Structural Properties and Quantum Chemical Analysis on a New Chalcone Derivative of \((E)-3-(4\text{-bromophenyl})-1-(4\text{-fluorophenyl})\text{prop-2-en-1-one}\)

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Abstract. The molecular structure of \((E)-3-(4\text{-bromophenyl})-1-(4\text{-fluorophenyl})\text{prop-2-en-1-one} (C_{15}H_{10}BrFO)\) was successfully synthesized and crystallized in the monoclinic system of \(P2_1/c\) space group. The unit cell dimensions are: \(a = 27.795 (3) \text{ Å}, b = 3.9690 (4) \text{ Å}, c = 11.3703 (11) \text{ Å}, \alpha = 90^\circ, \beta = 93.290 (2)^\circ, \gamma = 90^\circ\) and \(Z = 4\). The physical properties of this compound were characterized by \(^1\)H and \(^{13}\)C Nuclear Magnetic Resonance (NMR) and UV-Vis spectroscopic methods. The molecular structure and crystal packing of the compound was structurally determined via single crystal X-ray diffraction method. Quantum chemical investigations have been employed to investigate the structural and spectral properties where the molecular geometry parameters obtained were further optimized by density functional theory (DFT) using B3LYP/6-311G\(++(d, p)\) basis set in the ground state. The optimized structure was used to calculate the geometrical parameters and chemical shifts of the title compound. TD-DFT/B3LYP method has been carried out to obtain electronic properties and HOMO-LUMO energy gap. There was a slight discrepancy between the experimental and theoretical results obtained due to the different environmental state in which the compounds were analyzed.

1. Introduction

Organic chalcone is the most attractive research studies and yet promising a significant role in multiple fields such as electrochemical sensing [1], non-linear optical [2] and luminescent properties [3]. Chemically, chalcones have a structure formed by two aromatic rings with a various array of functional groups linked by \(\alpha, \beta\)-unsaturated carbonyl group. On both of benzene rings, chalcone possess a system of conjugated double bonds and completely delocalized electrons. Modification of \(\text{C} - \text{H}\) or \(\text{C} - \text{OH}\) to \(\text{C} - \text{F}\) were widely acknowledged since such substitutions showed alterations in physicochemical properties and biological activities of organic compounds, without introducing much major steric changes [4]. Due to this, fluorine substitution has become centre of attraction among researchers to develop wide range of various active materials. In addition, K. Thanigaimani et al. [5] reported bromo substitution at the forth-position on the acetophenone ring assists in enchancing the antimicrobial and antioxidant activities. This supports bioactive property of the molecule by lowering the HOMO-LUMO band gap.

In this study we designed and synthesized the bromo and fluoro substitutions at the 4-position of both benzene rings. The structure of the compound was characterized by NMR, UV-Vis and confirmed
by single-crystal X-ray diffraction studies. The theoretical part also was employed to predict the structural and spectroscopic parameters of the compound in the gas phase with the aid of DFT/B3LYP methods in 6-311++G(d,p) basis set.

2. Experimental

2.1 Synthesis

The title compound of (E)-3-(4-bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-one was successfully synthesized using standard Claisen-Schmidt condensation method at room temperature. The commercially available starting materials such as 4-fluoroacetophenone (0.1 mol) and 4-bromobenzaldehyde (0.1 mol) were used to prepare the title compound. The precursors were dissolved in 20 ml of methanol solution and stirred continuously. Catalytic amount of sodium hydroxide (NaOH) was added dropwise to the solution. The reaction was then stirred for about 5 – 6 hours at room temperature. The resultant crude products were filtered, rinsed successfully with distilled water and recrystallized from acetone to get the corresponding chalcone (Scheme 1). The obtained synthesized crystal was then characterized via single crystal XRD, ¹H NMR, ¹³C NMR and UV-Vis spectroscopy. The colourless plate crystals (CCDC No.: 1567481) is formed and obtained.

2.2 X-ray crystallographic analysis

The single crystal obtained was proceeded for X-ray analysis which performed on APEXII Duo CCD area-detector using MoKα radiation (λ = 0.71073 Å). Data collection was performed using the APEX2 software [6], whereas the cell refinement and data reduction were performed using the SAINT software [6]. The crystal structure was solved by direct method using the program SHELXTL [7] and refined by full-matrix least squares technique on F². Absorption correction was applied to the final crystal data using the SADABS software [6]. All geometrical calculations were generated using the program PLATON [8]. The molecular graphics were drawn using SHELXTL [7] and Mercury [9] programs. The non-hydrogen atoms were refined anisotropically. In this compound, all the hydrogen atom were positioned geometrically (C – H = 0.93 Å) and refined using a riding model with isotropic displacement parameters. In the final refinement, the most disagreeable reflections was omitted (3 1 1). Details of crystal data and the structure refinement parameters of the title compound are presented in Table 1.

