56		$\nu_{CH}(82)$

ν: Stretching, δ: In-plane bending, γ: Out-of-plane bending, τ: Torsion.
[a] Obtained from the wave number calculated at B3LYP/6-311G(d,p) using scaling factors 0.9682 [27].
[b] Relative absorption intensities normalized with highest peak absorption equal to 100.
[c] Total energy distribution calculated B3LYP/6-311G(d,p) level, PED less than 10% are not shown.

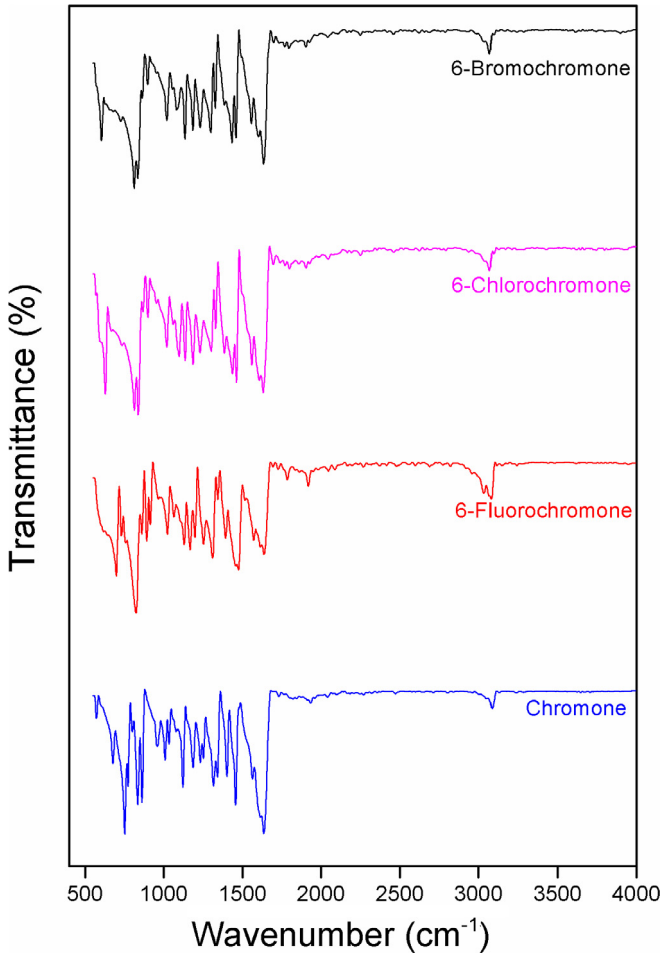


Fig. 2. Experimental FT-IR spectra of Chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

The carbon chemical shift values generally give resonances and overlapped areas from 100 to 150 ppm in NMR spectra [37,38]. The C7 atom has a most shielded signal because C_7 atom is attached to an electronegative oxygen atom O_{16}. The experimental signal of C_7 atom is observed at 176.7 ppm for chromone molecule. The same signal appeared at 175.6 ppm for 6-*Cl*chr and 176.1 ppm for 6-Brchr. The calculated value noticed that 179.6 ppm for chromone, 178.7 ppm for 6-*Cl*chr and 176.0 ppm for 6-Brchr by DFT calculations. The experimental signal of C_9 and C_3 atoms, which are connected to the oxygen atom O_{15}, are measured at 157.3 ppm, 156.3 ppm for chromone, 157.7 ppm for 6-*Cl*chr and 160.5 ppm and 157.7 ppm for 6-Brchr, respectively.

Fluorine atom has also more electronegative property than oxygen and other atoms. So, the sequence of the Carbon-13 chemical shifts of 6-Fluorochromone molecule expects C_6, C_7, C_9 and C_3, but this sequence is just reversed (C_7, C_6, C_9 and C_3). Because fluorine atoms highly sensitive to magnetic field, some uncounted effects exist in fluorine substituted molecules. In the 6-Flchr molecule, 175.5 ppm (C_7), 157.7 ppm (C_6) and 155.3 ppm (C_9 and C_3) signals detected in the NMR spectra [39].

