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SPECTRAL INFORMATIONS AND INTRAMOLECULAR INTERACTIONS OF 2-(4-FLUOROPHENYL)-3-HYDROXY-7-METHYLCHROMEN-4-ONE SUPPORTED BY NATURAL BOND ORBITAL ANALYSIS

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Abstract

Chromene (Benzopyran) is a polycyclic organic compound that results from the fusion of benzene ring to a heterocyclic pyran ring, which constitutes basic backbone of various types of polyphenol, widely found in alkaloids, tocopherols, flavonoids, and anthocyanins. These compounds are biologically active natural products and promising synthetic compounds in the field of medicinal, agrochemical, cosmetics and pigment industries. Harmonic vibrational frequencies of 2-(4-fluorophenyl)-3-hydroxy-7-methylchromen-4-one have been carried out with the help of density functional theory (DFT) method by employing B3LYP/6-311++G(d,p) basis set. Optimized geometric bond length parameters were calculated and analyzed. C-H…O and O-H…O intramolecular interactions were confirmed via both experimental and computational analysis.

***Keywords: Chromene; FT-IR; FT-Raman; DFT; NBO*.**

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1. INTRODUCTION

Chromene (Benzopyran) consists of a benzene ring fused to a γ-pyrone ring and are synthetically versatile substrates used as raw material for drug synthesis. Drug molecules bearing chromene unit have been investigated for their human immune deficiency virus-inhibitory (HIV),cytotoxic (anticancer), neuroprotective, antimicrobial, antifungal and antioxidant activity [1].Diverse applications in the fields of medicine, agriculture and related pharmacology of chromene derivatives have been developed during last several years.

Title compound 2-(4-fluorophenyl)-3-hydroxy-7-methylchromen-4-one (FPHMC) is a derivative of chromene belonging to flavonoid family having C3-C4 double bond.Spectroscopic techniques such asFourier-transform Infrared spectroscopy (FT-IR), Fourier-transform Raman spectroscopy (FT-Raman),along with density functional theory (DFT) computations aid to determine molecular structural elucidation of title compound. Experimental and computational investigations for determining mentioned properties of FPHMC have not been reported in literature so far. This article highlightshydrogen bonding interactions and aims to focus the chromophore characteristics including the free hydroxyl groups, carbonyl group, electronegative atom fluorine, C=C double bond, confirmed by both computational and FT-IR and FT-Raman spectral analytical studies.Computational studies such as Normal Coordinate Analysis (NCA) gathers detailed vibrational assignments and indicates the various intramolecular interactions that are responsible for the stabilization of title compound leading to its medicinal activity.

2 EXPERIMENTAL DETAILS

2-(4-fluorophenyl)-3-hydroxy-7-methylchromen-4-one was purchased (powder) with a stated purity of greater than 94% from OTAVA Chemicals, Canada. FT-IR spectrum of CFPHC was recorded using Perkin Elmer spectrophotometer in the region 4000-400 cm^{-1} with the spectral resolution of 1 cm^{-1} and FT-Raman spectrum of CFPHC was recorded in the region 4000-50 cm^{-1} using Bruker RFS 27 spectrophotometer using 1064 nm excitation from an Nd:YAG (neodymium-doped yttrium aluminium garnet) laser source with the spectral resolution of 2 cm^{-1}.

3 COMPUTATIONAL DETAILS

Geometry optimization and vibrational wavenumber were performed using Becke-3-Lee-Yang-Parr (B3LYP) gradient correlation functional with 6-311++G(d,p) the basis set [2-6] using Gaussian 09W program package developed by Frisch and coworkers [7]. To improve the agreement between predicted and observed wavenumbers, computed harmonic wavenumbers were scaled and scaling factor (0.9673) [8-9] for the corresponding basis set was used according to the scaled quantum mechanical force field (SQMFF) procedure [10]. Deviation from the experiments after scaling was found to be less than 10 cm^{-1} with a few exceptions. Descriptions of the predicted wavenumbers during the scaling process were followed by potential energy distribution matrix computed using MOLVIB 7.0 program package [10-11] and cartesian representation of the force constants were transferred to a non-redundant set of symmetry coordinates, chosen in accordance with the recommendations of Pulay et al. [13].

