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Synthesis and Theoretical Studies of Organic Chalcone Compound for Potential Optoelectronics Properties

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Abstract

Two organic chalcone compounds, both featuring a donor-pi-acceptor (D-π-A) configuration, specifically (*E*)-1-(4-nitrophenyl)-3-(4-phenylthiophen-2-yl)prop-2-en-1-one (**Ch1**) & (*E*)-4-(3-(4-phenylthiophen-2-yl) acryloyl)benzonitrile (**Ch2**) were meticulously designed and synthesized using the Claisen-Schmidt condensation reaction method. The resulting compounds were purified by repeated recrystallization in acetone solvent and single crystals were grown via a slow evaporation solution growth technique. This research centers on the computational modeling of these two chalcone compounds, employing Density Functional Theory (DFT). Molecular geometry, including bond lengths and bond angles, was determined from the DFT-optimized structures using the method B3LYP/6-311 G++(d,p) basis set in the ground state. Notably, the HOMO-LUMO energy gap, falling within the 3.1 to 3.4 eV range, indicates these compounds' suitability for facilitating efficient charge transfer. As a result, these specifically designed and computed materials hold great promise for potential use in optoelectronic devices due to their small energy gaps.

Keywords: Chalcone; DFT; HOMO-LUMO energy levels; Frontier orbitals

Introduction

In the pursuit of more effective and environmentally friendly optoelectronic devices, the crucial focus lies in designing and creating materials with improved charge transfer capabilities. Chalcones, a category of organic compounds renowned for their varied chemical and pharmacological characteristics, have recently emerged as promising contenders for optoelectronic applications, encompassing light-emitting diodes (LEDs) and solar cells. Their distinct molecular structure, marked by an α,β-unsaturated carbonyl system surrounded by two aromatic rings, presents captivating opportunities for facilitating the fundamental charge transfer processes required for these technologies. Optoelectronic devices depend on the efficient generation, transport, and utilization of charge carriers, including electrons and holes, across semiconductor interfaces.

The effective operation of such devices relies significantly on the active materials' capacity to expedite rapid and efficient charge transfer, which ultimately governs their overall effectiveness and performance. In this context, chalcones have gained notable recognition due to their adjustable electronic characteristics and straightforward synthesis. Chalcones are characterized by being α,β-unsaturated ketones, distinguished by their electron-rich and electron-deficient components. These structural features make them suitable candidates for charge transfer materials in optoelectronic devices (Sokolov *et al.,* 2018). Chalcones have the capability to facilitate the transfer of charge carriers (electrons and holes) within the material—an indispensable feature for the efficiency of optoelectronic devices. Notably, one of the primary merits of chalcones lies in their structural tunability. By modifying the chemical structure of chalcones through various substitutions and functionalizations, researchers have been able to fine-tune their optoelectronic properties (Gomez *et al.,* 2020). This tunability allows for the tailoring of chalcones to fulfill the specific requisites of various optoelectronic devices. This research paper explores the synthesis of chalcones, using 4-phenylthiophene-2-carbaldehyde as the aldehyde component and a variety of ketone components. 4-phenylthiophene-2-carbaldehyde is a compound comprising a thiophene ring with a phenyl group attached to the second carbon and an aldehyde functional group (CHO) attached to the third carbon of the thiophene ring. The aldehyde group within this compound is capable of undergoing nucleophilic addition reactions with a ketone or another aldehyde, resulting in the creation of a chalcone. The selection of this aldehyde is noteworthy due to its unique structure, which integrates a thiophene ring and a phenyl group, potentially conferring distinctive properties to the resulting chalcone (Verma *et al.,* 2020). The primary objective is to explore how distinct structural variations in the ketone components influence the charge transfer characteristics of the resulting chalcones. The array of structural variations among ketone derivatives provides researchers with the opportunity to customize the charge transfer features to align with specific requirements in optoelectronic applications. The existence of the carbonyl group (C=O) in the ketone compounds plays a vital role in chalcone synthesis. Steric effects arising from the size and orientation of substituents on the ketone compounds can influence how chalcone molecules are packed and arranged in solid-state materials. This, in turn, impacts the efficiency of charge transfer within the material (Song *et al.,* 2020). Understanding the interplay between steric factors and charge transfer properties is essential for optimizing material performance. Effective charge transfer materials are crucial for enhancing the performance of LEDs and solar cells. Chalcones synthesized using 4-phenylthiophene-2-carbaldehyde and specific ketones have demonstrated potential for use in these optoelectronic devices (Kumar *et al.,* 2021). Our goal is to determine which combination of 4-phenylthiophene-2-carbaldehyde and ketone derivatives promotes the most efficient charge transfer, making them excellent candidates for integration into optoelectronic devices.