The ^{13}C chemical shifts of C_6 atom which bonded to hydrogen or halogen calculated at 131.6 pp (attached to the hydrogen atom or chromone molecule), 169.8 ppm (attached to the fluorine atom or 6-Fluorochromone molecule), 145.4 ppm (attached to the chlorine atom or 6-Chlorochromone molecule) and 141.1 pp (attached to the bromine atom or 6-Bromochromone molecule). The experimental NMR signals of the title molecule were measured at 125.3 ppm (Chr), 157.7 ppm (6-Flchr), 154.9 ppm (6-*Cl*chr) and 152.8 ppm (6-Brchr). The sequence of the electronegativity properties of Hydrogen, Fluorine, Chlorine and Bromide atoms is the F > Cl > Br > H atom. Therefore, the chemical shifts value of the C_6 atom which bonded to fluorine is the highest.

The experimental ^{13}C NMR signal of hydrogen connected carbon atoms (C_1–H_{10}, C_2–H_{11}, C_5–H_{12} and C_8–H_{13}), which are not connected to the oxygen or halogen atoms, were appeared at 110–140 ppm region for all molecule. These NMR signal are good agreed well with those of reported in similar works [40,41]. C_4 environment has no attached oxygen or halogen atoms. Its NMR resonance appeared at 124.6 pp for Chr molecule, 137.2 ppm for 6-

Table 6
The experimental and calculated chemical shifts for the ^{1}H and ^{13}C nuclei.

	Chromone		6-Fluorochromone			6-Chlorochromone			6-Bromochromone		
	Theo.	Exp.	Theo.		Exp.	Theo.		Exp.	Theo.		Exp.
C_7	179.6	176.7	C_7	179.1	175.5	C_7	178.7	175.6	C_7	176.0	176.1
C_9	164.2	157.3	C_9	164.1	155.3	C_9	164.2	157.7	C_9	161.5	160.5
C_3	163.8	156.3	C_3	160.7	155.3	C_3	162.8	157.7	C_3	160.7	157.7
C_1	140.4	134.6	C_1	128.1	127.4	C_1	140.8	134.5	C_1	141.1	
C_5	131.8	125.8	C_5	116.5	112.7	C_5	131.7	124.3	C_5	132.6	125.8
C_6	131.6	125.3	C_6	169.8	157.7	C_6	145.4	154.9	C_6	141.1	152.8
C_4	131.4	124.6	C_4	133.2	137.2	C_4	132.6	130.3	C_4	130.21	125.7
C_2	124.8	118.8	C_2	127.5	126.1	C_2	126.9	121.4	C_2	124.4	122.9
C_8	119.4	112.7	C_8	118.6	118.3	C_8	119.4	112.6	C_8	116.9	111.9
H_{12}	8.43	8.32	H_{12}	7.94	7.80	H_{12}	8.20	8.35	H_{12}	8.33	“8.34
H_{14}	8.13	8.06	H_{14}	8.13	8.35	H_{14}	8.11	7.96	H_{14}	8.11	8.10
H_{10}	8.00	7.81	H_{10}	7.64	7.69	H_{10}	7.80	7.85	H_{10}	7.88	7.95
H_{11}	7.81	7.65	H_{11}	7.82	7.77	H_{11}	7.74	7.75	H_{11}	7.74	7.66
H_{17}	7.76	7.50									
H_{13}	6.34	6.38	H_{13}	6.34	6.39	H_{13}	6.35	6.41	H_{13}	6.35	6.41

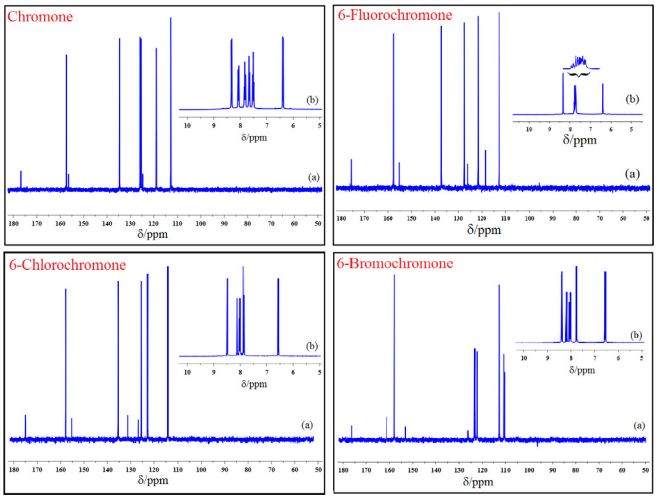


Fig. 3. Experimental NMR spectra of Chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

Flchr molecule, 130.3 ppm 6-*Cl*chr and 125.7 ppm for 6-Brchr molecule.