4RESULTS AND DISCUSSIONS

4.1 OPTIMIZED GEOMETRY

Optimized geometrical structure of 2-(4-fluorophenyl)-3-hydroxy-7-methylchromen-4-one **(**FPHMC) is as shown in figure 1 and optimized bond length are tabulated in Table 1. Double bond O11=C2 is 1.21 Å, andring C-O bond length is 1.43 Å agrees well [14] but bond lengths C4-O5=1.37Å and C6-O5=1.35Å are reduced due to the presence of electron donating oxygen atoms.Elongation of O12-H13=0.97bond length occursdue to hyperconjugation.Donor-acceptor distance of intramolecular hydrogen bond O12-H31 is 2.14Å which is supported by vander Waals radii (2.5 Å) [15].Bond lengths of methyl-phenylring vary due to the electron cloud surrounding each atom, which repels each other leading to a lot of destabilization that arises due to steric effect. Replacement of hydrogen by methyl group in C_8 alters bond lengths and electronic charge is back donated from the lone pair oxygen atom to σ* orbital of C-H bonds, followed by the increase in C-H bond distances.

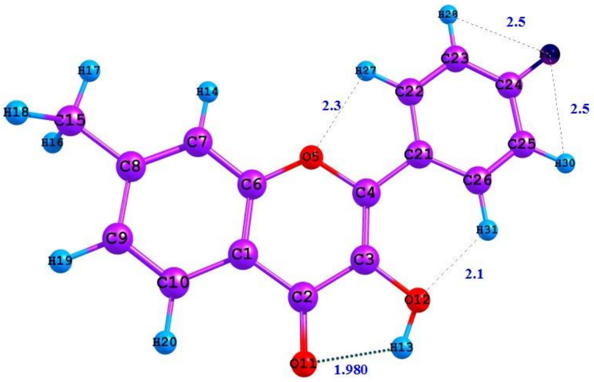

Fig1.OPTIMIZED STRUCTURE OF FPHMC

Table 1.OPTIMIZED BOND LENGTH OF FPHMC

Bond Length(Å)	
Parameters	Calc.
C1-C6	1.39
C1-C10	1.43
C2-C3	1.46
C2-O11	1.23
C3-C4	1.36
C3-O12	1.35
O5-C6	1.35
C8-C15	1.5
C9-H19	1.08
C10-H20	1.08
O12-H13	0.97
O12-H31	2.14
C15-H16	1.09
C15-H17	1.09
C15-H18	1.09

4.2 SPECTRAL ANALYSIS

FPHMChas 28 atoms and 78 normal modes of vibrations.Theoretical and simulated IR and Raman spectra of FPHMC have been constructed and shown in figures 2(a) and 2(b).Selected spectral assignments with PED contributions are summarized in Table 2.

Table2.SPECTRAL ASSIGNMENTS OF FPHMC

Observed fundamentals (cm^{-1})		**Assignment with (PED%)**
IR	**Raman**	
3438vs		υOH (100)
1633	1637	$υ_{db}$CO (60)υCC1 (20)
1265vs	1290,vs	υR3CC(48),βR1OH(20), υR2CC(16)
1393s	1393s	υR3CC(47), βR1OH(14), υR2CC(13)
	3064, 3089w	υCH (99)
1139,1166,1230s	1351s	βR3CH(53),υR3CF(17),υR3CC(17)
1107,1308m	1174m	βR3CH(33), βR2CH(21), υR3CC(10)
691m		βR1CO(23),R2ADO (17), R1TD(13)
842s	801m	R2TD (43), υR1CCl (13), υR1CC (11)
1205vs		υR3CC(30), υR3CF(18), υR1CC(15),
318vw		βR3CF(41), R3AD (24)
1473,1609 vs	1568,1605s	υR2CC (62), υR1CC (10)
1415,1509 m	1459,1510 m	υR2CC (56), R3CC (30)

vs: very strong; s: strong; m: medium; w: weak; υ: stretching; R–ring; β:bending; db: double bond;TD-trigonal deformation; AD- asymmetric deformation; ADO- out of plane asymmetric deformation.

4.2.1Hydroxyl Vibrations

Hydroxyl vibrations generally expected to occur around 3600 cm^{-1} [16]. Broad obvious band in the spectrum red shifts the frequency range at 3438 cm^{-1} in IR due to intramolecular O-H···O hydrogen bonding interaction. O-H in-plane bending modes occur as strong bands in the region 1440-1260 cm^{-1} [16] which appears as a very strong band at 1265 cm^{-1} in IR and at 1290 cm^{-1} in FT-Raman with medium intensity.

