



Analysis of the nonlinear optical properties, vibrational spectra, DFT method and photovoltaic performance of cyanidin-3-rutinoside chloride

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Abstract

This study aims to identify a cyanidin-3-rutinoside chloride that exhibits both photovoltaic performance and nonlinear optical properties, which may be utilized in the field of optoelectronics. Prior to investigating these properties, the stable structure must be determined. For this purpose, its conformational analysis is performed by the Molecular Force Field method with the spartan program. The exact nature of the stable configuration has been ascertained by empirical evidence. The energy of the stable configuration is -1654184.76 kcal/mol, and its dipole moment is 9.94 Debye. Cyanidin-3-rutinoside chloride has been investigated using experimental FT-IR and Raman spectroscopies. Meanwhile, the DFT method at the B3LYP/6-311++G(d, p) level was employed in order to study the simulated FT-IR and Raman spectra, the HOMO-LUMO analysis, the molecular electrostatic potentials (MEP), and the non-linear optical (NLO) characteristics of the title molecule. The HOMO and LUMO energies are **-6.45** and **-3.64** electron volts (eV), respectively, with a gap value of **2.81** eV. Additionally, the title compound's open-circuit voltage, the transition density matrix light-harvesting efficiency, driving force, and binding energy were calculated with by taking photovoltaic cell properties into account. Furthermore, investigations of hole reorganization energy, electron reorganization energy, and total reorganization energy were carried out at the B3LYP/6-31G(d, p) level for the cyanidin-3-rutinoside chloride of interest. In addition, density of state calculations and NBO were made at the B3LYP/6-31G(d, p) level. We calculated the following values for LHE, V_{oc} , ΔG_{inject} , E_b , λ_h , λ_e and λ_{total} : **0.06**, **2.45 eV**, **0.20 eV**, **0.56 eV**, **0.50 eV**, **0.57 eV** and **1.06 eV**, respectively.

Keywords DFT · Cyanidin-3-rutinoside chloride · Nonlinear optic · Photovoltaic performance

1 Introduction

Today, it is well-known that the energy demands have increased in parallel with concerns regarding greenhouse gas emissions and climate change as the global population continues to rise. This phenomenon has significantly inspired researchers across the globe to explore alternative and environmentally friendly approaches to energy generation. Solar energy, among the many renewable energy sources, provides abundant, passive, and environmentally favorable power with enormous potential to meet global energy consumption demands. The conversion of this abundant and environmentally friendly energy source into electrical power is made feasible and affordable through photovoltaics (El-Shishtawy et al. 2014; Kokkonen et al. 2021).

Dye-sensitized solar cells (DSSCs) have garnered significant interest as cost-effective and high-performing alternatives to traditional photovoltaic systems. Both academic and industry groups have shown significant interest in DSSCs due to their exceptional performance and affordable price. Enhancing the efficiency of converting solar energy into electricity is a significant focus of study in the field of DSSCs (Sen et al. 2023). Significant research efforts have been dedicated to the development of sensitizers for DSSCs. Improving the performance of DSSCs requires comprehensive knowledge of the absorption spectrum of the photosensitizer dye in visible light. This distinct attribute enhances the efficacy of the electron transfer process by facilitating the provision of electrons to the conduction band of titanium dioxide (TiO₂) (Yadav et al. 2021). Various varieties of light-sensitive paints described in the literature have the ability to generate an electric current. We categorize light-sensitive paints into two groups: artificial and natural pigments. Artificial dyes, despite their expensive prices, exhibit superior performance compared to natural dyes, which have lower performance and degrade over time. Natural dyes are derived only from the bark or essence of plants (Kh et al. 2021; Özgün et al. 2023; Roy et al. 2023).

Anthocyanins, a class of organic compounds, are naturally occurring pigments found throughout the natural world. They play a crucial role in the coloration of flowers, fruits, vegetables, and plants (Lee et al. 2014). Anthocyanins are a common class of water-soluble plant chemicals that are responsible for the spectacular color (red, orange, and blue) of fruits and flowers. Cyanidin and its glycosides are members of the anthocyanins family. Anthocyanins are a subset of flavonoids, which are a diverse and abundant category of plant compounds. Anthocyanins are pigments primarily responsible for the attractive colors in fruits, fruit juices, wines, flowers, and vegetables (Tulio et al. 2008; Li et al. 2021). Natural dyes consist of pigments that absorb light. Plant leaves, fruits, flowers, and stems can serve as sources for extracting dyes. The pigments responsible for light absorption are anthocyanins, chlorophyll, betalains, and other substances. These have been extensively investigated for their potential use in solar cells (Okello et al. 2021). In this content, as a member of the flavonoid family the cyanidin-3-rutinoside chloride (C₂₇H₃₁O₁₅Cl, here after referred as C3RC molecule) which is a light-sensitive dye derived from cherries, has been attracted by us.

Density Functional Theory (DFT) simulations are a computationally efficient and cost-effective method for analyzing and comprehending the optimal geometry, vibrational spectra, and possibly reactive locales of a molecule system (Divya et al. 2024). It also aids in the interpretation of the molecule's necessary information by comparing it to experimental results. In addition, they allow virtual imaging to provide three-dimensional views of the chemical and physical processes taking place within the molecule. In this study, the C3RC

molecule's quantum chemical characteristics were calculated using the Gaussian 09 program and the DFT/B3LYP/6-311++G(d, p) levels of theory. because, it provides the most accurate for computations of the ground and excited states (Reeda et al. 2023; Suja et al. 2024).

This work computationally tests the viability of a C3RC flavonoid as an optoelectronic material using DFT and time-dependent density functional theory (TD-DFT) computations. Therefore, in this work, the experimental FT-IR and Raman spectra and the simulated vibrational spectra and the non-linear optical (NLO) characteristics calculated at the B3LYP/6-311++G(d, p) level (Rao et al. 2021) of DFT theory. The HOMO-LUMO analysis, UV analysis, the MEP, and TDM of C3RC molecule were investigated at the B3LYP/6-311++G(d, p) level of TD-DFT theory. Moreover, DOS calculations were done at the B3LYP/6-31G(d, p) level of TD-DFT theory. Additionally, since the flavonoid family is employed as a dye in solar cells (Erdogdu et al. 2024). The photovoltaic characteristics of the C3RC molecule were also calculated. The objective of this investigation is to identify a C3RC molecule that possesses both nonlinear optical properties and photovoltaic performance, for potential application in the field of optoelectronics. We intend to ascertain whether C3RC is suitable for use as an optoelectronic material as a consequence of this investigation.

2 Computational methods

Theoretical computations are employed to examine a specific structure among alternatives. Scanning the potential energy region to generate conformers is the initial step in accomplishing this. The computations started with conformational analysis in order to get the accurate structure. The Spartan 14 (Irvine 2014) software was utilized to do conformational analysis, where the conformational space of molecules was explored using the Molecular Mechanics Force Fields (MMFF) (Halgren 1996) technique. Ten-degree rotations were applied to the sigma bonds (O_3-C_{22} , O_3-C_{26} , O_5-C_{18} , O_6-C_{19} , O_7-C_{25} , O_7-C_{29} , O_8-C_{20} , O_9-C_{21} , $O_{10}-H_{63}$, $O_{11}-C_{24}$, $C_{27}-C_{28}$, $O_{13}-C_{35}$, $O_{14}-C_{40}$, $O_{15}-C_{41}$, and $O_{16}-C_{43}$) of the compound in order to perform theoretical calculations. Following the conformation analysis of C3RC molecule, the bond lengths, bond angles, and dihedral angles of the most stable structure can be computed in this article. Using the density functional theory (DFT) technique Becke-3-Lee-Yang-Parr functional (B3LYP) functionality on a conventional 6-311++G(d, p) (Ans et al. 2019) ground set, the structural improvements of the obtained conformational isomers were achieved. The successful completion of optimization was indicated by the absence of imaginary frequency. The computation was performed utilizing the Gaussian 09 W program (Frisch 2009).

In addition, the wave numbers of harmonic vibrations were determined. However, it should be noted that the wavenumber values obtained at these levels are merely systematic errors. As a result, the calculated vibrational wavenumbers per factor were 0.955 (greater than 800 cm^{-1}) and 0.967 (less than 1800 cm^{-1}) (Erdogdu et al. 2012; Dereli et al. 2015; Dereli 2016). The NewFor Program (Pulay and Torok 1966) includes the Total Energy Distribution (TED) test, which was utilized to qualify the basic vibrational modes of C3RC molecule. The investigation involved the utilization of DFT to analyze both infrared and Raman vibrational properties, with theoretical outcomes being compared to empirical data.

Furthermore, in order to investigate the non-linear optical (NLO) characteristics, the DFT calculations were expanded to include the mean polarizability (α), the total dipole moment (μ), first-order hyperpolarizability (δ) and second-order hyperpolarizability (γ). Using a basis set of 6-311++G(d, p), NLO analysis were performed at the B3LYP level of DFT. The DFT/B3LYP approach was employed to calculate the highest filled molecular orbital - lowest empty molecular orbital energies (HOMO-LUMO) and atomic charges of C3RC molecule in its ground state. The calculations utilized the 6-311++G(d, p) ground set. In this work, all of these parameters were determined and evaluated using the DFT-TD/B3LYP technique and the 6-311++G(d, p) basis set. In order to determine the energy, we employed DFT with B3LYP/6-311++G(d, p) to analyze the time-dependent self-consistent field (TD-SCF) of C3RC molecule in the gaseous phases.

A transition density matrix (TDM) is another way to look at the exciton dynamics, which includes how the electron-hole pair is created, moved, and separated. The TDM for the C3RC molecule was constructed using TD-DFT calculations at the B3LYP/6-311++G(d, p) level, then it was plotted using Multiwfn 3.8 software (Lu and Chen 2012) in the form of a two-dimensional colored plot. At the B3LYP/6-311++G(d, p) level, MEP calculations were performed on the C3RC molecule. The three-dimensional (3D) MEP analysis was conducted using the Gauss View 5 (Dennington et al. 2009) software. At the surfaces denoted by blue, red, and green, the electrostatic potentials are also illustrated in the MEP figure. Non-covalent interaction (NCI) of molecule was carried out using the Multiwfn (Lu and Chen 2012) and Visual Molecular Dynamics (VMD) visualization tools (Humphrey et al. 1996).

In the present study, we also address the discussion of DOS, NBO and computed photo-voltaic parameters, including the open-circuit voltage (V_{oc}), electron reorganization energy (λ_e), hole reorganization energy (λ_h), light-harvesting efficiency (LHE), total reorganization energy (λ_{total}), short-circuit current density (J_{sc}), driving force (ΔG_{inject}), and binding energy (E_b) at the B3LYP/6-311G(d, p) level. PyMOLyze software (Tenderholt 2019) was used for DOS spectra.

3 Experimental

The C3RC molecule was employed following its acquisition from such wholesalers as Merck. The infrared spectrum of solid C3RC molecule was obtained using a Thermo Nicolet™ iS50 IR Spectrometer at room temperature with 2 cm⁻¹ resolutions covering a range of 3500–600 cm⁻¹. The prepared sample was compressed into self-supporting pellet and introduced into an IR cell equipped with KBr window. The Raman spectrum was acquired using 1064 nm excitation from the Nd: YAG laser on the Brucker FRA 106/S spectrometer. The detector was a Ge-diode cooled to liquid nitrogen temperature. The Raman spectrum was recorded by using laser irradiation with a wavelength of 785 nm and a power of 30 mW. The spectrum was recorded in the wavelength region of 3500–600 cm⁻¹.

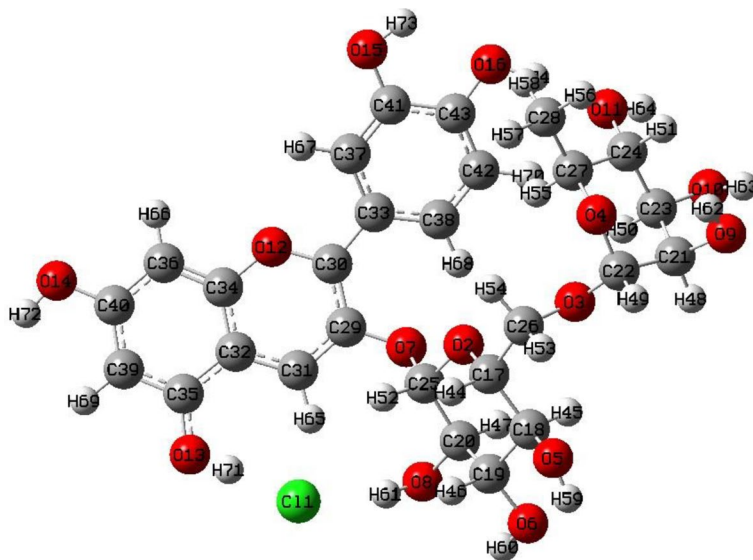


Fig. 1 Stable conformer of the C3RC molecule

Table 1 The calculated energies of C3RC molecule

Conf.	E (kcal/mol)	ΔE (kcal/mol)	Dip. Mom. (D)
1	-1654184.76	0.00	9.94
2	-1654183.74	1.02	8.51
3	-1654182.78	1.98	11.65

4 Results and discussions

4.1 Molecular geometry and optimization

The atomic numbering of the C3RC molecule, along with its molecular structure, is illustrated in Fig. 1. The conformational study involved rotating the free rotation bonds of the C3RC molecule at 10-degree intervals to explore its conformational space. Table 1 displays the most stable conformers of the C3RC molecule, along with the overall dipole moment of the compound. The simulations were performed using the optimized molecular structure provided in Conformer 1.

Three distinct configurations of the C3RC molecule were discovered throughout the investigation. The dipole moment of the most stable conformation, depicted in Fig. 1, was determined to be 9.94 Debye and its energy was -1654184.76 kcal/mol.