In the chromone molecule, it has six hydrogen atoms are attached to the Carbon atoms in the ring. ^{1}H experimental chemical shift of hydrogen atoms (i.e. H_{12}, H_{14}, H_{10}, H_{11} and H_{13}) were occurred at 8.32, 8.06, 7.81, 7.65, 7.50 and 6.38 ppm, respectively, whereas the predicted values of shift were at 8.43, 8.13, 8.00, 7.81, 7.76 and 6.34 ppm, respectively. In the 6-halogen substituted Chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules, it has five hydrogen atoms are attached to the carbon atoms in the ring.

The sequence of the ^{1}H NMR chemical shifts of 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecule expects H_{12}, H_{14}, H_{10}, H_{11} and H_{13}, but this sequence is just reversed (H_{14}, H_{12}, H_{11}, H_{10} and H_{13}) for fluorine substituted molecules. Because fluorine atoms are highly sensitive to magnetic field, some uncounted effects exist in fluorine substituted molecule [40]. In the 6-Flchr molecule, 8.35 ppm (H_{14}), 7.80 ppm (H_{12}), 7.77 ppm (H_{11}), 7.69 ppm (H_{10}) and 6.39 ppm (H_{13}) signals detected in the NMR spectra. We can easily state that theoretical results obtained from our studies for the title molecules are in good agreement with the experimental data.

2.4. UV–vis spectra

Ultraviolet spectra analysis of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules were investigated theoretically and experimentally. A UV–Vis spectrum was experimentally measured in DMSO solvent. Theoretical UV–Vis spectrum was calculated by DFT theory within 0–700 nm range. On the basis of fully optimized ground state structure, B3LYP/6-311G(d,p) calculations are used to determine the excited state of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules in DMSO solvent, as well. The theoretical and experimental UV–Vis spectra of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules have been indicated in Fig. 4.

The time dependent density functional theory (TD-DFT) calculations has been performed to the investigated the electronic absorption properties of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules. The calculated visible absorption maxima wavelengths (λ_{max}) [29], which are the function of electron availability, theoretical and experimental electronic excitation energies and oscillator strength are gathered in Table 7. The λ_{max} values for chromone molecule were predicted at

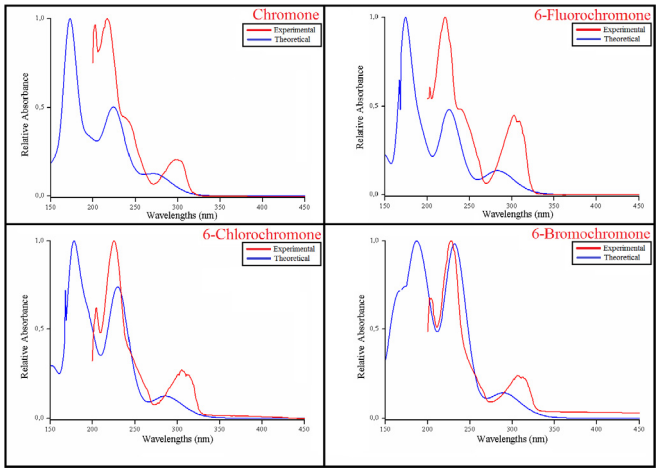


Fig. 4. Experimental and theoretical UV–Vis spectra chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

Table 7
Theoretical electronic absorption spectral data of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