4.2.2 Carbonyl Vibrations

Bands due to C-C=O-OH vibration is expected to occur in the region 1680-1720 cm^{-1} and the conjugated C=C-C=O grouping frequencies red shifts to 1633 and 1637 cm^{-1} in FT-IR, and FT-Raman respectively the C=O stretching modes [17]. Fundamental CC=O bending mode at 606 cm^{-1} (IR), 616 cm^{-1} (R) for chromenes appears as weak bands at 617 (IR) and 620 cm^{-1}(R) for FPHMC.

4.2.3Hydrocarbon Vibrations

Hydrocarbonstretching vibrations give rise to multiple band in the region 3100-3000 cm^{-1} which are observed as weak bands at 3100cm^{-1} and 3082 cm^{-1} in FT-Raman. In-plane aromatic C-H bending vibrations appear in the range 1400-1000 cm^{-1}[18-19] and C-H in-plane bending vibrations are assigned as strong bands at 1139,1166,1230cm^{-1} in FT-IR and at 1351cm^{-1} in FT-Raman. Medium bands at 1107, 1308 cm^{-1} in FT-IR and at 1174 cm^{-1} in FT-Raman are attributed to C-H in-plane bending vibrations.

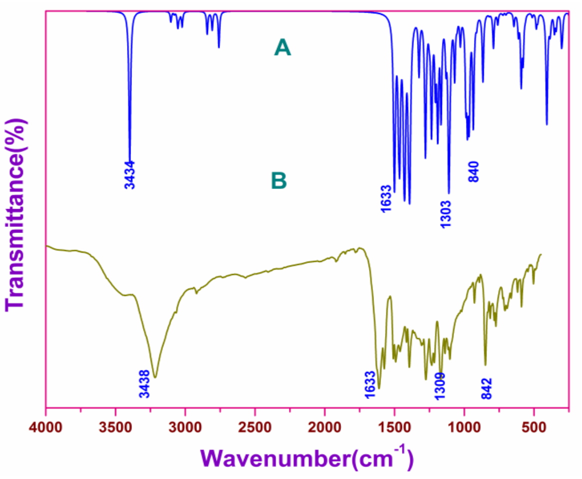

Fig 2(a) FT-IR SPECTRA OF FPHMC

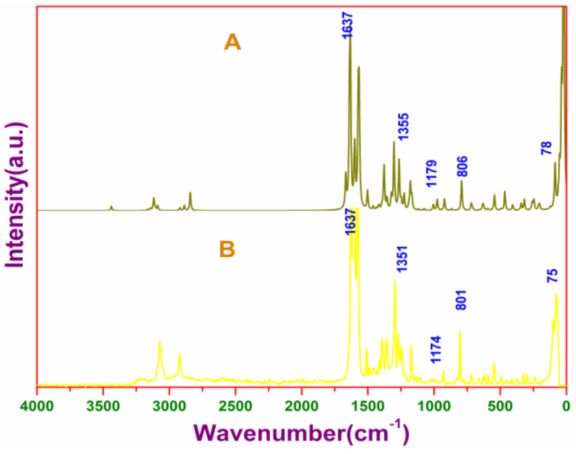

Fig..2(b) FT-RAMAN SPECTRA OF FPHMC

4.2.4 Ring Vibrations

Bands between 1400 and 1650 cm^{-1} in benzene derivatives are usually assigned to C=C and C-C stretching modes [18,19]. In FPHMC, the aromatic C-C stretching vibrations are observed as very strong bands at 1473 and 1609 cm^{-1} in FT-IR and at 1568 and 1605 cm^{-1} in FT-Raman. CCC in-plane bending vibrations are observed at 691cm^{-1}in FT-IR and out-of plane bending vibrations appear at 465cm^{-1} in FT-Raman. These assignments are in good agreement with literature indicating that the substitutions do not affect much the vibrations of these modes.

5 CONCLUSIONS

Optimized bond lengths and spectral assignments predicts the structural properties and hydrogen bonding interactions. Lowering of C=O stretching band is due to intra-molecular O-H…O hydrogen bonding with neighbouring hydroxyl group which was confirmed from wavenumber assignments that red shifts νOH thereby broad and sharp intense band is observed. Theoretical C-H stretching vibrations are in good agreement with each other and lies well within the expected range.

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