Table 2 displays the geometrical parameters of this conformer as calculated using the DFT/B3LYP technique with the 6-311++G(d, p) basis set, and it compares these parameters to their experimental values. Theoretical values of C3RC were compared to the results of a crystal structure analysis of Cyanidin Bromide Monohydrate (Ueno and Saito 1977). By comparing the experimental and predicted bond lengths of the four phenolic OH groups ($O_{13}-H_{71}$, $O_{14}-H_{72}$, $O_{15}-H_{73}$, and $O_{16}-H_{74}$) of the C3RC, it is clear from Fig. 1; Table 2 that there is no significant difference. Additionally, as can be seen in Table 2, the values that were

Table 2 The calculated geometric parameters of C3RC molecule by B3LYP/6-311++G(d, p) method, bond lengths in Angstrom (Å) and angles in degrees (°)

Bond Length	Teo.	Lit. ^a	Bond Angles	Teo.	Bond Angles	Teo.	Lit. ^a	Dihedral Angles	Teo.	Dihedral Angles	Teo.
Cl ₁ -H ₆₁	2.20	-	H ₆₁ -Cl ₁ -H ₆₅	64.2	O ₇ -C ₂₉ -C ₃₀	120.6	122.4	H ₅₉ -O ₅ -C ₁₈ -C ₁₇	166.3	O ₉ -C ₂₁ -C ₂₂ -O ₃	-168.6
Cl ₁ -H ₆₅	2.37	-	H ₆₁ -Cl ₁ -H ₇₁	115.1	O ₇ -C ₂₉ -C ₃₁	119.7	118.1	H ₅₉ -O ₅ -C ₁₈ -C ₁₉	46.4	O ₉ -C ₂₁ -C ₂₂ -O ₄	67.2
Cl ₁ -H ₇₁	1.98	-	H ₆₅ -Cl ₁ -H ₇₁	57.3	C ₃₀ -C ₂₉ -C ₃₁	119.7	119.5	H ₅₉ -O ₅ -C ₁₈ -H ₄₅	-74.9	O ₉ -C ₂₁ -C ₂₂ -H ₄₉	-46.9
O ₂ -C ₁₇	1.43	-	C ₁₇ -O ₂ -C ₂₅	114.0	O ₁₂ -C ₃₀ -C ₂₉	117.8	118.4	H ₆₀ -O ₆ -C ₁₉ -C ₁₈	-173.6	C ₂₃ -C ₂₁ -C ₂₂ -O ₃	69.3
O ₂ -C ₂₅	1.42	-	C ₂₂ -O ₃ -C ₂₆	114.7	O ₁₂ -C ₃₀ -C ₃₃	113.7	112.4	H ₆₀ -O ₆ -C ₁₉ -C ₂₀	-51.7	C ₂₃ -C ₂₁ -C ₂₂ -O ₄	-54.9
O ₃ -C ₂₂	1.40	-	C ₂₂ -O ₄ -C ₂₇	115.1	C ₂₉ -C ₃₀ -C ₃₃	128.5	129.2	H ₆₀ -O ₆ -C ₁₉ -H ₄₆	68.5	C ₂₃ -C ₂₁ -C ₂₂ -H ₄₉	169.0
O ₃ -C ₂₆	1.43	-	C ₁₈ -O ₅ -H ₅₉	107.2	C ₂₉ -C ₃₁ -C ₃₂	121.5	121.3	C ₂₉ -O ₇ -C ₂₅ -O ₂	-104.4	H ₄₈ -C ₂₁ -C ₂₂ -O ₃	-51.7
O ₄ -C ₂₂	1.43	-	C ₁₉ -O ₆ -H ₆₀	107.4	C ₂₉ -C ₃₁ -H ₆₅	118.4	118	C ₂₉ -O ₇ -C ₂₅ -C ₂₀	135.8	H ₄₈ -C ₂₁ -C ₂₂ -O ₄	-175.9
O ₄ -C ₂₇	1.45	-	C ₂₅ -O ₇ -C ₂₉	117.4	C ₃₂ -C ₃₁ -H ₆₅	120.0	121	C ₂₉ -O ₇ -C ₂₅ -H ₅₂	14.6	H ₄₈ -C ₂₁ -C ₂₂ -H ₄₉	70.0
O ₅ -C ₁₈	1.42	-	C ₂₀ -O ₈ -H ₆₁	110.0	C ₃₁ -C ₃₂ -C ₃₄	117.4	118.4	C ₂₅ -O ₇ -C ₂₉ -C ₃₀	119.2	O ₉ -C ₂₁ -C ₂₃ -O ₁₀	52.4
O ₅ -H ₅₉	0.97	-	C ₂₁ -O ₉ -H ₆₂	108.5	C ₃₁ -C ₃₂ -C ₃₅	124.4	124.5	C ₂₅ -O ₇ -C ₂₉ -C ₃₁	-61.9	O ₉ -C ₂₁ -C ₂₃ -C ₂₄	-70.5
O ₆ -C ₁₉	1.42	-	C ₂₃ -O ₁₀ -H ₆₃	107.0	C ₃₄ -C ₃₂ -C ₃₅	118.2	117.1	H ₆₁ -O ₈ -C ₂₀ -C ₁₉	68.7	O ₉ -C ₂₁ -C ₂₃ -H ₅₀	169.8
O ₆ -H ₆₀	0.97	-	O ₂ -C ₁₇ -C ₁₈	109.8	C ₃₀ -C ₃₃ -C ₃₇	119.4	119.4	H ₆₁ -O ₈ -C ₂₀ -C ₂₅	-54.3	C ₂₂ -C ₂₁ -C ₂₃ -O ₁₀	174.8
O ₇ -C ₂₅	1.43	-	O ₂ -C ₁₇ -C ₂₆	108.3	C ₃₀ -C ₃₃ -C ₃₈	121.6	121.8	H ₆₁ -O ₈ -C ₂₀ -H ₄₇	-172.6	C ₂₂ -C ₂₁ -C ₂₃ -C ₂₄	51.9
O ₇ -C ₂₉	1.36	-	O ₂ -C ₁₇ -H ₄₄	109.8	C ₃₇ -C ₃₃ -C ₃₈	119.0	118.9	C ₂₀ -O ₈ -H ₆₁ -C ₁₁	62.5	C ₂₂ -C ₂₁ -C ₂₃ -H ₅₀	-67.8
O ₈ -C ₂₀	1.41	-	C ₁₈ -C ₁₇ -C ₂₆	113.9	O ₁₂ -C ₃₄ -C ₃₂	118.8	118.6	H ₆₂ -O ₉ -C ₂₁ -C ₂₂	-36.8	H ₄₈ -C ₂₁ -C ₂₃ -O ₁₀	-64.3
O ₈ -H ₆₁	0.98	-	C ₁₈ -C ₁₇ -H ₄₄	108.4	O ₁₂ -C ₃₄ -C ₃₆	117.7	118.6	H ₆₂ -O ₉ -C ₂₁ -C ₂₃	85.1	H ₄₈ -C ₂₁ -C ₂₃ -C ₂₄	172.8
O ₉ -C ₂₁	1.43	-	C ₂₆ -C ₁₇ -H ₄₄	106.6	C ₃₂ -C ₃₄ -C ₃₆	123.5	124.1	H ₆₂ -O ₉ -C ₂₁ -H ₄₈	-155.9	H ₄₈ -C ₂₁ -C ₂₃ -H ₅₀	53.1
O ₉ -H ₆₂	0.97	-	O ₅ -C ₁₈ -C ₁₇	107.9	O ₁₃ -C ₃₅ -C ₃₂	123.5	125.2	H ₆₃ -O ₁₀ -C ₂₃ -C ₂₁	-37.6	O ₁₀ -C ₂₃ -C ₂₄ -O ₁₁	60.7
O ₁₀ -C ₂₃	1.43	-	O ₅ -C ₁₈ -C ₁₉	111.7	O ₁₃ -C ₃₅ -C ₃₉	118.3	114.8	H ₆₃ -O ₁₀ -C ₂₃ -C ₂₄	86.1	O ₁₀ -C ₂₃ -C ₂₄ -C ₂₇	-177.1
O ₁₀ -H ₆₃	0.97	-	O ₅ -C ₁₈ -H ₄₅	110.2	C ₃₂ -C ₃₅ -C ₃₉	118.1	120.0	H ₆₃ -O ₁₀ -C ₂₃ -H ₅₀	-156.3	O ₁₀ -C ₂₃ -C ₂₄ -H ₅₁	-57.4
O ₁₁ -C ₂₄	1.44	-	C ₁₇ -C ₁₈ -C ₁₉	109.0	C ₃₄ -C ₃₆ -C ₄₀	116.8	116.7	H ₆₄ -O ₁₁ -C ₂₄ -C ₂₃	-47.3	C ₂₁ -C ₂₃ -C ₂₄ -O ₁₁	-175.1
O ₁₁ -H ₆₄	0.97	-	C ₁₇ -C ₁₈ -H ₄₅	108.9	C ₃₄ -C ₃₆ -H ₆₆	122.0	123.0	H ₆₄ -O ₁₁ -C ₂₄ -C ₂₇	-170.1	C ₂₁ -C ₂₃ -C ₂₄ -C ₂₇	-52.9
O ₁₁ -H ₇₄	1.78	-	C ₁₉ -C ₁₈ -H ₄₅	109.0	C ₄₀ -C ₃₆ -H ₆₆	121.2	120.0	H ₆₄ -O ₁₁ -C ₂₄ -H ₅₁	71.5	C ₂₁ -C ₂₃ -C ₂₄ -H ₅₁	66.8
O ₁₂ -C ₃₀	1.35	1.35	O ₆ -C ₁₉ -C ₁₈	107.4	C ₃₃ -C ₃₇ -C ₄₁	120.5	120.4	C ₃₄ -O ₁₂ -C ₃₀ -C ₂₉	4.4	H ₅₀ -C ₂₃ -C ₂₄ -O ₁₁	-55.4

Table 2 (continued)