	Wavelength λ (nm)	Excitation energies (eV)	Excitedstate	Oscillator strengths (f)
Chromone	274.92 (298)[a]	4.5098	(H-2)→(L+1); (H-2)→(L+2); (H)→(L)	0.1050
	247.95	5.0004	(H-3)→(L); (H-2)→(L); (H-2)→(L+1); (H)→(L+1)	0.0337
	228.82	5.4185	(H-3)→(L); (H-2)→(L); (H-2)→(L+2); (H)→(L+1)	0.1795
	222.65 (217)[a]	5.5685	(H-3)→(L); (H)→(L+1); (H)→(L+2)	0.2587
	212.12	5.8449	(H-3)→(L+1); (H-2)→(L); (H-2)→(L+1); (H-2)→(L+2); (H)→(L); (H)→(L+2)	0.0475
	196.91	6.2966	(H-3)→(L); (H-3)→(L+1); (H-3)→(L+2); (H-2)→(L+1); (H-2)→(L+2); (H)→(L+2)	0.2384
	190.65	6.5032	(H-3)→(L); (H-3)→(L+1); (H-2)→(L+2); (H)→(L+2)	0.0196
	178.68	6.9387	(H-5)→(L); (H-3)→(L+1); (H-3)→(L+2); (H-2)→(L+2); (H)→(L+1); (H)→(L+2)	0.3446
	170.96 (203)[a]	7.2524	(H-3)→(L+1); (H-3)→(L+2); (H-2)→(L+1); (H-2)→(L+2); (H)→(L)	0.6824
	167.33	7.4095	(H-3)→(L+3); (H)→(L+3)	0.0011
	161.55	7.6747	(H-7)→(L); (H-4)→(L+1)	0.0004
	161.20	7.6913	(H-3)→(L+4); (H)→(L+4)	0.0086
6-Fluorochromone	283.59 (301)	4.3720	(H-2)→(L+1); (H-2)→(L+2); (H)→(L)	0.1126
	246.02	5.0395	(H-3)→(L); (H-2)→(L); (H)→(L+1)	0.0213
	230.63	5.3759	(H-3)→(L); (H)→(L+2)	0.0319
	226.09 (220)	5.4837	(H-2)→(L); (H-2)→(L+2); (H)→(L+1); (H)→(L+2)	0.3911
	212.77	5.8272	(H-3)→(L); (H-3)→(L+1); (H-2)→(L+1); (H)→(L+1); (H)→(L+2)	0.0269
	194.57	6.3721	(H-3)→(L+2); (H-2)→(L+1); (H)→(L+2)	0.2064
	190.04	6.5241	(H-3)→(L); (H-3)→(L+1); (H-2)→(L+1); (H-2)→(L+2); (H)→(L+2)	0.0613
	180.21	6.8800	(H-5)→(L); (H-3)→(L+1); (H-3)→(L+2); (H-2)→(L); (H-2)→(L+1); (H-2)→(L+2); (H)→(L+1); (H)→(L+2)	0.2980
	172.29 (203)	7.1963	(H-3)→(L+1); (H-3)→(L+2); (H-2)→(L+1); (H-2)→(L+2); (H)→(L)	0.7148
	164.65	7.5302	(H-5)→(L)	0.0176
	164.46	7.5391	(H-6)→(L); (H-4)→(L+1); (H-4)→(L+2)	0.0014
6-Chlorochromone	286.03 (307)[a]	4.3347	(H-2)→(L+1); (H)→(L)	
	250.04	4.9585	(H-2)→(L); (H)→(L+1)	
	232.26	5.3381	(H-3)→(L); (H)→(L+1); (H)→(L+2)	
	230.04 (225)[a]	5.3897	(H-3)→(L); (H-3)→(L+1); (H-2)→(L); (H-2)→(L+2); (H)→(L+1)	
	217.27	5.7065	(H-3)→(L); (H-3)→(L+1); (H-2)→(L+2); (H)→(L); (H)→(L+2)	
	200.41	6.1866	(H-3)→(L+1); (H-3)→(L+2); (H-2)→(L+1)	
	196.71	6.3030	(H-3)→(L); (H-3)→(L+1); (H-2)→(L+2); (H)→(L+2)	
	185.74	6.6750	(H-5)→(L); (H-3)→(L+1); (H-2)→(L+1); (H-2)→(L+2); (H-1)→(L+3)	
	177.70 (204)[a]	6.9771	(H-5)→(L); (H-3)→(L+2); (H-2)→(L+2); (H-1)→(L+3)	
	176.50	7.0247	(H-3)→(L+3); (H-2)→(L+3)	
	175.48	7.0655	(H-5)→(L); (H-5)→(L+1); (H-3)→(L+2); (H-2)→(L+1); (H-1)→(L+3); (H)→(L)	
	161.02	7.6999	(H-7)→(L); (H-4)→(L+2); (H-1)→(L+5)	
6-Bromochromone	289.83 (307)[a]	4.2778	(H-2)→(L+1); (H)→(L	0.0898
	234.85	5.2793	(H-1)→(L+1)	0.1275
	231.86 (227)[a]	5.3474	(H-3)→(L+3); (H-2)→(L+3); (H)→(L+3);	0.4769
	218.80	5.6665	(H-8)→(L); (H-5)→(L); (H-3)→(L)(H-3)→(L+1); (H-3)→(L+2); (H-2)→(L); (H-2)→(L+1); (H-2)→(L+2);	0.0273
	205.63	6.0296	(H-10)→(L); (H-5)→(L); (H-3)→(L+2); (H-2)→(L); (H-2)→(L+1); (H)→(L+1);	0.0824
	202.63	6.1188	(H-5)→(L); (H-5)→(L+1); (H-5)→(L+2); (H-3)→(L+2); (H-2)→(L+1); (H-2)→(L+2); (H)→(L	0.0579
	199.53	6.2137	(H-2)→(L+2); (H-1)→(L+3);	0.0416
	194.19	6.3848	(H-5)→(L); (H-3)→(L+1); (H-3)→(L+2); (H-2)→(L+1); (H-2)→(L+2); (H)→(L+2);	0.2686
	186.43 (202)[a]	6.6505	(H-4)→(L+3); (H-3)→(L); (H-3)→(L+1); (H-2)→(L+1); (H-2)→(L+2); (H-1)→(L+3);	0.1899
	180.49	6.8694	(H-5)→(L); (H-5)→(L+1); (H-3)→(L+2); (H-2)→(L+1);	0.3137
	166.94	7.4270	(H-5)→(L+1); (H-3)→(L+2); (H-2)→(L+1); (H)→(L+5);	0.3386
	160.72	7.7143	(H-3)→(L+4); (H-2)→(L+4); (H)→(L+4);	0.0058