Methodology

Material synthesis

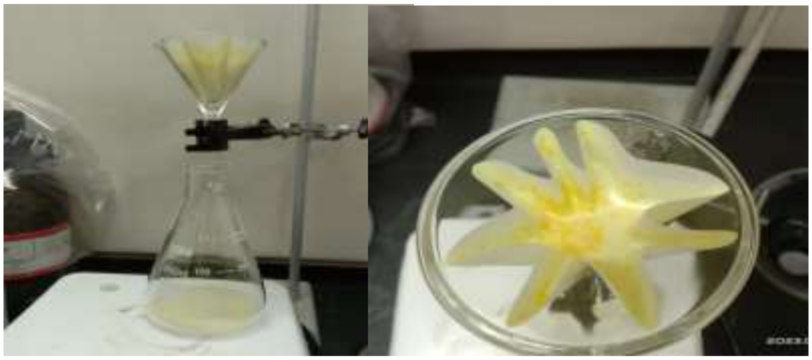
4-Phenylthiophene-2-carbaldehyde, 1-(4-nitrophenyl)ethan-1-one, and 4-acetylbenzonitrile were provided by Universiti Sains Malaysia. Figure 1, shows flow of synthesis chalcone derivatives using the Claisen-Schmidt reaction. To create them, two equivalent molar amounts (1 mmol) of 4-phenylthiophene-2-carbaldehyde (0.1883 g) and 1-(4-nitrophenyl)ethan-1-one (0.1651 g) in 20 mL of methanol (Figure 2). Then, 3 mL of 20% aqueous NaOH was added dropwise as a catalyst[1] and the solution was stirred vigorously at room temperature for 6 hours[2]. After precipitation occurred and the solution became cloudy, the solution was poured into ice-cold water. The resulting crude product was washed several times with distilled water and filtered with Whatman filter paper[3]. The washed precipitates were air-dried for a week. The dried products were further purified in acetone through slow evaporation for 6-7 days. The crystals of (*E*)-1-(4-nitrophenyl)-3-(4-phenylthiophen-2-yl)prop-2-en-1-one (Figure 3) were placed in a vial and labeled as Ch1. This procedure was replicated using 1 mmol of 4-phenylthiophene-2-carbaldehyde (0.1883 g) and 1-(4-nitrophenyl)ethan-1-one (0.1452 g). The resulting dried products were purified, and the crystals of (*E*)-4-(3-(4-phenylthiophen-2-yl)acryloyl)benzonitrile (Figure 4) were labeled as Ch2.

Add the NaOH solution into the round bottom flask.

↓

Stir the solution for 6 hours drop by drop, using a dropper.[1]