2.3 NMR and UV-Vis analysis

The ¹H and ¹³C NMR spectra were recorded at 500MHz, in DMSO-d₆, on Bruker 500MHz Avanze III spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) in the presence of tetramethylsilane (TMS) as internal reference. In addition, for electronic transition analysis, the
compound was characterized via UV-Visible analysis using UV-Visible Spectrophotometer Model Cary 5000 in 1 cm³ cuvette and the spectrum was recorded in the 800-200 nm region.

### Table 1. Crystal data and structure refinement parameters.

| Crystal data                      | Structure refinement parameters |
|-----------------------------------|---------------------------------|
| CCDC deposition numbers           | 1567481                         |
| Molecular formula                 | C₁₅H₁₀BrFO                      |
| Molecular weight                  | 305.14                          |
| Crystal system                    | Monoclinic                      |
| Space group                        | P2₁/c                           |
| a (Å) 27.795 (3)                   |                                |
| b (Å) 3.9690 (4)                   |                                |
| c (Å) 11.3703 (11)                 |                                |
| α (°) 90                           |                                |
| β (°) 93.290 (2)                   |                                |
| γ (°) 90                           |                                |
| V (Å) 1252.3 (2)                   |                                |
| Z                                  | 4                               |
| D_cal (g cm⁻³)                     | 1.618                           |
| Crystal dimensions (mm) 0.41 × 0.29 × 0.11 |                |
| µ (mm⁻¹)                           | 3.28                            |
| Radiation, λ (Å)                   | 0.71073                         |
| F(0 0 0)                           | 608                             |
| T_{min}/T_{max} 0.174/0.282       |                                |
| Reflection measured               | 5690                            |
| Ranges/indices (h, k, l)           | h = −33 → 33                    |
|                                   | k = −4 → 4                      |
|                                   | l = −13 → 13                    |
| θ limit (°)                       | 1.5–25.0                        |
| Unique reflections                | 2209                            |
| Observed reflections              | 1820                            |
| (I > 2σ(I))                       | 163                             |
| Parameters                        | 1.05                            |
| Goodness of fit (GOF) on F²        | 0.055, 0.157                    |
| R₁, wR₂[I > 2σ(I)]                | 0.043                           |
| Rint                              | 1.26 and −0.30                  |

2.4 Computational details
In computational procedures, the molecular geometries of the compound was obtained from X-ray refinement data. The optimization of the molecule geometries was carried out with GAUSSIAN 09 program package [10], using the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang and Parr (B3LYP) with the 6-311++G(d,p) as a basis set. The optimized structural parameters were used to calculate the geometrical parameters and isotropic chemical shifts.

3. Results and discussion
3.1 Molecular and optimized structure analysis
The molecular and optimized structure of the title compound [molecular formula: C₁₅H₁₀BrFO] is shown in Figure 1 and Figure 2 respectively. This compound crystallizes in the monoclinic crystal system of P2₁/c space group [a = 27.795 (3) Å, b = 3.9690 (4) Å, c = 11.3703 (11) Å, α = 90°, β =
The molecule exhibits an E configuration with respect to the C8–C9 double bond with the C7–C8–C9–C10 torsion angle being 179.7 (5)° and 179.17° for the experimental and calculated (B3LYP) respectively. The presence of the α-β-un saturated ketone is indicated by the shorter O1−C7 and C8−C9 bond lengths of 1.216 (6) and 1.318 (7) Å, respectively. The calculated O1−C7 and C8−C9 bond lengths are found to be 1.2242 and 1.3454 Å for B3LYP. The bond angles of O1−C7−C8 and C9−C8−C7 (Table 2) within the enone moiety (O1/C7−C9) are 120.7 (5) and 121.5 (5)°, respectively. The corresponding bond angles are 121.17 and 120.19° for B3LYP.

