Synthesis, Photochromism, and Dft Study of Substituted Chalcone Fulgide and Fulgimide

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***Abstract*—Stobbe condensation is an important C-C bond-forming reaction in which an Aldehydes or ketones were condensed with dimethyl succinate to give corresponding acid- ester product and subsequent Stobbe condensation gives fulgide followed by ammonolysis to give fulgimide. Substituted chalcone were synthesized by convenient method to carry out subsequent Stobbe condensation. Stobbe condensation on chalcone like (E)-1-phenyl-3-(p-tolyl) prop-2-en-1-one with dimethyl succinate in presence of strong base at room temperature were carried to give the corresponding acid-ester product as (3Z,5E)-3-(methoxycarbonyl)-4-phenyl-6-(p-tolyl) hexa-3,5-dienoic acid. Esterification of obtained product followed by subsequent Stobbe condensation with ketone gives acid-ester product as (3Z,5E)-3-(methoxycarbonyl)-4-phenyl-2-(propan-2-ylidene)-6-(p-tolyl) hexa-3,5-dienoic acid. This acid ester product was saponified to give the corresponding diacid (Fulgenic acids) (Z)-2-((E)-1-phenyl-3-(p-tolyl) allylidene)-3-(propan-2-ylidene) succinic acid. Acetylation of Fulgenic acid leads to fulgide (Z)-1-phenyl-3-((E)-1-phenyl-3-(p-tolyl) allylidene)-4-(propan-2-ylidene) pyrrolidine-2,5-dione. Further ammonolysis of fulgides were carried out with aniline to give the corresponding Fulgimide (Z)-1-phenyl-3-((E)-1-phenyl-3-(p-tolyl) allylidene)-4-(propan-2-ylidene) pyrrolidine-2,5-dione. Photochromism is a reversible change in color or shade when exposed to light of a particular frequency or intensity. This reversible change makes them applicable in optical memory devices, ophthalmic lenses, novelty printing sensors, etc. This Fulgide was irradiated at 254 nm wavelengths in an Immersion-well photochemical reactor for photochromic properties. Properties like bond length, bond angle, dipole moment, HOMO-LUMO gap, and vibrational frequencies were also studied by using Density Functional Theory (DFT) at B3LYP, utilizing a 6-311+ G** basis set.**

***Index Terms*—Stobbe condensation, Fulgide, Fulgimide, Photochromism, DFT.**

I. INTRODUCTION

A simple chemical compound, chalcone (1,3-diphenyl-2-propene-1-one) has two aromatic rings that are separated by α and β-unsaturated carbonyl groups. Chalcones are produced when aromatic aldehydes and acetophenones condense with a catalyst present. Chalcones facilitate the creation of beneficial medicinal substances [1]. Chalcones have received particular attention due to their varied pharmacological effects and straightforward architectures [2,3]. The synthesis of chalcones and chalcone-based functionalized derivatives is still carried out for the reasons mentioned. Schemes for the synthesis of these chemicals have been described by numerous researchers worldwide. Aldol condensation and Claisen-Schmidt condensation are still the most popular techniques among those mentioned.

Fulgide and fulgimide were synthesized by subsequent Stobbe condensation followed by acetylation and ammonolysis [4-8]. Fulgide and Fulgimide attract the attention of researchers for their photochromic behavior. A lot of research was carried out with Stobbe products for their photochromic properties [9-12]. Photochromic compounds can make reversible changes in color or shade when exposed to a particular wavelength of light. This reversible change makes them applicable in optical memory devices, ophthalmic lenses, novelty printing sensors, etc. One important potential application is utility as the photoactive medium in an erasable, rewriteable optical memory [13-15]. In the past decade, many important positive developments in the engineering of such devices have been made.