↓



Filtration process

Figure 1: Flow of synthesis chalcone derivatives

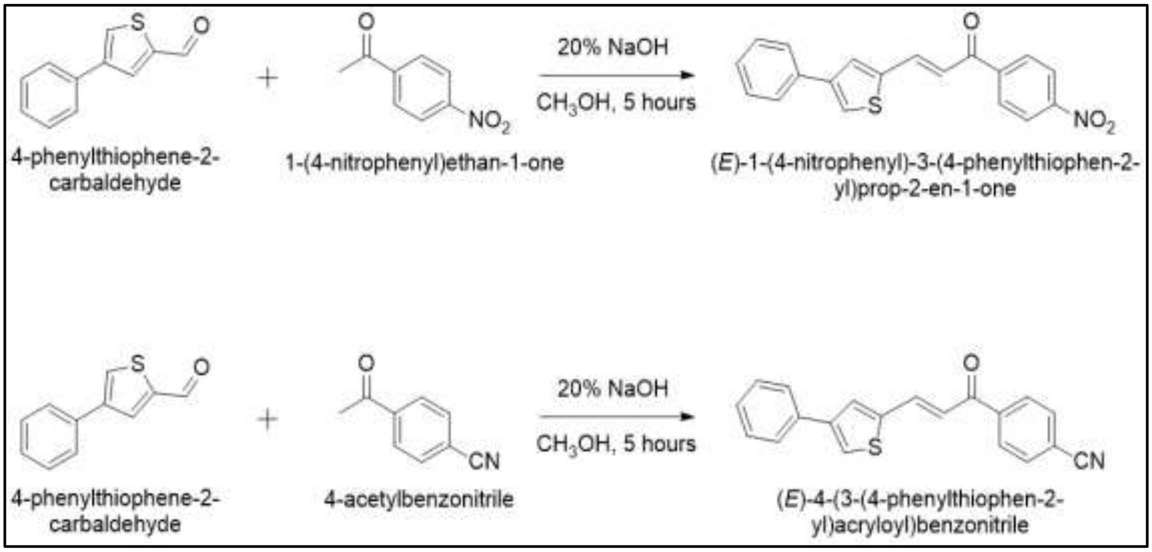
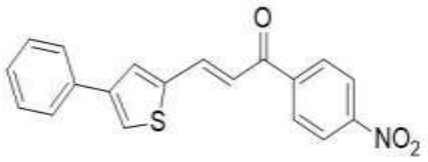


Figure 2: Overall Equation of the Reaction

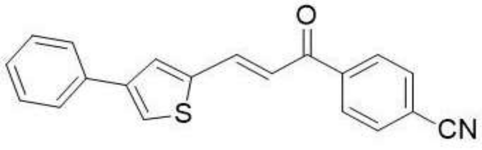
Draw 2D Structures

To generate 2D molecular representations of the chalcone compounds, ChemDraw was used according to the following procedure: Launch ChemDraw and sketch the chemical structure of both chalcone compounds (Ch1 and Ch2) on the workspace, ensuring the inclusion of all atoms, bonds, and pertinent functional groups. Appropriately label each compound as Ch1 and Ch2, and save the 2D structures as distinct files.