Table 2. Experimental and geometrical parameters of the title compound.

| Bond lengths | Value (Å) | Bond angles | Value (°) | Torsion angles | Value (°) |
|--------------|-----------|-------------|-----------|----------------|-----------|
| Br1−C13      | 1.905 (4) | C2−C1−C6   | 120.5 (5)| C6−C1−C2−C3   | −11.9 (9)|
| F1−C3       | 1.36 (6)  | C2−C1−H1A  | 119.8    | C1−C2−C3−F1   | −178.5 (5)|
| O1−C7       | 1.216 (6) | C2−C1−H1A  | 119.8    | C1−C2−C3−C4   | 1.7 (10)|
| C1−C2       | 1.372 (7) | C3−C2−C1   | 118.3 (5)| C1−C2−C3−C4   | 179.7 (5)|
| C1−C6       | 1.388 (6) | C3−C2−H2A  | 120.8    | C2−C3−C4−C5   | −1.5 (10)|
| C1−H1A      | 0.93      | C3−C2−H2A  | 120.8    | C3−C4−C5−C6   | 0.6 (9)|
| C2−C3       | 1.36 (8)  | C3−C2−C4   | 118.4 (5)| C4−C5−C6−C7   | −0.1 (9)|
| C2−H2A      | 0.93      | C3−C2−C4   | 118.5 (5)| C4−C5−C6−C7   | 179.6 (6)|
| C3−C4       | 1.36 (8)  | C3−C2−C4   | 122.5 (2)| C2−C1−C6−C5   | 0.3 (8)|
| C4−C5       | 1.368 (8) | C3−C4−C5   | 117.9 (5)| C2−C1−C6−C7   | −178.7 (5)|
| C4−H4A      | 0.93      | C3−C4−H4A  | 121.1    | C5−C6−C7−O1   | −8.3 (9)|
| C5−C6       | 1.382 (7) | C4−C3−H4A  | 121.2    | C6−C7−C8−C9   | −170.8 (5)|
| C5−H5A      | 0.93      | C4−C3−H4A  | 121.4 (5)| C7−C8−C9−C10  | 179.7 (5)|
| C6−C7       | 1.456 (6) | C5−C4−H5A  | 119.3    | C8−C9−C10−C15  | 12.9 (8)|
| C7−C8       | 1.473 (7) | C6−C5−H5A  | 119.3    | C8−C9−C10−C15  | −0.10119|
| C8−C9       | 1.318 (7) | C7−C6−C5   | 118.7 (4)| C9−C10−C11−C12| −0.39573|
| C9−H9A      | 0.93      | C7−C6−C5   | 118.4 (6)| C9−C10−C11−C12| 179.3 (4)|
| C10−C11     | 1.385 (7) | C8−C7−C6   | 119.9 (4)| C11−C12−C13−C14| 178.3 (4)|
| C11−C12     | 1.367 (7) | C8−C7−C6   | 119.5 (4)| C11−C12−C13−C14| 178.3 (4)|
| C11−H11A    | 0.93      | C8−C7−C6   | 119.3    | C11−C12−C13−C14| 178.3 (4)|
| C12−C13     | 1.36 (6)  | C9−C8−C7   | 119.3    | C11−C12−C13−C14| 178.3 (4)|
| C12−H2A     | 0.93      | C9−C8−C7   | 118.0 (4)| C11−C12−C13−C14| 178.3 (4)|
| C13−C14     | 1.374 (6) | C10−C9−C8  | 116.5    | C11−C12−C13−C14| 178.3 (4)|
| C14−C15     | 1.367 (7) | C10−C9−C8  | 116.5    | C11−C12−C13−C14| 178.3 (4)|
| C14−H4A     | 0.93      | C10−C9−C8  | 116.5    | C11−C12−C13−C14| 178.3 (4)|
| C15−H5A     | 0.93      | C10−C9−C8  | 119.2    | C11−C12−C13−C14| 178.3 (4)|

93.290 (2)°, γ = 90° and Z = 4].

Figure 1. (a) The molecular structure of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed line represent the intramolecular hydrogen bond. (b) The view of the twisted fluoro-substituted phenyl ring.
Table 3. Hydrogen bonding geometry for the title compound.

| Bond                | Bond length (Å) | Angle (°) |
|---------------------|-----------------|-----------|
| D‒H⋯A              | D‒H             | H⋯A       | D⋯A     | D‒H⋯A |
| C9‒H9A⋯O1          | 0.93            | 2.46      | 2.789(6) | 101   |

Table 4. Halogen ⋅⋅⋅ Halogen [ I ⋅⋅⋅ J = Br ⋅⋅⋅ Br ] interaction.

| X‒I⋯J            | Bond length, X‒I, (Å) | X‒I⋯J, (°) |
|------------------|-----------------------|-----------|
| C13‒Br(1)⋯Br(1)(i) | 3.699                 | 164.53(12) |

(i)Symmetry code: 1-x, -1/2+y, 3/2-z
Van der Waals radii (Å): Br = 1.85

Figure 2. The optimized structure of the title compound.