Bond Length	Teo.	Lit. ^a	Bond Angles	Teo.	Bond Angles	Teo.	Lit. ^a	Dihedral Angles	Teo.	Dihedral Angles	Teo.
O ₁₂ -C ₃₄	1.36	1.36	O ₆ -C ₁₉ -C ₂₀	111.3	C ₃₃ -C ₃₇ -H ₆₇	121.0	122.0	C ₃₄ -O ₁₂ -C ₃₀ -C ₃₃	-	H ₅₀ -C ₂₃ -C ₂₄ -C ₂₇	66.8
O ₁₃ -C ₃₅	1.32	1.34	O ₆ -C ₁₉ -H ₄₆	109.5	C ₄₁ -C ₃₇ -H ₆₇	118.4	118.0	C ₃₀ -O ₁₂ -C ₃₄ -C ₃₂	-1.5	H ₅₀ -C ₂₃ -C ₂₄ -H ₅₁	-
O ₁₃ -H ₇₁	1.01	0.79	C ₁₈ -C ₁₉ -C ₂₀	111.2	C ₃₃ -C ₃₈ -C ₄₂	120.2	119.9	C ₃₀ -O ₁₂ -C ₃₄ -C ₃₆	179.5	O ₁₁ -C ₂₄ -C ₂₇ -O ₄	176.5
O ₁₄ -C ₄₀	1.35	1.34	C ₁₈ -C ₁₉ -H ₄₆	108.8	C ₃₃ -C ₃₈ -H ₆₈	120.3	122.0	H ₇₁ -O ₁₃ -C ₃₅ -C ₃₂	22.6	O ₁₁ -C ₂₄ -C ₂₇ -C ₂₈	-65.3
O ₁₄ -H ₇₂	0.96	0.89	C ₂₀ -C ₁₉ -H ₄₆	108.6	C ₄₂ -C ₃₈ -H ₆₈	119.5	118.0	H ₇₁ -O ₁₃ -C ₃₅ -C ₃₉	-	O ₁₁ -C ₂₄ -C ₂₇ -H ₅₅	58.4
O ₁₅ -C ₄₁	1.36	1.36	O ₈ -C ₂₀ -C ₁₉	111.2	C ₃₅ -C ₃₉ -C ₄₀	121.0	120.0	H ₇₂ -O ₁₄ -C ₄₀ -C ₃₆	-	C ₂₃ -C ₂₄ -C ₂₇ -O ₄	54.9
O ₁₅ -H ₇₃	0.97	1.02	O ₈ -C ₂₀ -C ₂₅	113.2	C ₃₅ -C ₃₉ -H ₆₉	118.1	118.0	H ₇₂ -O ₁₄ -C ₄₀ -C ₃₉	-0.7	C ₂₃ -C ₂₄ -C ₂₇ -C ₂₈	173.2
O ₁₆ -C ₄₃	1.35	1.35	O ₈ -C ₂₀ -H ₄₇	106.4	C ₄₀ -C ₃₉ -H ₆₉	120.8	120.0	H ₇₃ -O ₁₅ -C ₄₁ -C ₃₇	177.4	C ₂₃ -C ₂₄ -C ₂₇ -H ₅₅	-63.2
O ₁₆ -H ₇₄	0.98	0.82	C ₁₉ -C ₂₀ -C ₂₅	108.9	O ₁₄ -C ₄₀ -C ₃₆	116.3	116.6	H ₇₃ -O ₁₅ -C ₄₁ -C ₄₃	-0.8	H ₅₁ -C ₂₄ -C ₂₇ -O ₄	-65.3
C ₁₇ -C ₁₈	1.53	-	C ₁₉ -C ₂₀ -H ₄₇	109.1	O ₁₄ -C ₄₀ -C ₃₉	121.5	121.2	H ₇₄ -O ₁₆ -C ₄₃ -C ₄₁	160.0	H ₅₁ -C ₂₄ -C ₂₇ -C ₂₈	52.9
C ₁₇ -C ₂₆	1.52	-	C ₂₅ -C ₂₀ -H ₄₇	107.9	C ₃₆ -C ₄₀ -C ₃₉	122.2	122.1	H ₇₄ -O ₁₆ -C ₄₃ -C ₄₂	-19.8	H ₅₁ -C ₂₄ -C ₂₇ -H ₅₅	176.6
C ₁₇ -H ₄₄	1.10	-	O ₉ -C ₂₁ -C ₂₂	110.8	O ₁₅ -C ₄₁ -C ₃₇	120.1	124.9	O ₂ -C ₁₇ -C ₁₈ -O ₅	-	O ₄ -C ₂₇ -C ₂₈ -H ₅₆	60.2
C ₁₈ -C ₁₉	1.52	-	O ₉ -C ₂₁ -C ₂₃	110.3	O ₁₅ -C ₄₁ -C ₄₃	120.0	114.7	O ₂ -C ₁₇ -C ₁₈ -C ₁₉	-57.0	O ₄ -C ₂₇ -C ₂₈ -H ₅₇	-59.5
C ₁₈ -H ₄₅	1.10	-	O ₉ -C ₂₁ -H ₄₈	106.2	C ₃₇ -C ₄₁ -C ₄₃	119.9	120.4	O ₂ -C ₁₇ -C ₁₈ -H ₄₅	61.8	O ₄ -C ₂₇ -C ₂₈ -H ₅₈	-
C ₁₉ -C ₂₀	1.53	-	C ₂₂ -C ₂₁ -C ₂₃	110.0	C ₃₈ -C ₄₂ -C ₄₃	120.5	120.9	C ₂₆ -C ₁₇ -C ₁₈ -O ₅	59.8	C ₂₄ -C ₂₇ -C ₂₈ -H ₅₆	-58.8
C ₁₉ -H ₄₆	1.10	-	C ₂₂ -C ₂₁ -H ₄₈	109.8	C ₃₈ -C ₄₂ -H ₇₀	120.2	119.0	C ₂₆ -C ₁₇ -C ₁₈ -C ₁₉	-	C ₂₄ -C ₂₇ -C ₂₈ -H ₅₇	-
C ₂₀ -C ₂₅	1.53	-	C ₂₃ -C ₂₁ -H ₄₈	109.8	C ₄₃ -C ₄₂ -H ₇₀	119.3	119.0	C ₂₆ -C ₁₇ -C ₁₈ -H ₄₅	-59.8	C ₂₄ -C ₂₇ -C ₂₈ -H ₅₈	61.7
C ₂₀ -H ₄₇	1.09	-	O ₃ -C ₂₂ -O ₄	113.5	O ₁₆ -C ₄₃ -C ₄₁	115.9	116.3	H ₄₄ -C ₁₇ -C ₁₈ -O ₅	-58.6	H ₅₅ -C ₂₇ -C ₂₈ -H ₅₆	178.4
C ₂₁ -C ₂₂	1.53	-	O ₃ -C ₂₂ -C ₂₁	108.0	O ₁₆ -C ₄₃ -C ₄₂	124.3	124.2	H ₄₄ -C ₁₇ -C ₁₈ -C ₁₉	62.9	H ₅₅ -C ₂₇ -C ₂₈ -H ₅₇	58.8
C ₂₁ -C ₂₃	1.53	-	O ₃ -C ₂₂ -H ₄₉	111.2	C ₄₁ -C ₄₃ -C ₄₂	119.8	119.5	H ₄₄ -C ₁₇ -C ₁₈ -H ₄₅	-	H ₅₅ -C ₂₇ -C ₂₈ -H ₅₈	-61.1
C ₂₁ -H ₄₈	1.09	-	O ₄ -C ₂₂ -C ₂₁	109.8	Cl ₁ -H ₆₁ -O ₈	168.4	-	O ₂ -C ₁₇ -C ₂₆ -O ₃	-64.8	O ₇ -C ₂₉ -C ₃₀ -O ₁₂	176.6
C ₂₂ -H ₄₉	1.10	-	O ₄ -C ₂₂ -H ₄₉	104.1	Cl ₁ -H ₆₅ -C ₃₁	139.6	-	O ₂ -C ₁₇ -C ₂₆ -H ₅₃	175.1	O ₇ -C ₂₉ -C ₃₀ -C ₃₃	-5.6
C ₂₃ -C ₂₄	1.53	-	C ₂₁ -C ₂₂ -H ₄₉	110.3	Dihedral Angles	Teo.		O ₂ -C ₁₇ -C ₂₆ -H ₅₄	56.3	C ₃₁ -C ₂₉ -C ₃₀ -O ₁₂	-2.3
C ₂₃ -H ₅₀	1.09	-	O ₁₀ -C ₂₃ -C ₂₁	112.0	H ₆₁ -Cl ₁ -O ₁₃ -C ₃₅	-68.6	-	C ₁₈ -C ₁₇ -C ₂₆ -O ₃	57.7	C ₃₁ -C ₂₉ -C ₃₀ -C ₃₃	175.6

Table 2 (continued)

Bond Length	Teo.	Lit. ^a	Bond Angles	Teo.	Bond Angles	Teo.	Lit. ^a	Dihedral Angles	Teo.	Dihedral Angles	Teo.
C ₂₄ -C ₂₇	1.53	-	O ₁₀ -C ₂₃ -C ₂₄	109.6	H ₆₅ -Cl ₁ -O ₁₃ -C ₃₅	-39.3	-	C ₁₈ -C ₁₇ -C ₂₆ -H ₅₃	-62.4	O ₇ -C ₂₉ -C ₃₁ -C ₃₂	178.5
C ₂₄ -H ₅₁	1.10	-	O ₁₀ -C ₂₃ -H ₅₀	106.5	H ₆₅ -Cl ₁ -H ₆₁ -O ₈	25.1	-	C ₁₈ -C ₁₇ -C ₂₆ -H ₅₄	178.8	O ₇ -C ₂₉ -C ₃₁ -H ₆₅	1.6
C ₂₅ -H ₅₂	1.10	-	C ₂₁ -C ₂₃ -C ₂₄	111.0	H ₇₁ -Cl ₁ -H ₆₁ -O ₈	52.3	-	H ₄₄ -C ₁₇ -C ₂₆ -O ₃	177.1	C ₃₀ -C ₂₉ -C ₃₁ -C ₃₂	-2.6
C ₂₆ -H ₅₃	1.10	-	C ₂₁ -C ₂₃ -H ₅₀	108.8	H ₆₁ -Cl ₁ -H ₆₅ -C ₃₁	-	-	H ₄₄ -C ₁₇ -C ₂₆ -H ₅₃	57.0	C ₃₀ -C ₂₉ -C ₃₁ -H ₆₅	-
C ₂₆ -H ₅₄	1.09	-	C ₂₄ -C ₂₃ -H ₅₀	108.8	H ₇₁ -Cl ₁ -H ₆₅ -C ₃₁	73.3	-	H ₄₄ -C ₁₇ -C ₂₆ -H ₅₄	-61.7	O ₁₂ -C ₃₀ -C ₃₃ -C ₃₇	16.7
C ₂₇ -C ₂₈	1.52	-	O ₁₁ -C ₂₄ -C ₂₃	109.3	C ₂₅ -O ₂ -C ₁₇ -C ₁₈	60.6	-	O ₃ -C ₁₈ -C ₁₉ -O ₆	-63.5	O ₁₂ -C ₃₀ -C ₃₃ -C ₃₈	-
C ₂₇ -H ₅₅	1.10	-	O ₁₁ -C ₂₄ -C ₂₇	110.4	C ₂₅ -O ₂ -C ₁₇ -C ₂₆	-	-	O ₃ -C ₁₈ -C ₁₉ -C ₂₀	174.6	C ₂₉ -C ₃₀ -C ₃₃ -C ₃₇	-
C ₂₈ -H ₅₆	1.09	-	O ₁₁ -C ₂₄ -H ₅₁	108.1	C ₂₅ -O ₂ -C ₁₇ -H ₄₄	-58.4	-	O ₃ -C ₁₈ -C ₁₉ -H ₄₆	55.0	C ₂₉ -C ₃₀ -C ₃₃ -C ₃₈	16.2
C ₂₈ -H ₅₇	1.09	-	C ₂₃ -C ₂₄ -C ₂₇	111.3	C ₁₇ -O ₂ -C ₂₅ -O ₇	-	-	C ₁₇ -C ₁₈ -C ₁₉ -O ₆	177.4	C ₂₉ -C ₃₁ -C ₃₂ -C ₃₄	5.4
C ₂₈ -H ₅₈	1.09	-	C ₂₃ -C ₂₄ -H ₅₁	109.3	C ₁₇ -O ₂ -C ₂₅ -C ₂₀	-59.7	-	C ₁₇ -C ₁₈ -C ₁₉ -C ₂₀	55.4	C ₂₉ -C ₃₁ -C ₃₂ -C ₃₅	-
C ₂₉ -C ₃₀	1.40	-	C ₂₇ -C ₂₄ -H ₅₁	108.4	C ₁₇ -O ₂ -C ₂₅ -H ₅₂	63.5	-	C ₁₇ -C ₁₈ -C ₁₉ -H ₄₆	-64.2	H ₆₅ -C ₃₁ -C ₃₂ -C ₃₄	-
C ₂₉ -C ₃₁	1.39	-	O ₂ -C ₂₅ -O ₇	105.3	C ₂₆ -O ₃ -C ₂₂ -O ₄	-69.1	-	H ₄₅ -C ₁₈ -C ₁₉ -O ₆	58.6	H ₆₅ -C ₃₁ -C ₃₂ -C ₃₅	1.1
C ₃₀ -C ₃₃	1.45	1.45	O ₂ -C ₂₅ -C ₂₀	111.5	C ₂₆ -O ₃ -C ₂₂ -C ₂₁	169.0	-	H ₄₅ -C ₁₈ -C ₁₉ -C ₂₀	-63.4	C ₂₉ -C ₃₁ -H ₆₅ -Cl ₁	109.0
C ₃₁ -C ₃₂	1.39	1.39	O ₂ -C ₂₅ -H ₅₂	110.5	C ₂₆ -O ₃ -C ₂₂ -H ₄₉	47.9	-	H ₄₅ -C ₁₈ -C ₁₉ -H ₄₆	177.1	C ₃₂ -C ₃₁ -H ₆₅ -Cl ₁	-68.0
C ₃₁ -H ₆₅	1.08	0.95	O ₇ -C ₂₅ -C ₂₀	109.1	C ₂₂ -O ₃ -C ₂₆ -C ₁₇	-	-	O ₆ -C ₁₉ -C ₂₀ -O ₈	61.4	C ₃₁ -C ₃₂ -C ₃₄ -O ₁₂	-3.4
C ₃₂ -C ₃₄	1.42	1.43	O ₇ -C ₂₅ -H ₅₂	109.8	C ₂₂ -O ₃ -C ₂₆ -H ₅₃	-43.1	-	O ₆ -C ₁₉ -C ₂₀ -C ₂₅	-	C ₃₁ -C ₃₂ -C ₃₄ -C ₃₆	175.6
C ₃₂ -C ₃₅	1.44	1.43	C ₂₀ -C ₂₅ -H ₅₂	110.5	C ₂₂ -O ₃ -C ₂₆ -H ₅₄	76.9	-	O ₆ -C ₁₉ -C ₂₀ -H ₄₇	-55.7	C ₃₅ -C ₃₂ -C ₃₄ -O ₁₂	177.7
C ₃₃ -C ₃₇	1.41	1.40	O ₃ -C ₂₆ -C ₁₇	110.3	C ₂₇ -O ₄ -C ₂₂ -O ₃	-58.6	-	C ₁₈ -C ₁₉ -C ₂₀ -O ₈	-	C ₃₅ -C ₃₂ -C ₃₄ -C ₃₆	-3.3
C ₃₃ -C ₃₈	1.41	1.40	O ₃ -C ₂₆ -H ₅₃	109.8	C ₂₇ -O ₄ -C ₂₂ -C ₂₁	62.3	-	C ₁₈ -C ₁₉ -C ₂₀ -C ₂₅	-53.5	C ₃₁ -C ₃₂ -C ₃₅ -O ₁₃	3.8
C ₃₄ -C ₃₆	1.38	1.38	O ₃ -C ₂₆ -H ₅₄	110.0	C ₂₇ -O ₄ -C ₂₂ -H ₄₉	-	-	C ₁₈ -C ₁₉ -C ₂₀ -H ₄₇	64.0	C ₃₁ -C ₃₂ -C ₃₅ -C ₃₉	-
C ₃₅ -C ₃₉	1.39	1.37	C ₁₇ -C ₂₆ -H ₅₃	108.3	C ₂₂ -O ₄ -C ₂₇ -C ₂₄	-61.5	-	H ₄₆ -C ₁₉ -C ₂₀ -O ₈	-59.3	C ₃₄ -C ₃₂ -C ₃₅ -O ₁₃	-
C ₃₆ -C ₄₀	1.40	1.39	C ₁₇ -C ₂₆ -H ₅₄	109.4	C ₂₂ -O ₄ -C ₂₇ -C ₂₈	175.9	-	H ₄₆ -C ₁₉ -C ₂₀ -C ₂₅	66.1	C ₃₄ -C ₃₂ -C ₃₅ -C ₃₉	3.7
C ₃₆ -H ₆₆	1.08	1.09	H ₅₃ -C ₂₆ -H ₅₄	109.1	C ₂₂ -O ₄ -C ₂₇ -H ₅₅	56.6	-	H ₄₆ -C ₁₉ -C ₂₀ -H ₄₇	-	C ₃₀ -C ₃₃ -C ₃₇ -C ₄₁	174.5

Table 2 (continued)