H: HOMO.
L: LUMO.
[a] Experimental wavelength.

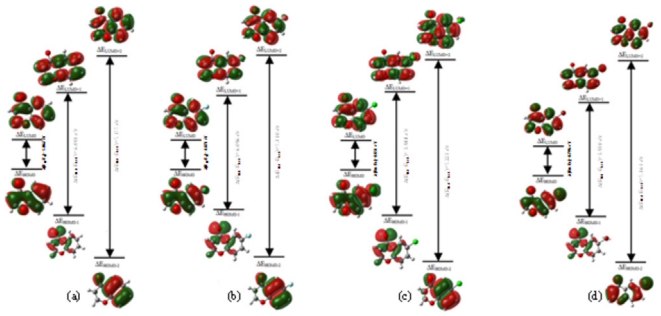


Fig. 5. HOMO-LUMO plots chromone (a) and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F (b), Cl (c) and Br (d))] molecules.

170 nm, 222 nm and 274 nm, which were experimentally measured at 203 nm, 217 nm and 298 nm. The λ_{max} values for 6-Fluorochromone determined at 172/203 nm, 226/220 nm and 283/301 nm in the experimental/theoretical procedure. The λ_{max} values of 6-Chlorochromone and 6-Bromochromone were experimentally detected at 204/225/302 nm and 202/227/307 nm, respectively.

2.5. HOMO-LUMO analysis

By using HOMO and LUMO energy values for a molecule, the global chemical reactivity descriptors of molecules such as chemical hardness (η), chemical potential (μ), softness (S), electronegativity (χ) and electrophilicity index (ω) were defined [42,43]. On the basis of E_{HOMO} and E_{LUMO}, these are calculated using below equations. Using Koopman's theorem [44] for closed shell molecules.

$I = -E_{HOMO}$ (Ionization potential).

$A = -E_{LUMO}$ (Electron Affinity).