Density Functional Theory (DFT) is a potent tool for figuring out ground-state parameters like electron density and total energy. Because it can handle complicated systems and offers a fair balance between accuracy and computational cost, DFT is widely employed to reduce the expectation value of the Hamiltonian concerning the electron density [16]. The present work reports a DFT analysis of the vibrational spectra of a photo-heterocyclic compound in the ground state. These calculations provide other important properties of the molecule beyond the harmonic vibrational frequency, including optimized geometry, molecular energy, and dipole moment. Good agreement with the experimental data is obtained by using DFT/B3LYP, utilizing a 6-311+G** as a basis set [17-18].

Experimental Detail:

1. General Procedures and Materials

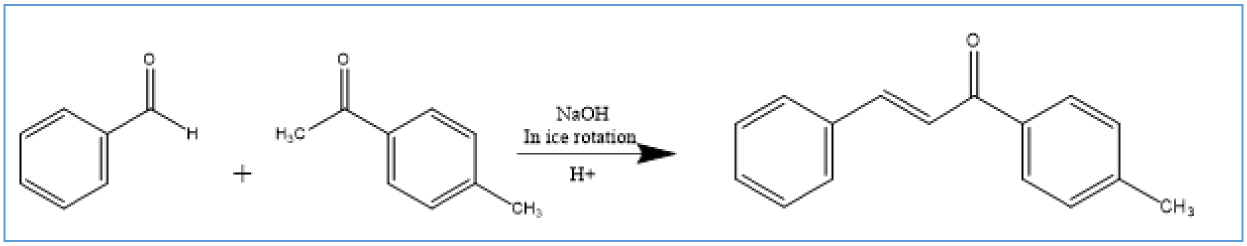
Commercial reagents and solvents of purest grade (A.R.) are used. Purification was carried out on a silica gel column by Chromatography. A photochromic study was done using an Immersion well photochemical reactor (SAIC-model IQW-I) and UV lamp (254nm). UV/VIS/NIR Spectrometer lambda-750 was used. A DFT study was carried out using Gaussian 09 software, and calculations were based on B3LYP and 6-311+G** basis set.

2. CHALCONE SYNTHESIS

Chalcone was synthesized using a known literature method, namely, a base-catalyzed Claisen-Schmidt condensation reaction of appropriately substituted Acetophenone and benzaldehyde [2,3].

Synthesis of (E)-1-phenyl-3-(p-tolyl) prop-2-en-1-one (1)

In a 500 cm^3 round-bottom flask fitted with a magnetic stirrer, 100 cm^3 of rectified spirit was used to dissolve 10.6g (0.1 mol) of benzaldehyde. After keeping the reaction flask submerged in a bath of crushed ice to maintain the appropriate temperature, 4-methylacetophenone (13.47 g, 0.1 mol) was added dropwise while being vigorously stirred for four to five hours. A 0.02M hydrochloric acid solution was used to neutralize the reaction mixture until precipitation occurred. Following vacuum filtering, the resultant product (E)-1-phenyl-3-(p-tolyl) prop-2-en-1-one (1) (see Scheme 01) was recrystallized in ethanol. Using column chromatography (silica gel with 10% ethyl acetate in hexane), the crystallized substance was purified. found: Yield 17.9 g (81%), Melting point:115°C, **UV**: λ_{max} (EtOH): 254 nm; **FTIR** cm^{-1}: 1662 (C=O), 1605 (C=C), 2960 (-CH), 979 (C=C-H); **^{1}H-Nmr** $CDCl_3$: δ 7.85 (2H, d, Aromatic CH), 7.58 (1H, d, Olefinic CH), 7.52 (1H, d, Olefinic CH), 2.20 (1H, s, CH_3).



Scheme 01: Synthesis of 4-methyl chalcone from Benzaldehyde and 4-methyl acetophenone.