(*E*)-1-(4-nitrophenyl)-3-(4-phenylthiophen-2-yl)prop-2-en-1-one

Figure 3: Chemical structure Ch1



(*E*)-4-(3-(4-phenylthiophen-2-yl)acryloyl)benzonitrile

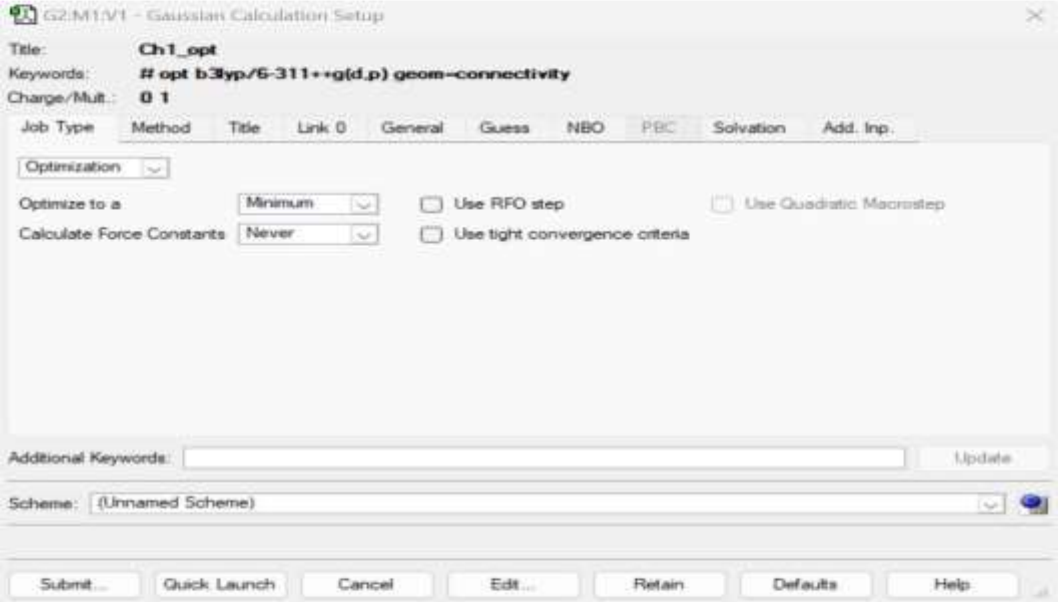
Figure 4: Chemical structure Ch2

Creating 3D Structures

To produce 3D molecular structures, CS Chem3D was used through the subsequent process (Figure 5): Begin by launching CS Chem3D and importing the 2D structures crafted in ChemDraw. Convert the 2D structures into 3D by introducing hydrogen atoms and optimizing the geometry. Save the resulting 3D structures as SYBL2 (*.mol2) files.

Computational methods

Density Functional Theory, DFT, is utilized to explore the crystal's properties at the molecular scale. To conduct Density Functional Theory (DFT) calculations on chalcone compounds, Gaussian 09W is used. First, launch Gaussian 09W and initiate a new calculation via the "Calculate" > "Gaussian Calculation Setup" route. Select "Optimization"[4] as the job type to optimize the geometry to its energetically stable configuration. Specify the method as "Ground State" and the DFT method as "B3LYP."[5] Set the basis set as "6-311G++(d,p)." Next, designate the spin as "Singlet" and provide a title for the chalcone compound before commencing the optimization calculation.[6] Gaussian will execute a geometry optimization to identify the most stable structure of each chalcone compound.[7] This process entails fine-tuning bond lengths and angles to minimize energy. Following optimization, retrieve the optimized geometric parameters, including bond lengths and angles for each compound. Lastly, compute the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy levels, along with the energy gap between them for each compound. These energy levels offer insights into the compounds' electronic properties and their potential for charge transfer.

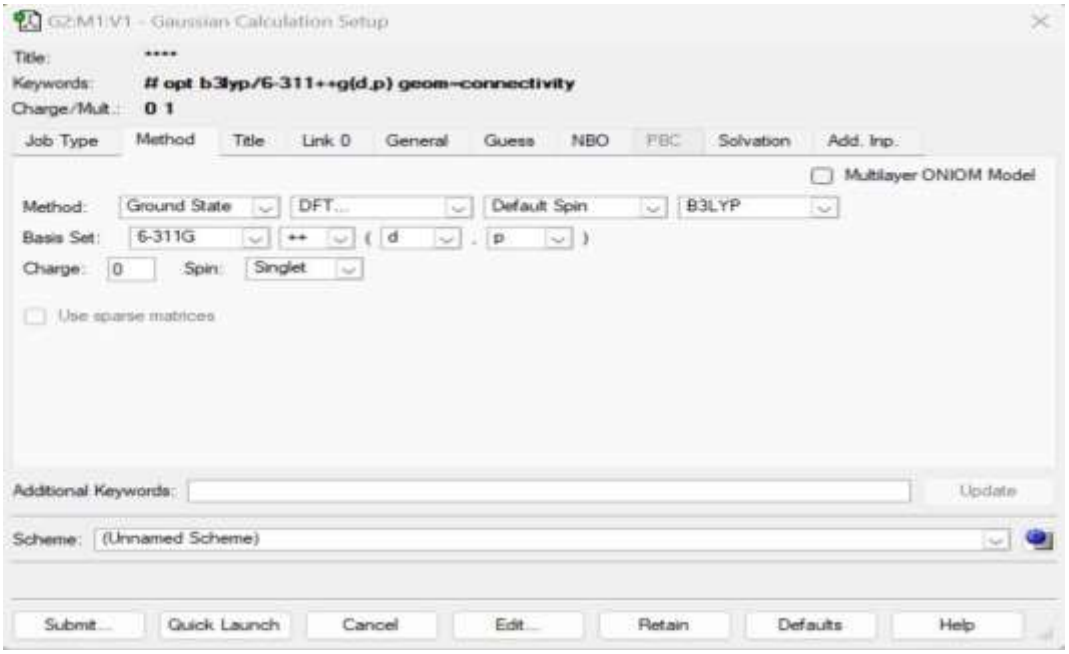


Title: Ch1_opt
Keywords: # opt b3lyp/6-311++g(d,p) geom=connectivity
Charge/Mult.: 0 1

Optimization
Optimize to a: Minimum
Calculate Force Constants: Never
☐ Use RFO step
☐ Use tight convergence criteria
☐ Use Quadratic Macrostep

Additional Keywords:
Scheme: (Unnamed Scheme)

Choose the job type as "Optimization.