The hardness of the molecule is

$$\eta = -\frac{I - A}{2}$$

The chemical potential of the molecule is

$$\mu = -\frac{I - A}{2}$$

The softness of the molecule is

$$S = \frac{1}{\eta}$$

The electronegativity of the molecule is

$$\chi = \frac{I + A}{2}$$

The electrophilicity index of the molecule is

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

whereas hard molecules have a large HOMO-LUMO gap, soft molecules have a small HOMO-LUMO gap. In terms of chemical reactivity, we can conclude that soft molecules will be more reactive than hard molecules for unimolecular reactions such as isomerization and dissociation. In the present study, $\Delta E_{H\text{-}L}$ gap value are reduced when 6-position of the chromone molecule are substituted halogen. As seen in Fig. 5 and Table 8, the sequence of HOMO-LUMO gap is the Chr>6-Flchr>6-*Cl*chr>6-Brchr. So, chromone is the hardest than 6-halogen substituted chromone molecule. In addition to, it can be said that all molecules are more polarizable than the urea because their energy gap are lower than the urea ($\Delta E_{H\text{-}L} = 6.7063$ eV) [45]. The chemical hardness is also a good indicator of chemical stability. The more the chemical hardness the more stable the compound will be. The chemical hardness of the chromone and some 6-halogen substituted [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules was determined at 2.531 eV, 2.436 eV, 2.426 eV and 2.398 eV, respectively. Chromone molecule is the more stable than 6-halogen substituted [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules [46–49].

Energy of HOMO is directly related to the ionization potential (IP) and LUMO energy is directly related to the electron affinity (EA). The IP value defined that the energies value of the 6.834 eV (Chr), 6.875 eV (6-Flchr), 6.916 eV (6-*Cl*chr) and 6.849 eV (6-Brchr) are required to remove an electron from the HOMO. The energies value of EA (1.772 eV (Chr), 2.003 eV (6-Flchr), 2.065 eV (6-*Cl*chr) and 2.052 eV (6-Brchr)) indicates that the studied molecules readily accept electrons to form bonds. The biological activity can be described using the electrophilicity index. For the chromone and some 6-halogen substituted [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules, the electrophilicity index were predicted at 3.658 eV, 4.045 eV, 4.157 eV and 4.130 eV, respectively. It can be showed that the all molecules are biologically active [46–49].

3. Conclusion

In conclusion, we report the first the spectral data such as FT-IR, NMR and UV–Vis spectra, optimized geometric parameters and some electronic properties of the chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F (b), *Cl* (c) and Br (d))] molecules. The FT-IR, NMR and UV–Vis spectra of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F (b), *Cl* (c) and Br (d))] molecules, show similar and relatively simple spectral

Table 8
Some selected electronic molecular properties of chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F, *Cl* and Br)] molecules.

	ΔE_{LUMO+2} (eV)	ΔE_{LUMO+1} (eV)	ΔE_{LUMO} (eV)	ΔE_{HOMO} (eV)	ΔE_{HOMO+1} (eV)	ΔE_{HOMO+2} (eV)	$\Delta E_{H\text{-}L}$ (eV)	$\Delta E_{(H\text{-}1)\text{-}(L+1)}$ (eV)	$\Delta E_{(H\text{-}2)\text{-}(L+2)}$ (eV)
Chr	−0.301	−0.883	−1.772	−6.834	−6.884	−7.478	5.062	6.001	7.177
6-Flchr	−0.478	−0.971	−2.003	−6.875	−7.067	−7.789	4.871	6.096	7.310
6-*Cl*chr	−0.619	−1.187	−2.065	−6.916	−7.131	−7.844	4.851	5.944	7.225
6-Brchr	−0.610	−1.190	−2.052	−6.849	−7.121	−7.772	4.796	5.930	7.161
	I (eV)	A (eV)	η (eV)	S $(eV)^{-1}$	χ (eV)	μ (eV)	ω (eV)		
Chr	6.834	1.772	2.531	0.396	4.303	4.303	3.658		
6-Flchr	6.875	2.003	2.436	0.410	4.439	4.439	4.045		
6-*Cl*chr	6.917	2.065	2.426	0.412	4.491	4.491	4.157		
6-Brchr	6.849	2.053	2.398	0.417	4.451	4.451	4.130		

patterns, suggesting that they have similar structures. Theoretical calculations showed that chromone and some 6-halogen substituted chromone [$C_9O_2H_5X$ (X: F (b), Cl (c) and Br (d))] molecules have Cs symmetry.

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