Bond Length	Teo.	Lit. ^a	Bond Angles	Teo.	Bond Angles	Teo.	Lit. ^a	Dihedral Angles	Teo.	Dihedral Angles	Teo.
C ₃₇ -C ₄₁	1.38	1.37	O ₄ -C ₂₇ -C ₂₄	107.9	C ₃₂ -C ₃₄ - C ₃₆ -C ₄₀	0.8	-	O ₈ -C ₂₀ - C ₂₅ -O ₂	178.5	C ₃₀ -C ₃₃ - C ₃₇ -H ₆₇	-2.8
C ₃₇ -H ₆₇	1.08	0.97	O ₄ -C ₂₇ -C ₂₈	106.8	C ₃₂ -C ₃₄ - C ₃₆ -H ₆₆	-	-	O ₈ -C ₂₀ - C ₂₅ -O ₇	-65.6	C ₃₈ -C ₃₃ - C ₃₇ -C ₄₁	-3.1
C ₃₈ -C ₄₂	1.38	1.38	O ₄ -C ₂₇ -H ₅₅	108.9	O ₁₃ -C ₃₅ - C ₃₉ -C ₄₀	179.2	-	O ₈ -C ₂₀ - C ₂₅ -H ₅₂	55.3	C ₃₈ -C ₃₃ - C ₃₇ -H ₆₇	179.6
C ₃₈ -H ₆₈	1.08	1.0	C ₂₄ -C ₂₇ -C ₂₈	113.8	O ₁₃ -C ₃₅ - C ₃₉ -H ₆₉	0.8	-	C ₁₉ -C ₂₀ - C ₂₅ -O ₂	54.2	C ₃₀ -C ₃₃ - C ₃₈ -C ₄₂	-
C ₃₉ -C ₄₀	1.40	1.41	C ₂₄ -C ₂₇ -H ₅₅	108.9	C ₃₂ -C ₃₅ - C ₃₉ -C ₄₀	-1.9	-	C ₁₉ -C ₂₀ - C ₂₅ -O ₇	170.2	C ₃₀ -C ₃₃ - C ₃₈ -H ₆₈	4.2
C ₃₉ -H ₆₉	1.08	0.94	C ₂₈ -C ₂₇ -H ₅₅	110.4	C ₃₂ -C ₃₅ - C ₃₉ -H ₆₉	179.7	-	C ₁₉ -C ₂₀ - C ₂₅ -H ₅₂	-69.0	C ₃₇ -C ₃₃ - C ₃₈ -C ₄₂	2.5
C ₄₁ -C ₄₃	1.41	1.4	C ₂₇ -C ₂₈ -H ₅₆	110.5	C ₃₄ -C ₃₆ - C ₄₀ -O ₁₄	-	-	H ₄₇ -C ₂₀ - C ₂₅ -O ₂	-64.0	C ₃₇ -C ₃₃ - C ₃₈ -H ₆₈	-
C ₄₂ -C ₄₃	1.39	1.38	C ₂₇ -C ₂₈ -H ₅₇	110.0	C ₃₄ -C ₃₆ - C ₄₀ -C ₃₉	1.2	-	H ₄₇ -C ₂₀ - C ₂₅ -O ₇	51.9	O ₁₂ -C ₃₄ - C ₃₆ -C ₄₀	179.8
C ₄₂ -H ₇₀	1.08	1.0	C ₂₇ -C ₂₈ -H ₅₈	110.7	H ₆₆ -C ₃₆ - C ₄₀ -O ₁₄	0.2	-	H ₄₇ -C ₂₀ - C ₂₅ -H ₅₂	172.7	O ₁₂ -C ₃₄ - C ₃₆ -H ₆₆	-0.1
Bond Angles	Teo.	Lit.^a	H ₅₆ -C ₂₈ -H ₅₇	108.4	H ₆₆ -C ₃₆ - C ₄₀ -C ₃₉	-	-	H ₆₇ -C ₃₇ - C ₄₁ -O ₁₅	-0.5	C ₃₅ -C ₃₉ - C ₄₀ -O ₁₄	-
C ₂₄ -O ₁₁ - H ₆₄	106.4	-	H ₅₆ -C ₂₈ -H ₅₈	108.6	C ₃₃ -C ₃₇ - C ₄₁ -O ₁₅	-	-	H ₆₇ -C ₃₇ - C ₄₁ -C ₄₃	177.7	C ₃₅ -C ₃₉ - C ₄₀ -C ₃₆	-0.6
C ₃₀ -O ₁₂ - C ₃₄	124.5	123.7	H ₅₇ -C ₂₈ -H ₅₈	108.5	C ₃₃ -C ₃₇ - C ₄₁ -C ₄₃	0.3	-	C ₃₃ -C ₃₈ - C ₄₂ -C ₄₃	0.9	H ₆₉ -C ₃₉ - C ₄₀ -O ₁₄	-1.3
C ₃₅ -O ₁₃ - H ₇₁	116.8	110			C ₃₇ -C ₄₁ - C ₄₃ -O ₁₆	-	-	C ₃₃ -C ₃₈ - C ₄₂ -H ₇₀	179.7	H ₆₉ -C ₃₉ - C ₄₀ -C ₃₆	177.7
C ₄₀ -O ₁₄ - H ₇₂	110.4	110			C ₃₇ -C ₄₁ - C ₄₃ -C ₄₂	3.1	-	H ₆₈ -C ₃₈ - C ₄₂ -C ₄₃	-	O ₁₅ -C ₄₁ - C ₄₃ -O ₁₆	1.6
C ₄₁ -O ₁₅ - H ₇₃	108.2	115			C ₃₈ -C ₄₂ - C ₄₃ -O ₁₆	176.0	-	H ₆₈ -C ₃₈ - C ₄₂ -H ₇₀	0.4	O ₁₅ -C ₄₁ - C ₄₃ -C ₄₂	-
C ₄₃ -O ₁₆ - H ₇₄	110.9	112			C ₃₈ -C ₄₂ - C ₄₃ -C ₄₁	-3.8	-	H ₇₀ -C ₄₂ - C ₄₃ -O ₁₆	-2.8	H ₇₀ -C ₄₂ - C ₄₃ -C ₄₁	177.5

*Experimental values have been taken from ref (Ueno and Saito 1977)

computed and those that were observed for the C-C bond lengths of the rings are showing a good agreement with each other. The discrepancies observed between the calculated and experimental outcomes may be attributed to the dissimilarities in the structural environments. Specifically, the experimental data for Cyanidin Bromide Monohydrate (Ueno and Saito 1977) was acquired from a crystal structure, whereas the theoretical calculations pertain to the gaseous phase. It is important to note that the study utilized cyanidin data of the chemical-based under investigation. The findings on rutinoides could not be compared by experimental means.

4.2 Vibrational properties

Since the C3RC molecule comprises 74 atoms, it has 216 fundamental vibrational modes according to 3N-6 freedom degrees. In all modes of the molecule, infrared and Raman spectroscopy activity is present. For the C3RC molecule, theoretical calculations provided

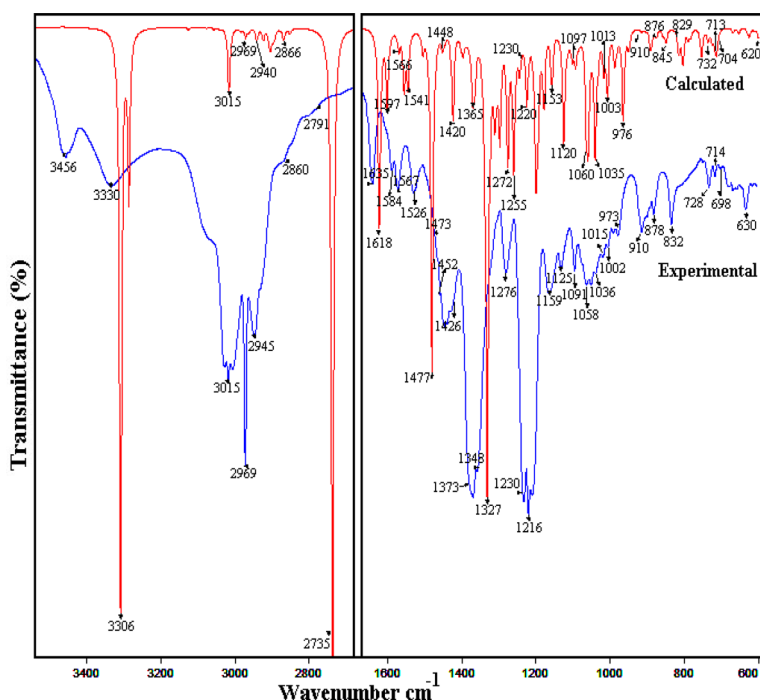


Fig. 2 FT-IR spectra of the C3RC molecule, both experimental and computational

support for the assignment of bands identified in the solid-state FT-IR and Raman spectra. While employing the B3LYP/6-311++G(d, p) basis set, frequencies are computed using the harmonic approximation.

Figures 2 and 3, separated into two sections (IR; 3500–2500 cm^{-1} and 1700–600 cm^{-1} and Raman; 3450–2550 cm^{-1} and 1700–600 cm^{-1}), display the experimental and simulated wavenumbers of the C3RC molecule at the B3LYP/6-311++G(d, p) level, respectively.

The frequency values of these vibrational modes were subsequently utilized to assess the vibrational motions of diverse atomic groups. The vibration frequencies obtained through experimentation are compared with the frequencies computed in Table 3.

4.2.1 Stretching vibrations

By considering Table 3, the observed /calculated at the mentioned level hydroxyl (OH) stretching mode originated from cyaniding group of title molecule were found as 3330 (IR) and 3307 (R) cm^{-1} / 3306 cm^{-1} . However, the vibrational wavenumber shifting between IR experimental and the calculated values is 24 cm^{-1} while the observed Raman wavenumber and the calculated value are in a very good agreement. On the other hand, the combination of the $\nu(\text{OH})$ and $\nu(\text{C}_1\text{--H}_{61})$ stretching modes was found as 3276 (R) / 3284 cm^{-1} (which has the shifting of 8 cm^{-1}) for the title molecule and according to PED analysis these values take place with the pure modes by the 37% and 34% PED contributions, respectively, (Colthup et al. 1964; Stuart 2004; Varsányi 2012; Bellamy 2013; Silverstein et al. 2005; 2014). The $\nu(\text{CH})$ stretching vibrations of cyanidin were observed at 3104 and 3041 (R)

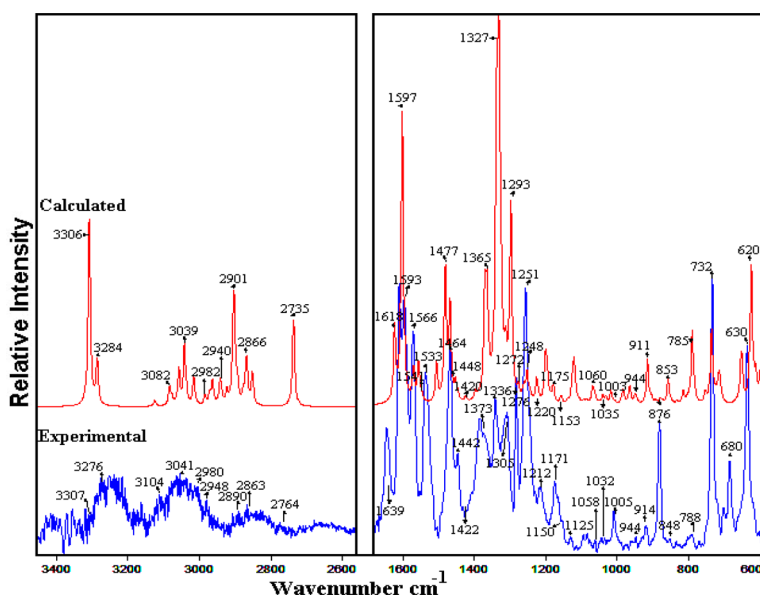


Fig. 3 Raman spectra of the C3RC molecule, both experimental and computational

cm^{-1} while the computed values were found in ranging from 3082 to 3014 cm^{-1} with the pure mode of 73% PED contributions (Silverstein et al. 2014; Rajkumar et al. 2023; Kumar et al. 2024). Furthermore, the combination of the ν (CH) and ν ($\text{Cl}_1\text{-H}_{65}$) stretching modes of cyanidin group was found as 3015 (IR) / 3014 cm^{-1} (which has just the shifting of 1 cm^{-1}) for the title molecule and according to PED analysis this value takes place with the pure modes by the 31% and 34% PED contributions, respectively.

The peaks at 2969 (IR) / 2969 and 2980 (R) / 2982 cm^{-1} can be attributed to the C-H asymmetric vibrational mode of CH_3 methyl group (Silverstein et al. 2014; Thirunavukkarasu et al. 2018; Kanagathara et al. 2023). However, the C-H symmetric vibrational mode of CH_3 methyl group is not observed. Similarly, the vibrational stretching CH_2 methylene group are no observed as seen in Table 3.

On the other hand, the combination of the ν (O-H_{71}) and ν ($\text{Cl}_1\text{-H}_{71}$) stretching modes in cyanidin were found as 2791 (IR) and 2764 (R) / 2735 cm^{-1} with the pure modes by the 36% and 34% PED contributions, respectively (Rajkumar et al. 2023). In accordance with our studies, we can state that the observed / computed single bonded C-O vibrations take place at 1348 (IR) and 1336 (R) / 1327 cm^{-1} , 1058 (IR) and 1058 (R) / 1060 cm^{-1} and 1015 (IR) / 1013 cm^{-1} (Kumar et al. 2024).

As for the aromatic $\text{C}=\text{C}$ double-bonded stretching vibrations can be attributed to the observed /calculated peaks at 1567 (IR) and 1566 (R) / 1566 cm^{-1} and 1426 (IR) and 1422 (R) / 1420 cm^{-1} (Thirunavukkarasu et al. 2018).