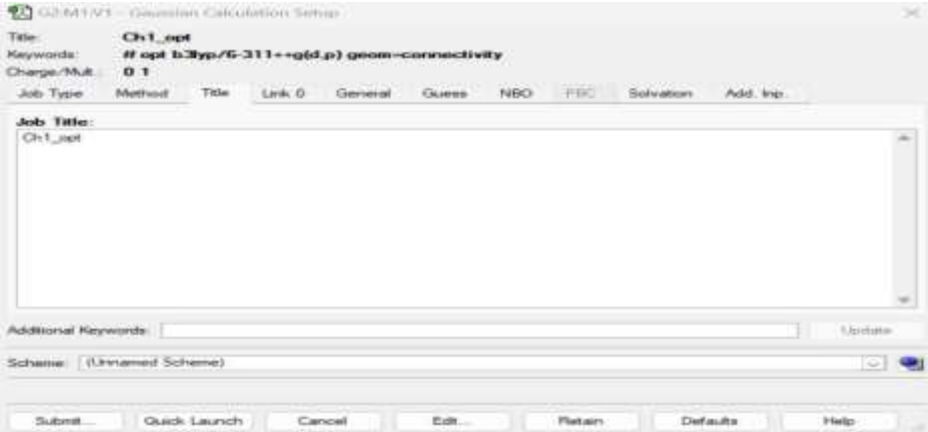


Title: ****
Keywords: # opt b3lyp/6-311++g(d,p) geom=connectivity
Charge/Mult.: 0 1

☐ Multilayer ONIOM Model
Method: Ground State | DFT... | Default Spin | B3LYP
Basis Set: 6-311G | ++ | (d , p)
Charge: 0 Spin: Singlet
☐ Use sparse matrices

Additional Keywords:
Scheme: (Unnamed Scheme)

Select "Ground State" and "B3LYP."[4]



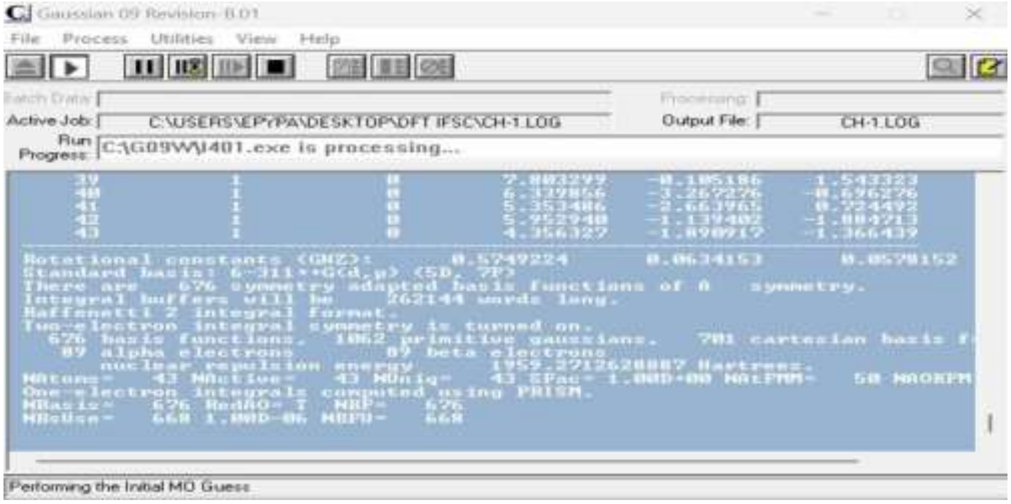
Title: Ch1_opt
Keywords: # opt b3lyp/6-311++g(d,p) geom=connectivity
Charge/Mult.: 0 1

Job Title: Ch1_opt

Additional Keywords:

Scheme: (Unnamed Scheme)

Add a title of the chalcone compound.[5]



Active Job: C:\USERS\EPYPA\DESKTOP\DFT IFSC\CH-1.LOG
Output File: CH-1.LOG
Run Progress: C:\G09W\l401.exe is processing...