3: SYNTHESIS OF (3Z,5E)-3-(METHOXYCARBONYL)-4-PHENYL-6-(P-TOLYL) HEXA-3,5-DIENOIC ACID (3)

A mixture of (E)-1-phenyl-3-(p-tolyl) prop-2-en-1-one (1) (17.5g, 0.08 mol) and dimethyl succinate (2) (12.5 mL, 0.08 mol) was dissolved in 50 mL of tert-butyl alcohol and slowly added to a solution of anhydrous potassium tertiary butoxide (13.46 g, 0.15 mol) in a 500 mL round-bottomed flask. The reaction mixture is refluxed for 30 minutes at room temperature and then allowed to stand for another 10 minutes. Then alcohol is distilled off under reduced pressure, and acidified with 3M Hydrochloric acid. Acidic substances were separated using 10% Na_2CO_3. Further acidification gives orange semi-solid acid ester (3Z,5E)-3-(methoxycarbonyl)-4-phenyl-6-(p-tolyl) hexa-3,5-dienoic acid (3) (see Scheme 02), which was recrystallized with n-hexane/Benzene petroleum ether, giving pure acid ester (3). Found :Yield: 19.5 g (61%), Melting point: 178°C, eq. wt. 336.20 required for $C_{21}H_{20}O_4$ (337.60), UV: λ_{max} (EtOH): 282 nm, FTIR (cm^{-1}): 1736 (C=O, ester), 1710 (C=O, acid), 1630 (C=C); ^{1}H-Nmr ($CDCl_3$): δ(ppm): 2.76 (3H, s, -CH_3), 7.17 (5H, Ar-H), 7.80 (1H, =CH-CO) 7.54 (1H, =CH). 2.15 (3H, d, -CH_3).

4. SYNTHESIS OF DIMETHYL (Z)-2-((E)-1-PHENYL-3-(P-TOLYL) ALLYLIDENE) SUCCINATE (4)

Acid ester (3) (19.2 g, 0.06 mol) was dissolved in 200 mL of methanol, and acetyl chloride (45 mL, 0.06 mol) was added under argon gas. After stirring for 24 hours, the solution was concentrated in vacuo. The residue was quenched with 100 mL of saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting orange liquid dimethyl (Z)-2-((E)-1-phenyl-3-(p-tolyl) allylidene) succinate (4) (see Scheme 02) was distilled in vacuo. Yield: 10.6 g (56%), Melting point: 190°C, **UV**: λ_{max} (EtOH): 268 nm, FTIR (cm^{-1}): 1734 (C=O, ester), 1719 (C=O, ester), 1630 (C=C); ^{1}H-Nmr ($CDCl_3$): δ (ppm): 2.42 (3H, s, $-CH_3$), 3.3 (3H, s, O-(C=O)), 3.5 (3H, s, O-(C=O)), 7.17 (5H, Ar-H), 6.80 (1H, =CH), 2.14 (3H, d, $-CH_3$).

5. SYNTHESIS OF (3Z,5E)-3-(METHOXYCARBONYL)-4-PHENYL-2-(PROPAN-2-YLIDENE)-6-(P-TOLYL) HEXA-3,5-DIENOIC ACID (6)

A mixture of diester (4) (10.3g, 0.03 mol) and Acetone (5) (1.8 g, 0.03 mol) was added dropwise to a solution of anhydrous potassium tertiary butoxide (4.5 g, 0.05 mol) in a 250 mL round-bottomed flask. The reaction mixture is refluxed for 30 minutes at room temperature and then allowed to stand for another 10 minutes. Alcohol was then distilled off under reduced pressure and then acidified with 3M Hydrochloric acid dropwise. Further acidification gives acid ester (3Z,5E)-3-(methoxycarbonyl)-4-phenyl-2-(propan-2-ylidene)-6-(p-tolyl) hexa-3,5-dienoic acid (6) (see Scheme 02), which has again recrystallized with n-hexane/benzene-pet ether. Yield: 7.4 g (58%), Melting Point: 208°C, eq. wt. 336.20 required for $C_{21}H_{20}O_4$ (337.60), **UV**: λ_{max} (EtOH): 288 nm, **IR** (cm^{-1}): 3090 (O-H, acid), 1748 (C=O, ester), 1709 (C=O, acid), 1630 (C=C), 1468 (aliphatic CH_2); **^{1}H-Nmr** ($CDCl_3$): δ (ppm): 2.40 (3H, s, $-CH_3$), 3.41 (3H, s, O-(C=O)), 3.42 (aliphatic CH_2), 7.05 (5H, Ar-H), 6.72 (1H, =CH), 2.09 (3H, d, $-CH_3$).