4.2.2 Bending vibrations

The CCH in-plane bending vibrational modes are observed at the interval 1635–1159 cm^{-1} in IR and 1639–1150 cm^{-1} in Raman spectra, respectively (Silverstein et al. 2014; Mohan

Table 3 Analysis of the observed and computed vibrational spectra of the C3RC molecule

Mode Nos.	Exp. Wave-numbers (cm ⁻¹)		Theoretical wavenumbers (cm ⁻¹)		TED ^b (%)	
	IR	Raman	Scaled Freq. ^a	I _{IR}	I _{Raman}	
1	-	-	3648	10	2	89 ν(OH), cyanidin
2	-	-	3635	4	1	83 ν(OH), rutinoid
3	-	-	3625	3	1	83 ν(OH), rutinoid
4	-	-	3618	2	0	80 ν(OH), rutinoid
5	-	-	3604	7	1	87 ν(OH), cyanidin
6	-	-	3597	4	0	82 ν(OH), rutinoid
7	-	-	3590	5	1	81 ν(OH), rutinoid
8	3330	3307	3306	84	11	81 ν(OH), cyanidin
9	-	3276	3284	24	2	37 ν(OH)+34 ν(Cl ₁ -H ₆₁)
10	-	-	3123	0	0	73 ν(CH), cyanidin+6 δ(CCC)+6 ν(CC)
11	-	3104	3082	0	1	73 ν(CH), cyanidin+6 ν(CC)+5 δ(CCC)
12	-	-	3074	0	0	72 ν(CH), cyanidin+6 ν(CC)+5 δ(CCC)
13	-	-	3056	0	2	72 ν(CH), cyanidin+6 δ(CCC)+5 δ(CCH)
14	-	3041	3039	0	3	73 ν(CH), cyanidin+6 ν(CC)+5 δ(CCC)
15	3015	-	3014	9	1	31 ν(CH), cyanidin+25 ν(Cl ₁ -H ₆₅)
16	-	2980	2982	0	0	89 vas, (CH ₃)
17	2969	-	2969	1	1	82 vas, (CH ₃)
18	-	-	2961	1	1	51 ν(CH), rutinoid
19	2945	2948	2940	1	1	48 ν(CH), rutinoid
20	-	-	2938	1	0	82 vas, (CH ₂)
21	-	-	2921	2	1	49 ν(CH), rutinoid
22	-	-	2906	2	1	70 vs (CH ₃)
23	-	-	2902	1	3	57 ν(CH), rutinoid
24	-	2890	2901	1	2	60 ν(CH), rutinoid
25	-	-	2895	1	1	67 vas, (CH ₂)
26	-	-	2890	1	0	53 ν(CH), rutinoid
27	-	-	2875	0	1	49 ν(CH), rutinoid
28	2860	2863	2866	2	2	47 ν(CH), rutinoid+5 τ(CCCH)
29	-	-	2850	1	2	48 vs (CH), rutinoid
30	-	-	2846	0	0	50 vas (CH), rutinoid
31	2791	2764	2735	100	4	36 ν(O-H ₇₁)+34 ν(Cl ₁ -H ₇₁)
32	1635	1639	1618	29	14	26 δ(CCH), cyanidin+19 ν(CC)
33	1584	1593	1597	11	56	25 δ(CCH), cyanidin+18 ν(CC)
34	1567	1566	1566	3	6	21 ν(CC)+18 δ(CCH), cyanidin+11 δ(CCC)+10 δ(OCC)
35	-	-	1552	8	7	35 δ(CCH), cyanidin+10 ν(CC)
36	1526	1533	1541	8	1	23 δ(CCH), cyanidin+18 ν(CC)+10 δ(CCC)+10 δ(OCC)
37	-	-	1501	3	8	25 δ(CCH), cyanidin+17 ν(CC)
38	1473	1464	1477	50	24	21 δ(CCH), cyanidin+12 ν(CC)
39	-	-	1464	0	17	15 ν(CC)+12 δ(CCH), cyanidin
40	1452	1442	1449	1	1	35 δ deformation (CH ₃)+24 δ(CH ₂), Scissoring
41	-	-	1449	0	0	38 δ(CH ₂) Scissoring+20 δ deformation (CH ₃)
42	-	-	1447	1	3	12 ν(CC)+11 δ(CCH)

Table 3 (continued)

Mode Nos.	Exp. Wave-numbers (cm ⁻¹)		Theoretical wavenumbers (cm ⁻¹)		TED ^b (%)	
	IR	Raman	Scaled Freq. ^a	I _{IR}	I _{Raman}	
43	-	-	1441	1	1	66 δ deformation (CH ₃)
44	1426	1422	1420	13	1	8 δ (CCH)+8 ν (CC)
45	-	-	1398	2	0	36 γ (HClH)+20 γ (COH)+11 γ (OCCH), rutinocide
46	-	-	1395	0	0	17 δ (CCH)+15 γ (OCH), rutinocide
47	-	-	1393	1	1	12 γ (HClHO)+8 δ (CCH)
48	-	-	1392	1	1	24 δ deformation (CH ₃) + 8 δ (COH)+8 δ (OCH)
49	-	-	1388	1	0	23 δ (CH ₂), wagging+15 δ (OCH)+7 γ (COCH)
50	-	-	1382	1	1	15 δ (OCH)+12 δ (CCH)+7 γ (HClHO)
51	-	-	1376	1	0	29 δ s (CH ₃) umbrella+13 δ (OCH)
52	-	-	1370	2	0	31 δ (CCH)+13 δ s (CH ₃) umbrella
53	-	-	1368	1	0	15 δ (CH ₂), wagging+10 δ (OCH)
54	-	-	1367	1	4	17 δ (CCH)
55	1373	1373	1365	6	13	17 δ (CCH)+7 δ (OCH)
56	-	-	1361	3	3	10 δ (CCH)+7 δ (OCH)
57	-	-	1360	3	14	10 δ (OCH)+7 δ (COH)+7 δ (CCH)
58	-	-	1352	0	1	32 δ (CCH)+6 δ (OCH)
59	-	-	1343	0	0	22 δ (OCH)+16 δ (CCH)
60	-	-	1334	10	32	5 δ (CCH)+5 δ (COH)
61	1348	1336	1327	64	100	14 ν (OC) + 10 δ (CCH)
62	-	-	1321	1	0	13 δ (CCH)+8 δ (OCH)+8 δ (COH)
63	-	-	1318	2	1	14 δ (CCH)+11 δ (OCH)
64	-	-	1316	1	1	16 δ (CCH)+8 δ (COC)
65	-	-	1313	1	1	33 γ (HCCH)+13 δ (OCH)
66	-	-	1307	9	7	6 δ (CCH)+6 ν (CC)
67	-	-	1302	5	0	18 δ (CCH)+16 δ (OCH)+8 δ (COH)
68	-	-	1294	7	15	15 δ (CHH)+5 δ (OCH)
69	-	1305	1293	7	20	12 δ (CCH)
70	-	-	1290	1	1	19 δ (CCH)+10 δ (OCH)+9 δ (COH)
71	1276	1276	1272	18	2	21 δ (CCH)+8 ν (OC) + 6 ν (CC)
72	-	-	1260	0	1	24 δ (CCH)+12 δ (OCH)+7 δ (COH)
73	-	-	1256	16	2	9 δ (CH ₂), twisting+5 δ (COH)
74	-	-	1255	3	0	13 δ (CH ₂), twisting+9 δ (COH)
75	-	1251	1248	1	5	13 δ (CCH)+11 δ (COH)
76	-	-	1240	4	1	16 δ (CCH)+9 δ (OCH)+8 δ (COH)
77	-	-	1238	1	0	21 δ (HClH)+14 δ (COH)+9 δ (CCH)
78	1239	-	1230	1	0	13 δ (HClH)+14 δ (CCH)+12 δ (COH)+11 δ (OCH)
79	1216	1212	1220	10	4	8 δ (COH)+6 δ (CCH)
80	-	-	1215	1	0	19 δ (CCH)+12 δ (OCH)+12 δ (HClH)+11 δ (COH)
81	-	-	1206	1	0	19 δ (CH ₃), rocking+10 δ (OCH)+8 δ (COH)
82	-	-	1196	19	8	10 δ (CCH)+8 δ (COH)
83	-	-	1191	9	3	11 δ (CCH)+8 δ (COH)+8 ν (C=C)+8 ν (OC)
84	-	-	1188	3	0	21 δ (CCH)+14 δ (OCH)+10 δ (COH)

Table 3 (continued)

Mode Nos.	Exp. Wave-numbers (cm ⁻¹)		Theoretical wavenumbers (cm ⁻¹)			TED ^b (%)
	IR	Raman	Scaled Freq. ^a	I _{IR}	I _{Raman}	
85	-	-	1181	0	0	28 δ (CCH)+6 ν (CC)+5 δ (CCC)+7 δ (COH)
86	-	1171	1175	8	2	13 δ (CCH)+5 γ (HClHO)+6 ν (OC)
87	-	-	1174	3	0	17 δ (CCH)+13 δ (OCH)+7 γ (HClHO)
88	1159	1150	1153	7	1	11 δ (CCH)+8 δ (COH)+7 ν (OC)+5 ν (CC)
89	-	-	1135	0	0	12 δ (CH ₃), deformation+10 δ (OCH)
90	-	-	1122	5	2	12 δ (CCH)
91	1125	1125	1120	12	1	10 δ (CCH)+4 ν (CC)
92	-	-	1116	0	7	12 δ (CCH)
93	-	-	1109	1	1	6 ν (OC)
94	-	-	1102	1	0	7 δ (OCH)+5 ν (OC)
95	1091	-	1097	3	0	6 δ (CH ₂), twisting+4 ν (OC)
96	-	-	1089	4	1	6 ν (CC)+6 ν (OC)
97	-	-	1082	1	0	7 ν (OC)
98	-	-	1077	1	0	16 δ (CH ₃), rocking
99	-	-	1065	0	3	12 δ (ClHC)
100	1058	1058	1060	9	0	5 ν (OC)+6 γ (HClHO)
101	-	-	1060	2	1	9 γ (CCCH)+5 ν (OC)
102	-	-	1055	14	1	8 ν (OC)
103	-	-	1045	1	0	17 γ (HClHO)+8 γ (COHCl)
104	-	-	1037	6	1	4 γ (HClHO)+4 γ (CCCH)+4 ν (OC)
105	1036	1032	1035	12	0	8 γ (CCCH)+6 ν (OC)
106	-	-	1028	2	1	6 ν (OC)
107	1015	-	1013	5	2	8 ν (OC)
108	1002	1005	1003	8	0	8 γ (HClHO)
109	-	-	1001	1	0	8 γ (HClHO)
110	-	-	984	4	1	8 γ (HClHO)
111	-	-	979	1	2	8 δ (CCH)+7 ν (CC)
112	973	-	976	1	0	11 γ (HClHO)+7 ν (OC)+5 ν (CC)
113	-	-	961	13	3	7 ν (OC)+8 γ (HClHO)
114	-	944	946	3	1	16 γ (CCCH)+6 ν (OC)
115	-	-	941	0	1	28 γ (CCCH)+12 γ (HCCH)+7 γ (CCCC)+5 γ (OCCH)
116	910	914	911	0	7	23 γ (HClHC)+17 γ (CCCH)+7 γ (CCCC)+7 γ (OCCH)
117	-	-	899	0	1	17 δ (CH ₂), rocking
118	-	-	888	0	0	7 τ (COCH)
119	-	-	886	3	0	10 δ (CH ₃), wagging
120	878	876	876	1	1	4 δ (CCH)+4 ν (CC)
121	-	-	870	1	0	35 γ (CCCH)+14 γ (CCCC)+13 γ (OCCH)
122	-	848	853	1	4	8 δ (CCC)
123	-	-	845	2	0	5 ν (CC)
124	832	-	829	0	1	13 γ (HOCC)+13 γ (OCCH)+10 γ (CCCH)+6 γ (CCCC)
125	-	-	811	2	1	5 γ (CCCH)
126	-	-	810	2	1	34 γ (CCCH)+10 γ (OCCH)+9 γ (CCCC)

Table 3 (continued)