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     39          1           0        7.803299   -0.105186    1.543323
     40          1           0        6.329856   -3.267276   -0.696276
     41          1           0        5.353486   -2.663965    0.224492
     42          1           0        5.952940   -1.139402   -1.884713
     43          1           0        4.356327   -1.890917   -1.366439
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.5749224      0.0634153      0.0578152
 Standard basis: 6-311++G(d,p) (5D, 7F)
 There are   676 symmetry adapted basis functions of A   symmetry.
 Integral buffers will be    262144 words long.
 Raffenetti 2 integral format.
 Two-electron integral symmetry is turned on.
   676 basis functions,  1062 primitive gaussians,   701 cartesian basis f
    89 alpha electrons       89 beta electrons
       nuclear repulsion energy      1959.2712628887 Hartrees.
 NAtoms=   43 NActive=   43 NUniq=   43 SFac= 1.00D+00 NAtFMM=    50 NAOKFM
 One-electron integrals computed using PRISM.
 NBasis=   676 RedAO= T  NBF=   676
 NBsUse=   668 1.00D-06 NBFU=   668
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Performing the Initial MO Guess

Gaussian will perform a geometry optimization to find the most stable structure of each chalcone compound.[6]

Figure 5 : Flow to run DFT

Results and Discussion

Computational optimization of compounds

The compounds' structures have been fine-tuned, and their geometric properties, bond angles and lengths have been analyzed and tabulated in Table 1. Using a computational method known as Density Functional Theory (DFT) with the B3LYP/6-311G++(d,p) approach, highly accurate molecular structures were obtained. These computed parameters align well with experimental data and can serve as a foundation for calculating additional molecular properties, aiding in the interpretation of experimental results and predictions.

All bond lengths and bond angles obtained from DFT for these two compounds are mutually comparable to the other reported studies performed by a similar basis set of DFT. (Alsaee *et al.,* 2022)

Table 1: Geometrical Parameters obtained from DFT calculations

Nitro substituent chalcone (Ch1)		**Cyano substituent chalcone (Ch2)**	
Bonds	**DFT (Å, °)**	**Bonds**	**DFT (Å, °)**
C13-O1	1.224	C13-O1	1.224
N1-O2	1.224	C20-N1	1.156
N1-O3	1.224	C1-C2	1.392
C17-N1	1.481	C2-C3	1.394
C1-C2	1.392	C3-C4	1.394
C2-C3	1.394	C4-C5	1.392
C3-C4	1.394	C5-C6	1.403
C4-C5	1.392	C6-C7	1.478
C5-C6	1.403	C7-C8	1.377
C6-C7	1.478	C7-C9	1.426
C7-C8	1.377	C9-C10	1.379
C7-C9	1.426	C8-S1	1.725
C9-C10	1.379	C10-S1	1.754
C8-S1	1.725	C10-C11	1.437
C10-S1	1.754	C11-C12	1.350
C10-C11	1.437	C12-C13	1.475
C11-C12	1.350	C13-C14	1.507
C12-C13	1.475	C14-C15	1.401
C13-C14	1.509	C15-C16	1.390
C14-C15	1.401	C16-C17	1.401
C15-C16	1.391	C17-C18	1.404
C17-C18	1.392	C5-C6-C7	120.7
C18-C19	1.387	C6-C7-C8	124.4
C19-C14	1.402	C9-C10-C11	126.1
C5-C6-C7	120.7	C10-C11-C12	127.7
C6-C7-C8	124.4	C11-C12-C13	120.3
C9-C10-C11	126.0	C12-C13-C14	118.8
C10-C11-C12	127.8	C13-C14-C15	123.5
C11-C12-C13	120.3	C12-C13-O1	121.9
C12-C13-C14	118.7	O1-C13-C14	119.3
C13-C14-C15	123.2	C17-C20-N1	180.0
C12-C13-O1	122.1	C5-C6-C7-C9	−35.6
O1-C13-C14	119.2	C5-C6-C7-C8	144.3
O2-N1-O3	124.8	C9-C10-C11-C12	−178.8
C5-C6-C7-C9	35.7	C10-C11-C12-C13	−179.2
C5-C6-C7-C8	−144.2	C11-C12-C13-C14	−176.8
C9-C10-C11-C12	178.6	C12-C13-C14-C15	16.3