6: SYNTHESIS OF (Z)-2-((E)-1-PHENYL-3-(P-TOLYL) ALLYLIDENE)-3-(PROPAN-2-YLIDENE) SUCCINIC ACID (7)

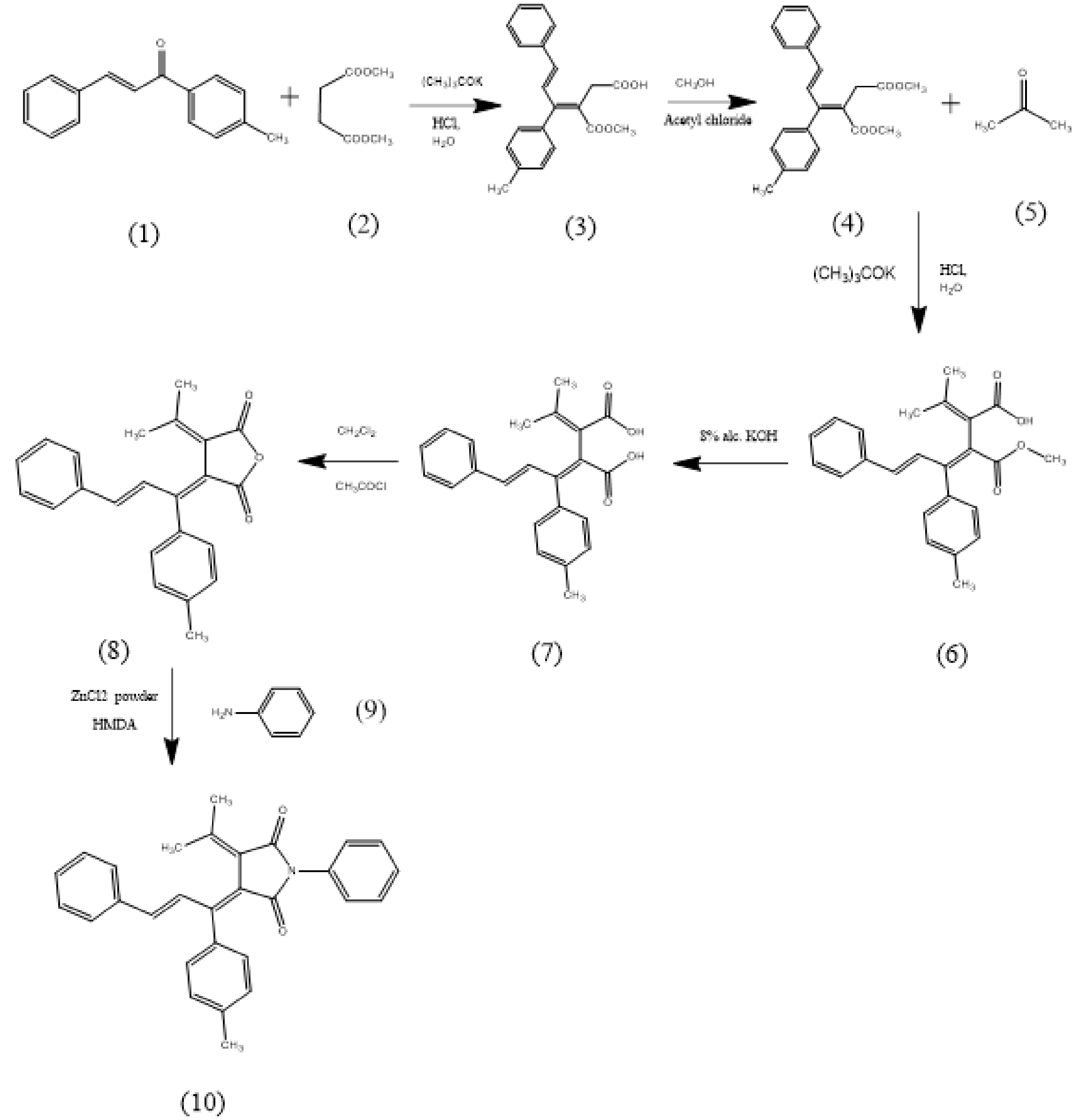
Acid ester (6) (7.2 g, 0.06 mol) was dissolved in alcoholic KOH (80 mL, 8%) and refluxed for 8 hours in a water bath, followed by acidification and recrystallized with n-hexane/Benzene petroleum ether, which would give a Yellow crystalline nature of diacids (Z)-2-((E)-1-phenyl-3-(p-tolyl) allylidene)-3-(propan-2-ylidene) succinic acid (7) (see Scheme 02), Yield: 3.9 g (53.8%), Melting point: 194°C, eq. wt. 181.20 required for $C_{23}H_{22}O_4$ (362.60), UV: λ_{max} (EtOH): 269 nm, IR (cm^{-1}): 1710,1735 (C=O, acid) stretch, 1322,1580 (C=C); ^{1}H-Nmr ($CDCl_3$): δ (ppm): 7.49 (1H,s, vinylic), 6.7-7.49 (Ar-H, m), 2.44 (3H, s, $-CH_3$), 2.15 (3H, d, $-CH_3$).