Mode Nos.	Exp. Wave-numbers (cm ⁻¹)		Theoretical wavenumbers (cm ⁻¹)			TED ^b (%)
	IR	Raman	Scaled Freq. ^a	I _{IR}	I _{Raman}	
127	-	-	800	5	1	17 γ (OCCH)+11 γ (CCCH)+10 γ (HOCC)+8 γ (CCCC)+5 γ (HClHO)
128	-	-	796	0	0	22 γ (OCCH)+20 γ (CCCH)+6 γ (HOCC)+9 γ (CCCC)
129	-	788	785	1	12	10 γ (HOCC)
130	-	-	779	1	1	4 ν (OC)+4 δ (CCH)
131	-	-	749	4	2	24 γ (HOCC)+6 γ (CCCC)
132	728	732	732	2	11	8 τ (HClHO)+5 τ (COHCl)
133	-	-	721	2	1	5 γ (CCCC)+7 γ (COHCl)+12 γ (HClHO)+5 γ (HOCC)
134	714	-	713	1	1	14 τ (HClHO)+8 τ (COHCl)+7 τ (CCCC)+5 τ (HOCC)
135	-	-	712	1	2	7 τ (CCCC)+6 τ (HClHO)
136	-	-	708	3	2	22 γ (HClHO)+12 γ (COHCl)+6 γ (HOCC)
137	698	-	704	0	1	11 τ (CCCC)+8 τ (CCCH)+6 τ (HClHO)
138	-	-	664	1	0	5 δ (OCC)+5 δ (CCC)
139	-	-	649	1	5	1 τ (COHCl)+1 τ (HOCC)+1 τ (OCCH)+1 τ (OCCO)+1 δ (OCC)
140	-	-	647	0	4	2 δ (OCC)+2 ν (ClH)
141	-	-	626	0	2	14 γ (CCCH)+11 γ (CCCC)+8 γ (HOCC)+7 γ (OCCH)+5 γ (OCCC)
142	630	630	620	1	20	2 γ (HClHO)+2 γ (CCCC)
143	-	-	608	0	4	5 γ (CCCC)
144	-	-	597	1	1	4 τ (HClHO)
145	-	-	594	1	4	4 τ (CCCH)+4 τ (CCCO)
146	-	-	584	1	1	4 τ (OCCC)
147	-	-	567	0	1	7 τ (CCCH)+6 τ (CCCC)
148	-	-	564	1	1	4 τ (CCCC)
149	-	-	554	0	1	4 τ (HClHO)
150	-	-	532	3	1	4 τ (HClHO)
151	-	-	528	2	4	12 γ (HOCC)+6 γ (HOCH)
152	-	-	523	3	3	16 γ (HOCC)
153	-	-	517	5	3	14 γ (HOCC)+7 γ (HOCH)
154	-	-	507	0	3	4 τ (HClHO)
155	-	-	473	1	1	4 τ (HClHO)
156	-	-	467	0	1	5 τ (COCC)
157	-	-	463	0	2	6 τ (HOCC)
158	-	-	459	0	9	7 τ (HOCC)+6 δ (CCC)
159	-	-	454	3	1	27 γ (HOCC)+10 γ (CCCC)+8 γ (CCCH)+6 γ (OCCC)
160	-	-	450	0	0	12 γ (HOCC)+6 γ (HOCH)
161	-	-	438	2	2	24 γ (HOCC)+11 γ (HOCH)
162	-	-	434	3	0	18 γ (HOCC)+11 γ (CCCC)+10 γ (CCCH)+5 γ (OCCC)
163	-	-	428	1	1	8 γ (HOCC)
164	-	-	417	0	1	5 γ (HOCC)
165	-	-	409	1	3	8 γ (HOCC)+5 γ (CCCC)
166	-	-	407	0	1	8 γ (HOCC)
167	-	-	396	5	1	17 γ (HOCC)+8 γ (HOCH)

Table 3 (continued)

Mode Nos.	Exp. Wave-numbers (cm ⁻¹)		Theoretical wavenumbers (cm ⁻¹)			TED ^b (%)
	IR	Raman	Scaled Freq. ^a	I _{IR}	I _{Raman}	
168	-	-	393	1	1	35 γ (HOCC)+18 γ (HOCH)
169	-	-	389	1	1	24 γ (HOCC)+11 γ (HOCH)
170	-	-	383	4	2	39 γ (HOCC)+5 γ (HOCH)
171	-	-	378	4	2	18 γ (HOCC)+8 γ (HClHO)+7 γ (HOCH)
172	-	-	360	0	9	10 τ (HOCC)
173	-	-	353	1	1	10 τ (HOCC)+5 τ (HOCH)
174	-	-	349	0	0	7 τ (HOCC)+6 τ (OCCH)
175	-	-	339	1	2	2 τ (CCCC)+2 ν (ClH)
176	-	-	333	0	2	4 τ (COCC)+2 ν (OH)
177	-	-	319	0	6	3 τ (COCC)+3 τ (HClHO)
178	-	-	310	0	2	6 τ (OCCC)+5 τ (CCCC)+5 τ (COCC)
179	-	-	298	0	1	10 τ (HClHO)+5 τ (OCCH)+5 τ (COHCl)
180	-	-	274	0	1	6 τ (HClHO)
181	-	-	271	1	0	6 τ (HOCC)
182	-	-	261	1	1	5 τ (HOCC)
183	-	-	258	0	1	13 τ (OCCC)+12 τ (CCCC)+7 τ (COCC)
184	-	-	256	0	1	4 τ (OCCH)+3 τ (CCCH)
185	-	-	251	0	6	3 τ (OCCC)
186	-	-	247	0	7	4 τ (CCCH)+3 τ (OCCH)
187	-	-	229	0	1	4 τ (HOCC)+3 τ (OCCH)+3 τ (HCCH)+3 τ (CCCH)
188	-	-	228	0	2	3 τ (OCCH)+3 τ (HCCH)+3 τ (CCCH)
189	-	-	222	1	0	4 τ (HOCC)+4 τ (OCCH)+4 τ (HCCH)+4 τ (CCCH)
190	-	-	212	0	3	5 τ (CCCC)
191	-	-	209	0	4	11 τ (OCCC)+9 τ (CCCC)
192	-	-	204	0	0	10 δ (CH ₃), twisting
193	-	-	193	0	1	10 τ (OCCC)+7 τ (CCCC)
194	-	-	190	0	4	5 τ (OCCH)
195	-	-	183	0	1	7 τ (OCCH)+6 τ (CCCH)+6 τ (HCCH)+5 τ (COCH)
196	-	-	165	0	1	7 τ (HClHO)+7 ν (ClH)
197	-	-	156	2	4	12 ν (ClH)+5 τ (CCCC)
198	-	-	153	0	3	7 τ (COCH)
199	-	-	146	0	2	4 τ (CCCH)+4 τ (OCCC)+4 τ (OCCH)
200	-	-	132	0	2	4 τ (CCCH)
201	-	-	127	0	1	6 τ (HOCC)
202	-	-	104	1	2	10 τ (HClHO)+5 τ (COHCl)
203	-	-	99	0	18	8 τ (OCCH)+3 τ (CCCH)
204	-	-	96	0	2	7 τ (HClHO)
205	-	-	85	0	4	5 τ (OCCH)
206	-	-	77	0	3	4 τ (COCC)+3 τ (CCCH)+3 τ (HCCH)+3 τ (OCCH)
207	-	-	69	0	2	7 τ (HClHO)
208	-	-	63	0	12	8 τ (HClHO)+6 τ (HOCC)+5 τ (CCCC)
209	-	-	52	0	4	3 τ (CCCH)
210	-	-	46	0	5	5 τ (HClOC)

Table 3 (continued)

Mode Nos.	Exp. Wave-numbers (cm ⁻¹)		Theoretical wavenumbers (cm ⁻¹)			TED ^b (%)
	IR	Raman	Scaled Freq. ^a	I _{IR}	I _{Raman}	
211	-	-	38	0	13	14 τ (HClHO)+7 τ (COHCl)+6 τ (CCCC)
212	-	-	37	0	10	6 τ (HClHO)
213	-	-	33	0	6	7 τ (CCCC)+7 τ (COCH)+7 τ (OCCC)+6 τ (COCC)+5 τ (HClOC)
214	-	-	28	0	5	8 τ (HClOC)+6 τ (HClHO)
215	-	-	21	0	23	8 τ (COCC)+6 τ (COCH)
216	-	-	10	0	73	7 τ (HClOC)+6 τ (COCC)+6 τ (COCH)+6 τ (HOCC)

^aCalculated by applying the scale constants 0.967 (under 1800 cm⁻¹) and 0.955 (above 1800 cm⁻¹) at B3LYP/6-311++G(d, p) for the wave numbers

^b ν , stretching; δ , in-plane bending; γ , out-of-plane bending ; τ torsion

2004; Stuart 2004). On the other hand, the computed values for this mode were found within the range of 118–1153 cm⁻¹.

The combination of the deformations in-plane bending methyl and methylene groups are observed/calculated at 1426 (IR) and 1422 (R) / 1449 cm⁻¹ with the pure modes by the 35% and 24% PED contributions, respectively (Silverstein et al. 2014; Kanagathara et al. 2023).

The observed peaks at 910 (IR) and 914 (R) cm⁻¹ are assigned to the out-of-plane bending mode of HCLHC group and its computed value was found as 911 cm⁻¹. Furthermore, the torsional HClHO vibrational mode are found as 728 (IR) and 732 (R) / 732 cm⁻¹.

4.3 Nonlinear optical properties

NLO materials have gained significant attention from the scientific community in recent times. This is because NLO materials provide a diverse range of applications in the field of optical signal processing (Hussain et al. 2020). For the purpose of researching optical switching, optical memory, optical modulation, and optical logic for new technologies in fields like signal processing, optical interconnections, and telecommunications, it is crucial to consider the NLO properties (Andraud et al. 1994; Ekincioglu et al. 2021). In order to investigate the correlation between the molecule and NLO properties. The NLO parameters such as dipole moment (μ), polarizability (α), first-order hyperpolarizability (δ) and second-order hyperpolarizability (γ) were calculated using DFT (Fonseca Guerra et al. 1998) with B3LYP (Gill et al. 1992) and 6-311++G(d, p) basis set (Andersson and Uvdal 2005). Table 4 is presented by the dipole moment, polarizability, and first-order hyperpolarizability components of molecules. As a result of the calculations, the obtained values from atomic unit were converted to Stat coulomb (esu) units (for μ , 1 a.u. = 2.541 Debye; for α , 1 a.u. = 0.1482×10^{-24} esu, for δ , 1 a.u. = 8.6393×10^{-33} esu and for γ 1 a.u. = 5.03717×10^{-40} e.s.u) (Prasad and Williams 1991; de Silva et al. 2005; Ekincioglu et al. 2021) Thanks to the transformed values, it is easier to compare and analyze values within the framework of electrodynamic properties. Using the x, y, and z components, the values of μ , (α), and (δ) are defined as follows.

Table 4 The dipole moment (D), polarizability (in a.u. and esu, first-order hyperpolarizability and second-order hyper polarizability (in a.u. and esu) values for C3RC molecule

μ	Values	α_{tot}	Values	β_{tot}	Values	$\langle \gamma \rangle$	Values
μ_x	-3.99	α_{xx}	628.22	β_{xxx}	4077.04	γ_{xxxx}	361,421
μ_y	-8.89	α_{yy}	461.10	β_{xyy}	2780.89	γ_{yyyy}	475,221
μ_z	1.01	α_{zz}	276.21	β_{xyy}	338.42	γ_{zzzz}	4,785,221
μ_{tot} (D)	9.79	α_{tot} (a.u)	455.18	β_{yyy}	-1991.13	γ_{xyyy}	102,260
		α_{tot} (esu)	67.45×10^{-24}	β_{xxz}	190.95	γ_{xxzz}	24635.8
				β_{xyz}	293.56	γ_{yyzz}	28,929
				β_{yyz}	-286.96	$\langle \gamma \rangle$ (a.u)	239230.12
				β_{xzz}	-69.74	$\langle \gamma \rangle$ (esu)	1.20×10^{-34}
				β_{yzz}	50.11		
				β_{zzz}	4.79		
				β_{tot} (a.u)	4427.08		
				β_{tot} (esu)	38246.86×10^{-33}		

Total dipole moment (μ_{tot}) for molecule is defined as in Eq. 1

$$\mu_{tot} = (\mu_x + \mu_y + \mu_z)^{1/2} \quad (1)$$

Total polarizability (α_{tot}) for molecule can be evaluated by Eq. 2

$$\alpha_{tot} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

The total first order hyper polarizability (β_{tot}) can be calculated by Eq. 3

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3)$$

where β_x , β_y and β_z are defined to be

$$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz}) \quad (4)$$

$$\beta_y = (\beta_{yyy} + \beta_{yzz} + \beta_{yxx}) \quad (5)$$

$$\beta_z = (\beta_{zzz} + \beta_{zxx} + \beta_{zyy}) \quad (6)$$

Total first order hyper polarizability from Gaussian 09 output is given in Eq. 7.

$$\beta_{tot} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2} \quad (7)$$

Total second-order hyper polarizability is calculated using Eq. 8.

$$\langle \gamma \rangle = \frac{1}{5} [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \quad (8)$$

The dipole moment values of a molecule give information about the charge distribution of the molecule and it can be represented as a three-dimensional vector. As a result, it can be employed as a descriptor to represent charge mobility across a molecule based on the locations of positive and negative charge centers.

As stated in Table 4, the obtained dipole moment is **9.79 D**. The highest dipole moment is achieved for component μ_z , which is equivalent to **1.01 D**. The smallest dipole moment is obtained for component μ_y , which is **-8.89 D**. The calculated Polarizability and first-order hyperpolarizability values are equal to 67.45×10^{-24} esu (455.18 a.u) and 38246.86×10^{-33} esu (**4427.08 a.u**) respectively. In the literature, urea is a model molecule used when examining and interpreting the properties of molecules (Dixon and Matsuzawa 1994). Therefore, it seems from the results obtained that the dipole moment values of the molecule examined are 7.13 times higher than those of urea. In addition, the polarizability and first-order hyperpolarizability values are 17.60 times and 196.43 times higher than those of urea respectively. The second-order hyperpolarizability value was also calculated and found to be 1.20×10^{-34} esu for the studied molecule.

4.4 Frontier molecular orbital and global reactivity descriptors analysis

The HOMO and the LUMO are known as the frontier molecular orbitals (FMOs), FMOs are an important influence on the quantum chemistry, UV–Visible spectra, electrical, electronic and optical properties (Fleming 1976). The HOMO corresponds to the ability to donate an electron and to electrophilic attacks, whereas the LUMO corresponds to the ability to accept an electron and sensitivity to nucleophilic attacks (Karelson et al. 1996). The energy gap which is defined as the energy difference between the HOMO and LUMO energies allows one to characterize the kinetic stability and chemical reactivity of the molecule. The energies HOMO and LUMO of the molecule are **-6.45** and **-3.64 eV** respectively. In addition, the energy gap value is **2.81 eV** and these values were presented Table 5. The presence of this band gap in the C3RC molecule indicates its high stability, and also facilitates the movement of charges inside the molecule (Galappaththi et al. 2017). The red and green colors on molecules represent positive and negative phases respectively and are shown in Fig. 4.