C10-C11-C12-C13	179.1	C11-C12-C13-O1	3.9
C11-C12-C13-C14	177.0	O1-C13-C14-C15	−164.4
C12-C13-C14-C15	−19.1	O1-C13-C14-C19	14.2
C11-C12-C13-O1	−3.9		
O1-C13-C14-C15	161.7		
O1-C13-C14-C19	−16.7		

Analysis of HOMO and LUMO Energy Levels

In this study, calculations to determine the energy levels of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) for two chalcone compounds were conducted. Each contained different substituents: one with a nitro (NO2) substituent (Figure 6) and the other with a cyano (CN) substituent (Figure 7). Density Functional Theory (DFT) with the B3LYP/6-311G++(d,p) basis set in the ground state was employed to gain insights into the electronic characteristics of these compounds. For the chalcone compound with a nitro substituent (Ch1), it was found that the HOMO energy level was calculated to be -6.5267 eV, and the LUMO energy level was -3.3345 eV. This resulted in an energy gap between the HOMO and LUMO orbitals, known as the HOMO-LUMO energy gap, measuring 3.192 eV. In contrast, the chalcone compound with a cyano substituent (Ch2) exhibited a HOMO energy level of -6.4880 eV and a LUMO energy level of -3.0518 eV, with a calculated HOMO-LUMO energy gap of 3.436 eV. These findings suggest that both chalcone compounds possess energy gaps conducive to efficient charge transfer processes. The HOMO-LUMO energy gap is a critical parameter for assessing a material's ability to facilitate charge transfer. A smaller energy gap typically indicates a material's suitability for charge transfer, making it potentially valuable in optoelectronic devices. Comparing the nitro-substituted chalcone (Ch1) with the cyano-substituted chalcone (Ch2) demonstrates how different substituents can influence the electronic properties of these compounds. Researchers and device designers can utilize these results to tailor chalcone-based materials to meet specific requirements for optoelectronic applications, such as light-emitting diodes (LEDs) and solar cells. The tunability of chalcone compounds makes them promising candidates for optimizing charge transfer efficiency in these devices.