The molecular conformation is stabilized by a weak intra-molecular C9‒H9A⋯O1 hydrogen-bond interaction (Table 3), shown in Figure 1(a). This interaction forms an S(5) graph set notation [11] which stabilizes the molecular structure. In the structure, the enone moiety (O1/C7‒C9) is slightly twisted at the C7‒C8 bond where the experimental and calculated torsion angles of O1–C7–C8–C9 are 10.4 (9) and −3.50 (Table 2), respectively. Furthermore, the molecule structure is twisted about C6‒C7 bond evidenced by the torsion angle value of −8.1 (8)° for C1‒C6–C7–C8. In the crystal packing, the obvious existence of the Van der Waals inter-molecular contact by the short halogen⋯halogen interaction (Table 4) between bromine atoms further stabilized the crystal structure. The molecular structure is arranged like sandwich along the c-axis as shown in Figure 3(b).

In the crystal structure, the molecules are centrosymmetrically arranged, interconnected via short inter-molecular contact Van der Waals interactions between the bromine atom of the phenyl ring and the other bromine atom C13‒Br(1)⋯Br(1). The observed Van der Waals interactions connect the molecules together into infinite supra-molecular one-dimensional chain arrangement along the b-axis as shown in Figure 3.
Figure 3. (a) Halogen-halogen interactions (Br ··· Br contact) observed in the crystal structure, forming one-dimensional chain along $b$-axis. The hydrogen atoms in the crystal structure have been omitted for clarity. (b) The sandwich arrangement of crystal structure along $c$-axis.

3.2 NMR spectra analysis

GIAO $^1$H and $^{13}$C chemical shift values with respect to tetramethylsilane (TMS) were calculated at DFT/B3LYP/6-311+g(d,p) level of theory and compared to the corresponding experimental values. The $^1$H NMR and $^{13}$C NMR chemical shifts values are presented in Table 5 and Table 6 respectively. For the title compound, $^1$H NMR chemical shift values were observed in the range 8.27–7.38 ppm, while the DFT values were calculated at 8.65–7.16 ppm. Two doublets observed at regions 7.86 and 7.65 ppm in the $^1$H NMR spectrum was assigned to vinylene group hydrogen and corresponding values were calculated at 7.91 and 7.52 ppm. Signal observed at 187.56 ppm in the $^{13}$C NMR spectrum was assigned to C7 atom of the carbonyl group and the calculated at 187.88 ppm. Signals recorded at 164.08 ppm and 166.09 ppm attribute to carbon atom in the bromine and fluorine atom respectively which are slightly conflict with the calculated at 150.80 ppm and 174.96 ppm respectively. $^{13}$C NMR spectrum of the title compound show signals in the range 166.09–115.78 ppm corresponds to benzene rings (C1–C2–C3–C4–C5–C6) and 164.08–130.79 ppm for (C10–C11–C12–C13–C14–C15). The calculated signals for $^{13}$C NMR spectrum corresponds to (C1–C2–C3–C4–C5–C6) and (C10–C11–C12–C13–C14–C15) in the range 174.96–118.50 ppm and 150.80–129.86 ppm respectively. Comparing the experimental data with the theoretical, it shows that DFT values are closer to the experimental data.
Table 5. Experimental and theoretical $^1$H NMR isotropic shifts (ppm) for the title compound.

| Atom  | Chemical shifts, $\delta$ (ppm) |
|-------|---------------------------------|
|       | Experimental (DMSO) | DFT/B3LYP |
| H1A   | 8.00                      | 8.10      |
| H2A   | 7.39                      | 7.16      |
| H4A   | 7.41                      | 7.30      |
| H5A   | 8.27                      | 8.65      |
| H8A   | 7.73                      | 7.75      |
| H9A   | 8.25                      | 8.17      |
| H11A  | 7.67                      | 7.52      |
| H12A  | 7.65                      | 7.52      |
| H14A  | 7.70                      | 7.60      |
| H15A  | 7.97                      | 8.07      |

Table 6. Experimental and theoretical $^{13}$C NMR isotropic shifts (ppm) for the title compound.