The ionization potential (I) and electron affinity (A) are connected to the LUMO and HOMO orbitals, respectively. Additionally, the electron affinity and ionization potential

Table 5 The theoretically calculated some molecular properties of C3RC molecule

Parameters	Values (eV)
Total Energy	-71749.887
E_{HOMO}	-6.45
E_{LUMO}	-3.64
Gap	2.81
Ionization potential	6.45
Electron affinity	3.64
Electronegativity	5.05
Chemical hardness	1.41
Chemical softness	0.71
Electrophilicity index	9.06

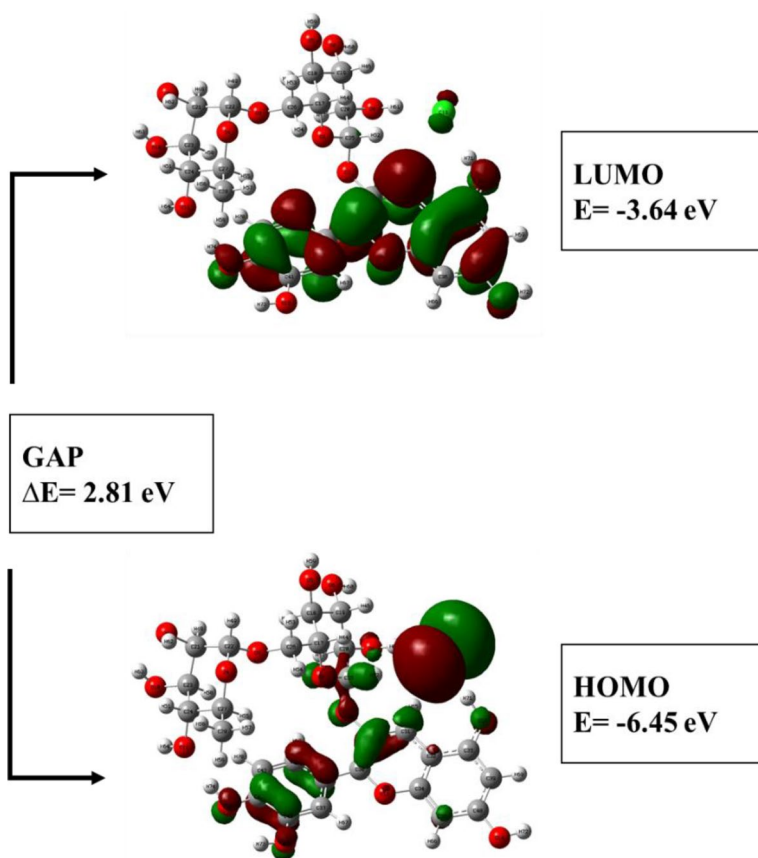


Fig. 4 HOMO and LUMO orbitals of C3RC molecule

can be expressed using the LUMO and HOMO orbital energies as $A = -E_{LUMO}$ and $I = -E_{HOMO}$. Thanks to Koopman's theorem (Koopmans 1934), The electronegativity and chemical hardness and are given Eqs. 9 and 10, respectively (Pearson 1988; Parr et al. 1999).

$$\chi = -\frac{E_{HOMO} + E_{LUMO}}{2} \quad (9)$$

$$\eta = -\frac{E_{HOMO} - E_{LUMO}}{2} \quad (10)$$

The chemical soft indexes and the global electrophilicity index are given Eqs. 11 and 12, respectively

$$\sigma = \frac{1}{\eta} \quad (11)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (12)$$

Global reactivity descriptors were calculated using the density functional theory level with the 6-311++G(d, p) basis set in gas phase and these values were presented Table 5. Hardness is known as the resistance to change in the electron distribution in a molecule. Softness is the inverse of hardness (Pearson 2005).

Additionally, Soft systems are large and highly polarizable, whereas hard systems are small and significantly less polarizable. Electrophilicity index is one of the most crucial global reactivity descriptors to determine the susceptibility of chemical species to accept electrons (Pearson 2005). As a result, greater electrophilicity index values indicate the presence of a good electrophile, whereas lower electrophilicity index values indicate a good nucleophile. The chemical Hardness, chemical softness and electrophilicity index are calculated as $\eta = 1.406$, $\sigma = 0.711$ and $\omega = 9.056$ eV, respectively.

4.5 Mulliken population and natural population analysis

In this study, The Mulliken charge and natural charge (evaluated utilizing the NBO procedure) were calculated at the B3LYP/6-311++G(d, p) level of theory and represented in Table 6. Atomic charges play a crucial role in applying quantum mechanical calculations to molecular systems. It has an important impact on the system's molecular characteristics, dipole moment, electronic structure, molecule polarizability and bond formation (Kumar et al. 2023).

In the present study, the calculated Mulliken atomic charges are found to be from -1.116 e to 1.116 e. The results demonstrate that oxygen atoms O₂, O₃, O₄, O₇, and O₁₂ are positively charged, while oxygen atoms O₅, O₆, O₈, O₉, O₁₀, O₁₁, O₁₃, O₁₄, O₁₅, and O₁₆ are negatively charged, demonstrating their capacity to donate electrons. The Cl atom is seen as negative, which is the location of possible electrophilic attacks. The carbon atoms C₁₇, C₂₉, C₃₀, C₃₁, C₃₂, C₃₃, C₃₄, C₃₈, C₃₉, and C₄₂ are positively charged, indicating their capacity to accept electrons. while the rest of the carbon atoms are negatively charged. All hydrogen atoms contain net positive charges, which serve as electron acceptors. The findings obtained here are generally consistent with the results from the molecular electrostatic potential analysis.

The carbon and oxygen atoms of the molecule contain both positive and negative charges in mulliken and natural charges. Moreover, the charges of the hydrogen and chlorine atoms are positive and negative, respectively. Mulliken and natural charge studies show that when the charges are analyzed in terms of oxygen and carbon atoms, the Mulliken charges are larger than the natural charges, but the opposite is true for hydrogen atoms. The obtained atomic charge results indicate that the O₂, C₁₇, H₄₄, and H₇₄ have values (**0.05e (Mulliken), -0.60e (natural)**), (**0.17e (Mulliken), 0.05e (natural)**), (**0.23e (Mulliken), 0.24e (natural)**), and (**0.46e (Mulliken), 0.534e (natural)**) respectively.

4.6 Transition density matrix

In photovoltaic applications, the performance of organic semiconductors is substantially governed by the dynamics of excitons (electron-hole pairs). Meanwhile, the transition density matrix (TDM) was also used to look at how charge moves between electrons and holes

Table 6 Calculated net charge by Mulliken population method and natural population analysis (NPA) of C3RC molecule

Atom	Mulliken charges	Atom	Mulliken charges	Atom	Natural charges	Atom	Natural charges
Cl ₁	-0.49	C ₃₈	0.03	Cl ₁	-0.76	C ₃₈	-0.18
O ₂	0.05	C ₃₉	0.25	O ₂	-0.60	C ₃₉	-0.38
O ₃	0.22	C ₄₀	-0.57	O ₃	-0.60	C ₄₀	0.39
O ₄	0.00	C ₄₁	-0.42	O ₄	-0.61	C ₄₁	0.29
O ₅	-0.17	C ₄₂	0.27	O ₅	-0.77	C ₄₂	-0.31
O ₆	-0.17	C ₄₃	-0.47	O ₆	-0.78	C ₄₃	0.31
O ₇	0.21	H ₄₄	0.23	O ₇	-0.55	H ₄₄	0.24
O ₈	-0.09	H ₄₅	0.29	O ₈	-0.79	H ₄₅	0.23
O ₉	-0.15	H ₄₆	0.26	O ₉	-0.77	H ₄₆	0.23
O ₁₀	-0.15	H ₄₇	0.27	O ₁₀	-0.77	H ₄₇	0.24
O ₁₁	-0.26	H ₄₈	0.28	O ₁₁	-0.80	H ₄₈	0.26
O ₁₂	0.05	H ₄₉	0.23	O ₁₂	-0.43	H ₄₉	0.23
O ₁₃	-0.14	H ₅₀	0.30	O ₁₃	-0.68	H ₅₀	0.25
O ₁₄	-0.18	H ₅₁	0.27	O ₁₄	-0.67	H ₅₁	0.22
O ₁₅	-0.19	H ₅₂	0.13	O ₁₅	-0.69	H ₅₂	0.22
O ₁₆	-0.33	H ₅₃	0.21	O ₁₆	-0.73	H ₅₃	0.23
C ₁₇	0.17	H ₅₄	0.18	C ₁₇	0.05	H ₅₄	0.23
C ₁₈	-0.18	H ₅₅	0.39	C ₁₈	0.05	H ₅₅	0.24
C ₁₉	-0.55	H ₅₆	0.16	C ₁₉	0.04	H ₅₆	0.24
C ₂₀	-0.10	H ₅₇	0.17	C ₂₀	0.03	H ₅₇	0.25
C ₂₁	-0.31	H ₅₈	0.15	C ₂₁	0.03	H ₅₈	0.25
C ₂₂	-0.06	H ₅₉	0.27	C ₂₂	0.37	H ₅₉	0.50
C ₂₃	-0.75	H ₆₀	0.27	C ₂₃	0.04	H ₆₀	0.50
C ₂₄	-0.27	H ₆₁	0.15	C ₂₄	0.05	H ₆₁	0.50
C ₂₅	-0.91	H ₆₂	0.27	C ₂₅	0.38	H ₆₂	0.49
C ₂₆	-1.12	H ₆₃	0.28	C ₂₆	-0.12	H ₆₃	0.49
C ₂₇	-0.36	H ₆₄	0.29	C ₂₇	0.06	H ₆₄	0.51
C ₂₈	-0.56	H ₆₅	0.06	C ₂₈	-0.70	H ₆₅	0.29
C ₂₉	0.05	H ₆₆	0.20	C ₂₉	0.24	H ₆₆	0.27
C ₃₀	0.05	H ₆₇	0.25	C ₃₀	0.42	H ₆₇	0.26
C ₃₁	0.63	H ₆₈	0.19	C ₃₁	-0.13	H ₆₈	0.27
C ₃₂	0.43	H ₆₉	0.18	C ₃₂	-0.19	H ₆₉	0.26
C ₃₃	0.27	H ₇₀	0.20	C ₃₃	-0.14	H ₇₀	0.25
C ₃₄	0.52	H ₇₁	0.21	C ₃₄	0.38	H ₇₁	0.50
C ₃₅	-0.84	H ₇₂	0.28	C ₃₅	0.43	H ₇₂	0.50
C ₃₆	-0.64	H ₇₃	0.29	C ₃₆	-0.37	H ₇₃	0.51
C ₃₇	-0.03	H ₇₄	0.46	C ₃₇	-0.24	H ₇₄	0.53

during electronic transitions. The TDM is an effective tool for demonstrating, analyzing, and interpreting electronic excitation events in molecular systems. furthermore, it produces a characteristic map that shows distribution of the associated electron-hole pairs and aids in determining the precise location of electrons (Li and Ullrich 2011). The TDM map is analyzes and evaluates the possibility of the exciton transfer from one part of the molecule to another. Also, it is a two-dimensional color representation that depicts the number of atoms and electron density distribution. To construct the TDM for the title molecule, TD-DFT was implemented at the B3LYP/6-311++G(d, p) level, and a graphic depiction was created

Fig. 5 The transition density matrix map of C3RC molecule

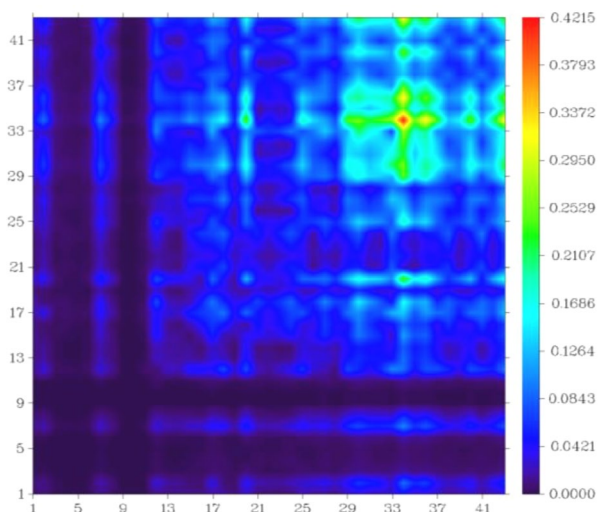
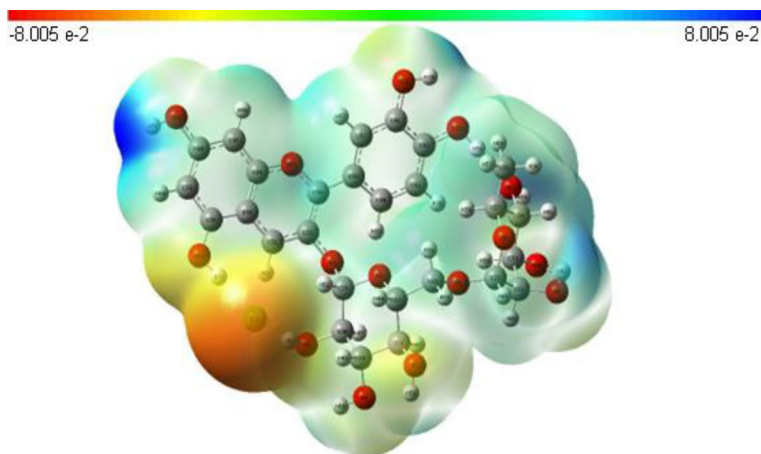


Fig. 6 The MEP maps of C3RC molecule

using the Multiwfn 3.8 software (Lu and Chen 2012). The obtained TDM map for molecule is presented in Fig. 5. This map illustration includes a color gradient from blue to red along the right-vertical axis. This gradient represents the increase in electron density from minimal to highest levels for a given molecule. In this regards, brighter sections of the matrix in this map indicate higher population densities for charge transitions. The electron density of title molecule was generally accumulated in the acceptor region.