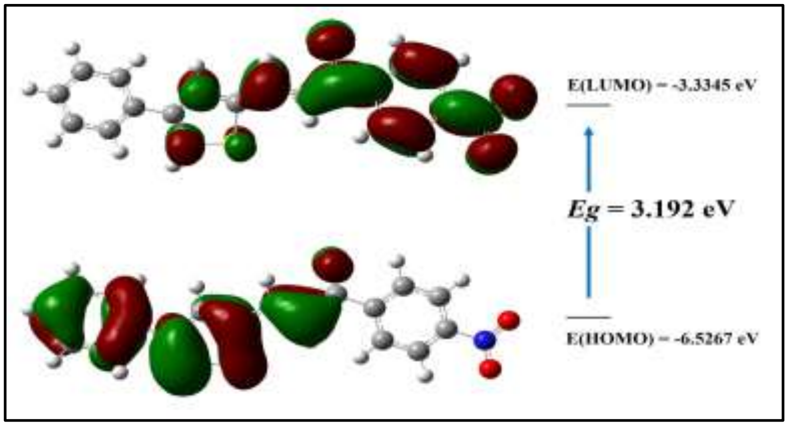

Figure 6: HOMO & LUMO diagram for nitro substituent chalcone

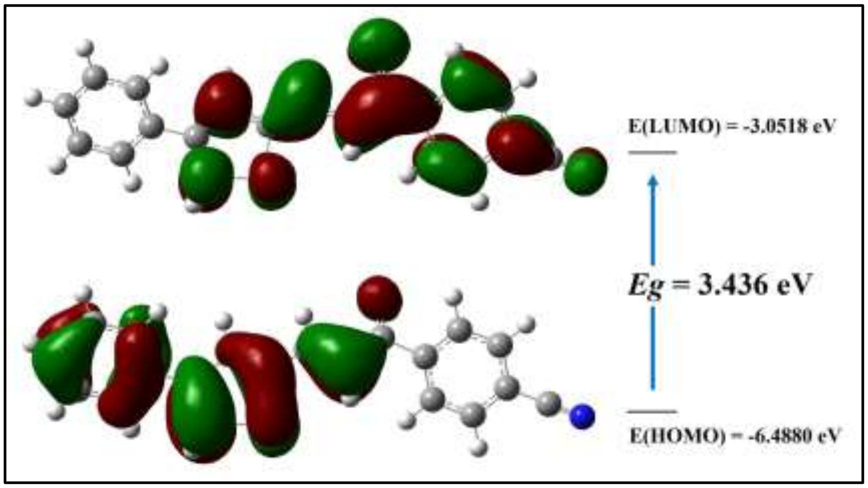

Figure 7: HOMO & LUMO diagram for cyano substituent chalcone

Exploration of Frontier Molecular Orbitals (FMOs)

Frontier molecular orbitals are essential quantum chemical properties, specifically the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). These quantum parameters play a crucial role in assessing a compound's reactivity and its capacity to absorb light. Dreuw and Head-Gordon's work in 2005 sheds light on how the energy gap between the HOMO and LUMO influences light absorption. Typically, in the HOMO state, electron density primarily resides in the donor region, whereas in the LUMO state, it concentrates in the acceptor region. The proximity of the HOMO and LUMO underlines their roles as electron donors and acceptors, respectively. Given that our compounds are configured in a D-π-A (donor-pi-acceptor) arrangement, the frontier molecular orbitals are clearly defined, spanning from the donor to the acceptor. In the HOMO state, electron density gathers at the phenylthiophene, which acts as the donor. In the LUMO state, electron density is centered at the nitro and cyano substituents, which serve as the acceptors. As our designed molecules exhibit a D-π-A structure, the transition of electrons from the donor to the acceptor results in a diminished energy gap. Consequently, our chalcone compounds hold the potential to bring about significant advancements in the realm of optoelectronics.

Conclusion

Two chalcone derivatives were intricately designed, synthesized, and rigorously analyzed through molecular electronic analysis using DFT theory, all with the objective of evaluating their potential as materials for optoelectronic applications. Our comprehensive theoretical investigations, encompassing quantum chemical computations and computational simulations, provided invaluable insights into the electronic structure, charge transfer characteristics, and optical properties of these chalcone compounds, as well as the importance of geometric alterations in shaping their performance. According to our DFT calculations, all bond lengths and bond angles in the two compounds closely align with those previously documented in research with a similar basis set of DFT.

Furthermore, our research presented the finding that, in addition to the electronic aspects, geometric parameters also played a pivotal role in shaping the reactivity and light absorption capabilities of these chalcone compounds. Specifically, the frontier molecular orbitals, particularly the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), were closely intertwined with the compounds' geometrical arrangements. Our investigation highlighted the fundamental role of frontier molecular orbitals, particularly HOMO and LUMO, in elucidating the reactivity and light absorption capabilities of these chalcone compounds.

Our research has revealed that (*E*)-1-(4-nitrophenyl)-3-(4-phenylthiophen-2-yl)prop-2-en-1-one (Ch1) surpasses (*E*)-4-(3-(4-phenylthiophen-2-yl) acryloyl)benzonitrile (Ch2) due to its narrower energy gap. Ch1 exhibits a 3.912 eV energy gap with the nitro substitution, while Ch2, with the cyano substitution, possesses a 3.436 eV energy gap. In summary, our synthesis and theoretical investigations of organic chalcone compounds have illuminated a promising pathway for the advancement of cutting-edge optoelectronic materials. The adaptability of chalcones, combined with our deepened comprehension of their electronic attributes, lays the groundwork for future innovations in optoelectronic devices, including light-emitting diodes (LEDs) and solar cells.

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