| Atom  | Chemical shifts, $\delta$ (ppm) |
|-------|---------------------------------|
|       | Experimental (DMSO) | DFT/B3LYP |
| C1    | 131.52                    | 133.94    |
| C2    | 115.78                    | 118.50    |
| C3    | 166.09                    | 174.96    |
| C4    | 124.02                    | 120.75    |
| C5    | 131.84                    | 138.23    |
| C6    | 134.08                    | 139.80    |
| C7    | 187.56                    | 187.88    |
| C8    | 122.54                    | 119.64    |
| C9    | 142.74                    | 148.84    |
| C10   | 133.89                    | 139.26    |
| C11   | 134.08                    | 139.74    |
| C12   | 131.59                    | 137.45    |
| C13   | 164.08                    | 150.80    |
| C14   | 131.59                    | 137.16    |
| C15   | 130.79                    | 129.86    |

3.3 UV-Vis analysis

The absorption spectrum of the title compound was carried out in acetonitrile by diluting the sample to obtain a solution with concentration of $10^{-5}$ M. Two major bands were observed as shown in Figure 4. The strongest band observed in the region of 313 nm which attributed to $\pi - \pi^*$ transition from HOMO to LUMO and this was expected to arise from phenyl ring connected to bromine atom [12]. The second band appeared in the region of 226 nm was assigned also as $\pi - \pi^*$ transition, which indicates the presence of phenyl rings. Consequently, the energy band gap ($E_g$) of the compound was determined from the UV-Vis absorption maximum ($\lambda_{\text{max}}$) within the range 200 – 500 nm. The optical band gap was further calculated using an equation (1) as shown [13].
\[ E_g = \frac{1240}{\lambda_{\text{edge}}} \]  

where \( \lambda_{\text{edge}} \) is the onset value of the absorption spectrum in the direction of longer wavelengths. From the UV-Vis data, the \( E_g \) for the title compound is 3.569 eV in which this value is responsible for the charge and electron transition within the molecule.

![Figure 4. The absorbance spectrum for the title compound.](image)

3.4 Frontier molecular orbitals
The frontier molecular orbitals analysis is significant in the development of the molecular electronic properties and yet it is crucial to determine the excitation energy of an organic compound. This is useful to study the movement of electrons and may have a substantial influence on the ICT. The TD-DFT/B3LYP/6-311++G(d,p) is employed to study the energy levels of the frontier molecular orbitals. The electron density plots of the HOMO and LUMO for the title molecule is illustrated in Figure 5 At the LUMO state, we seen that the molecular orbital covers over the entire molecular skeleton. LUMO is centred on the enone system and small contribution at the substituted phenyl rings from fluorine and bromine atoms. HOMO is more localized at enone system and phenyl ring attached to bromine atom. However, small molecular orbital contribution observed in phenyl ring that attached to fluorine atom. The energy values of the highest occupied molecular orbital (\( E_{\text{HOMO}} \)) and lowest unoccupied molecular orbital (\( E_{\text{LUMO}} \)) of the title compound are about -6.7638 eV and -2.7733 eV, respectively. The energy gap is calculated using \( E_{\text{LUMO}} - E_{\text{HOMO}} \) and it is found to be -3.9905 eV. Indeed, the energy gap obtained from TD-DFT is 4.0 eV and thus slightly deviates with the maximum absorption wavelength obtained from experimental UV-Vis spectrum.
3.5 Molecular electrostatic potential
MEP surfaces are very useful quantum molecular descriptor to visualize the charge distributions of the molecules particularly in locating their electron density. The spherical red region observed on the oxygen atom in the carbonyl group as shown in Figure 6 indicates the lowest electrostatic potential energy where the electron density is higher than the other atoms like fluorine and bromine. In addition, highest electrostatic potential energy is clearly can be seen by the blue region that appeared surrounds the hydrogen atoms where electron density is highest.

4. Conclusion
A novel chalcone derivative, (E)-3-(4-bromophenyl)-1-(4-fluorophenyl)prop-2-en-1-one, was synthesized and characterized by X-ray diffraction, $^1$H and $^{13}$C NMR spectra and UV-Vis spectrum. The compound crystallizes in monoclinic crystal system of $P2_1/c$ space group, unit cell parameters $a = 27.795 (3)$ Å, $b = 3.9690 (4)$ Å, $c = 11.3703 (11)$ Å, $\alpha = 90^\circ$, $\beta = 93.290 (2)^\circ$, $\gamma = 90^\circ$ and $Z = 4$. The
Density Functional Theory (DFT) calculations were performed to predict the structural geometry, chemical shifts and molecular orbitals HOMO-LUMO of the title compound. The experimental geometric parameters of the compound are comparable to the calculated values. The molecular structure was stabilized by the presence of intra-molecular and short contact interactions. The $^1$H and $^{13}$C NMR chemical shifts calculations showed an excellent agreement with the experimental data. Overall, the agreement between theoretical and experimental values is agreeable for every structural and spectroscopic calculations.

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