4.7 Molecular electrostatic potential

The MEP maps were generated using the B3LYP/6-311++G(d, p) basis set at the density functional theory level. The obtained MEP map for molecule is presented in Fig. 6. These

maps are a significant tool for depicting the charge distributions of molecules. It is also utilized as a reactivity map to better understand the locations of electrophilic and nucleophilic reactions, as well as hydrogen bond interactions. The color ranges from blue to red at the surface corresponds to different values of the electrostatic potential. the strongest attraction is corresponded to blue color (positive) region, whereas the strongest repulsion is corresponded to red color (negative) region. Additionally, the red, orange, and yellow colors (negative) regions at the surface of MEP correspond to electrophilic reactivity, while the blue color (positive) corresponds to nucleophilic reactivity (Lengsfeld and Yarkony 1992; Politzer and Murray 1996, 2002).

As can be seen Fig. 6. The color code of these map is the range of -8.005 e-2 a.u and 8.005 e-2 for C3RC molecule. Additionally, The MEP map of the analyzed molecule clearly shows that the strongest attraction positive potential regions localized on the O₉, O₁₁, O₁₃, O₁₄, and O₁₅ atoms and these regions are locations of possible nucleophilic attacks. Furthermore, this map indicates that the strongest repulsion negative potential region is localized on the Cl₁ atom and this region is a location of possible electrophilic attacks.

4.8 Reduced density gradient analysis

Reduced density gradient (RDG) analysis is important method to uncover and display non-covalent interactions (NCI) such as hydrogen bonds, repulsive and van der Waals interconnections (Reeda et al. 2023). The identification of noncovalent interactions involves the examination of electron density and its derivatives to pinpoint the precise regions where these interactions occur. According to Johnson et al., RDG scatter chart is shown RDG versus $\text{sign}(\lambda_2)\rho(r)$ (second eigenvalue of ED (electron density)), which provides information about the strength and type of contacts (Johnson et al. 2010). In this study, when (λ_2) is negative, Bonding interactions occur, while (λ_2) is positive non-bonding interactions occur and is shown in Fig. 7.

The scatter plot in Fig. 7 can be seen many spikes in the area between -0.04 and $+0.04$ a.u. herein, the steric repulsion in the RDG scatter chart is shown in red spikes from 0.00 to 0.04 a.u. The Wan der Waals interaction is detected in green spikes from 0.00 to -0.02 a.u.,

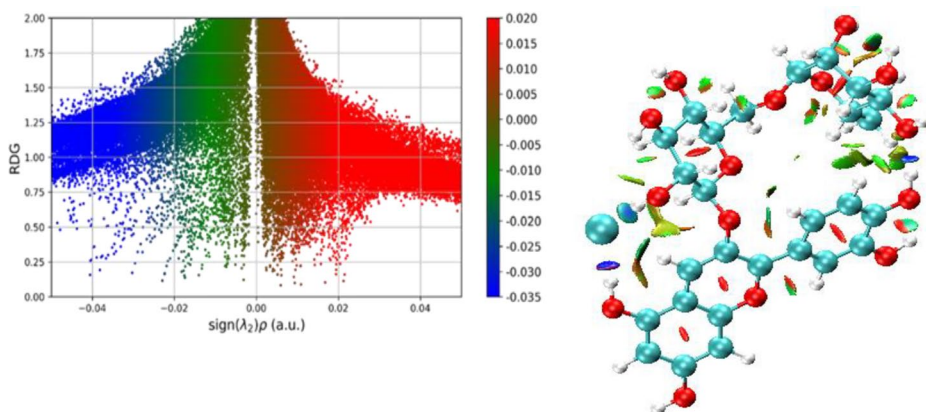


Fig. 7 2D scatter and iso-surface density plot of C3RC molecule

and strong attractive interactions, particularly strong hydrogen bonds, are indicated in blue spikes from -0.02 to -0.04 a.u.

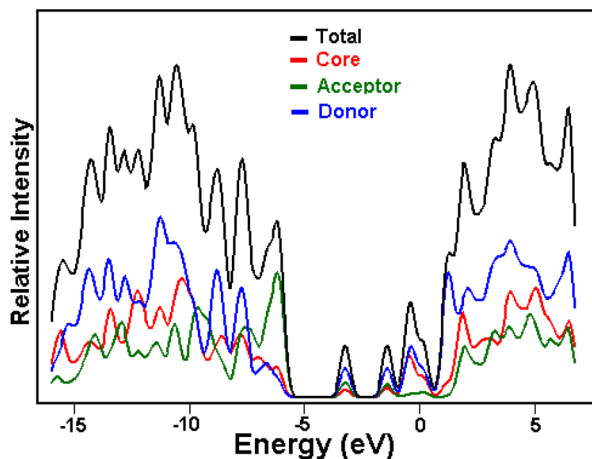
4.9 Density of states analysis

The density of states (DOS) graphs plays a vital role in understanding and interpreting charge transfer and FMO analysis in the molecular system. In DOS graphs, the positive values along the x-axis represent the LUMO (conduction band), whereas the negative values show the HOMO (valance band). The red, green, and blue lines characterize the comparative intensity of the donor, acceptor, and core parts, respectively. Light absorption occurs in semiconductor materials, which in a solar cell leads to the formation of electron-hole pairs. An electrical current is therefore able to be established as a result of these pairings being separated by the internal electric field that is present within the cell. If charge carriers are easily accessible and can move about without expense, then this technique will work. Understanding the energy levels of the semiconductor material and the densities of states that correspond to those levels may be gained via the investigation of the DOS. Determining the energy needed for the creation of electron-hole pairs and the energy required for their subsequent recombination depends critically on understanding this information. Determining the DOS contributes to our comprehension of the processes behind charge transfer and recombination inside cells. DOS has been calculated using DFT /B3LYP/6-31G(d, p). The highest density on LUMO is recorded -3.23 eV, while the maximum density on HOMO is -6.02 eV, as seen in Fig. 8, the molecule under study exhibits a degree of symmetry DOS.

4.10 The light-harvesting efficiency, the open circuit voltage, and the binding energy

The photovoltaic parameters were calculated utilizing the B3LYP functional and 6-31G (d, p) ground set, with the optimized structures acquired through the DFT method serving as the foundation. This is used to assess the photovoltaic characteristics of the C3RC molecule. The parameters of interest in this context are the short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), the efficiency (η), the incident photon-to-current efficiency

Fig. 8 Graphical representation for DOS



(IPCE), and the external quantum efficiency (EQE). The power conversion efficiency η of solar cells is often correlated with the highest open-circuit voltage (V_{oc}) as shown by Eq. (13).

$$\eta = FF \frac{V_{oc} J_{sc}}{P_{inc}} \quad (13)$$

The form, mobility, and lifespan of charge carriers have a significant impact on J_{sc} . The following is the equation for calculating short circuit current density: $LHE(\lambda)$ is the light harvesting efficiency at a certain wavelength. The term " Φ_{inject} " refers to the efficiency of injecting electrons, whereas " $\eta_{collect}$ " represents the efficiency of collecting charges. The LHE is closely linked to the oscillator strengths (f). f of the C3RC molecule is **0.0280**. For maximum photocurrent generation, set LHE to its maximum value. Equation 14 is employed for the present examination of LHE.

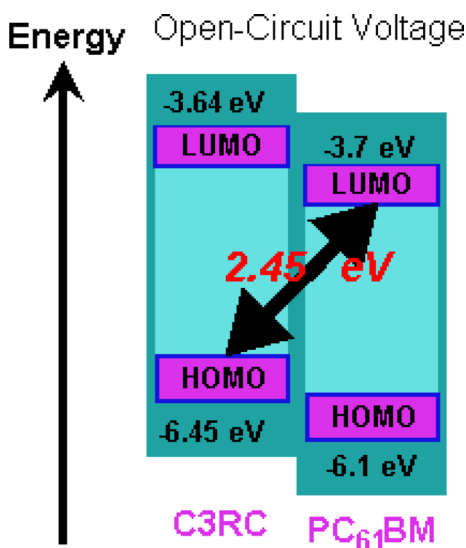
$$LHE = 1 - 10^{-f} \quad (14)$$

LHE is calculated as **0.062** using Eq. 14 for C3RC molecule. Theoretically, V_{oc} is determined by dividing the energy of the donor (HOMO) by the energy of the acceptor (LUMO) ($PC_{61}BM$), as shown in Eq. (15).

$$V_{oc} = ((|E_{HOMO(donor)}| - |E_{LUMO(acceptor)}|) - (0.3)) \quad (15)$$

In order to investigate the photovoltaic characteristics of C3RC molecule, it is imperative to assess the potential for electron transfer from the excited molecules under investigation to the conductive band of the acceptor ($PC_{61}BM$), which is an extensively employed acceptor in solar cell apparatus. A C3RC molecule has V_{oc} value of **2.45 eV**. According to Fig. 9, the HOMO level of C3RC molecule is greater than of the PCBM. The results suggest that C3RC molecule demonstrated a greater potential difference across the solar cell, which signifies

Fig. 9 The V_{oc} of C3RC molecule calculated with $PC_{61}BM$ acceptor



enhanced charge separation and a more effective conversion of light energy to electrical energy.

Until now, we calculated LHE and V_{oc} . Φ_{inject} is linked to the driving force (ΔG_{inject}) (Bourass et al. 2017) that facilitates the injection of electrons from the surface of the semiconductor from the photoinduced excited states of organic dyes. It can be mathematically represented as Eqs. 16 and 17, respectively.

$$\Delta G_{inject} = E^{dye*} - E_{CB} \quad (16)$$

$$E^{dye*} = E^{dye} - E_{exc} \quad (17)$$

Where E_{exc} is excitation energy (2.25 eV) and E^{dye} is $-E_{HOMO}$ (6.45 eV), respectively. By comparing the LUMO levels of C3RC molecule to the conduction band of TiO_2 (-4.00 eV), we determined that when in an excited state, C3RC molecule is likely to contribute an electron to the conduction band of the semiconductor. The given Eq. 17 yields an E^{dye*} value of 4.20 eV. ΔG_{inject} 's adverse effect on the selected dye suggests that the excited electron within the dye can readily evade detection by transitioning to the conduction band of TiO_2 . The value of ΔG_{inject} is 0.20 eV. Extremely significant and deeply linked to the E_b is the efficient segregation of excitons into free charge carriers. E_b represents the energy required to separate an electron-hole pair and generate independent charge carriers. Typically, there is a larger link between lower binding energies and higher exciton dissociation. It is represented by Eq. 18 (Sikandar et al. 2021). In the ethanol phase, the C3RC molecule has a binding energy of 0.56 eV.

$$E_b = E_{gap} - E_{exc} \quad (18)$$

In this context, E_{gap} represents the difference in energy between HOMO and LUMO in their ground state, while E_{exc} signifies the amount of energy necessary to initiate the excitation process.

4.11 The charge mobilities

Reorganization energies were computed and analyzed in order to create an approximation of the charge transfer property of organic substances. Reduced reorganization energy confirms faster electron transport. Hole reorganization energy (λ_h) and electron reorganization energy (λ_e) can be calculated using Eqs. 19 and 20, respectively (Fei et al. 2021).

$$\lambda_h = (E_0^+ - E_+) + (E_+^0 - E_0) \quad (19)$$

$$\lambda_e = (E_0^- - E_-) + (E_-^0 - E_0) \quad (20)$$

Where E_0^+ is energy of cation calculated with neutral optimized structure, E_0^- is energy of anion calculated with neutral optimized structure, E_+ is energy of cation calculated with cation optimized structure, E_- is energy of anion calculated with anion optimized structure; E_+^0 is energy of neutral molecule calculated with cation optimized structure, E_-^0 is energy of neutral molecule calculated with anion optimized structure and E_0 is

energy of neutral molecule at ground state. The value of λ_h for the C3RC molecule is determined to be **0.50 eV**, while the value of λ_e is found to be **0.57 eV**. Additionally, the value of λ_{total} is also determined to be **1.06 eV**.

5 Conclusion

In this paper, C3RC molecule is evaluated for its opto-electronic properties for organic solar cells. For this purpose, the stable structure of the C3RC molecule was determined. Calculations were performed for the first time to determine the equilibrium geometries, harmonic wavenumbers, ground state energy, and dipole moment of the C3RC molecule. The Raman and Fourier transform infrared spectra of the C3RC molecule were investigated. A comparison of the estimated vibrational values with the experimental data obtained from FT-IR and Raman reveals that they are in good agreement with one another. The NLO properties such as dipole moment (μ), polarizability (α), first-order hyperpolarizability (δ) and second-order hyperpolarizability (γ) of the C3RC molecule were determined using DFT with the B3LYP and 6-311++G(d, p) basis set. In addition, when calculating FMO properties $E_{gap} = 2.81$ eV, $\eta = 1.41$ eV, $\sigma = 0.71$ eV and $\omega = 9.07$ eV are found. In addition, TDM, MEP and DOS analyzes were performed and the acceptor-donor maps of the molecule were examined. Finally, LHE, V_{oc} , ΔG_{inject} , E_b , λ_h , λ_e and λ_{total} values were calculated as **0.06**, **2.45 eV**, **0.20 eV**, **0.56 eV**, **0.50 eV**, **0.57 eV** and **1.06 eV**, respectively. Consequently, the molecule's stable structure was determined and its Nonlinear Optical (NLO) and Photovoltaic characteristics were analyzed. The outcomes demonstrated the applicability of the C3RC molecule to optoelectronic devices.

Author contributions Ebru Karakaş Sarıkaya is the corresponding author, and she wrote the main manuscript text. She made all the calculations. Yavuz Ekincioglu wrote NLO, TDM, MEP, and FMO in the manuscript. Semiha Bahçeli wrote FT-IR and Raman in the manuscript. Ömer Dereli provided resources. All authors reviewed the manuscript.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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