7. SYNTHESIS OF (Z)-3-((E)-1,3-DIPHENYLALLYLIDENE) DIHYDROFURAN-2,5-DIONE (8)

The diacid (7) (3.5 g, 0.02 mol) was dissolved in dichloromethane (100 mL), and to this mixture was added acetyl chloride (110 mL) dropwise; then the mixture was refluxed for 21 hours. The excess acetyl chloride was removed in vacuo, and the crude product was recrystallized with n-hexane/Benzene-pet ether to give the corresponding Fulgide (Z)-3-((E)-1,3-diphenylallylidene) dihydrofuran-2,5-dione (8) (see Scheme 02), Yield: 2.1 g (61%), Melting point: 232°C, UV: λ_{max} (EtOH): 296 nm, IR (cm^{-1}): 1747 (CO-O-CO anhydride), 1742 (Conjugate anhydride), 1466 (C-H, d-2H), 740 (C=C benzene), 2920 (C-H, d-2H), ^{1}H-NMR ($CDCl_3$): δ (ppm): 7.51 (1H,s, vinylic), 6.72-7.48 (Ar-H, m), 2.40 (3H, s, $-CH_3$), 2.15 (3H, d, $-CH_3$).

8. SYNTHESIS OF (Z)-1-PHENYL-3-((E)-1-PHENYL-3-(P-TOLYL) ALLYLIDENE)-4-(PROPAN-2-YLIDENE) PYRROLIDINE-2,5-DIONE (10)

A Flask is charged with a solution of Fulgide (9) (1.9 g, 0.96 mmol) in benzene (20 mL). Through a dropping funnel, aniline (9) (0.8 g, 0.96 mmol) in benzene (10 mL) was added dropwise, and the reaction mixture was stirred for 1 hour at room temperature. Zinc chloride powder (0.4 g, 0.1 mmol) was added to this reaction mixture in one portion. Subsequently, the reaction mixture was raised to reflux temperature, followed by adding Hexamethyldisilazane (HMDA) (0.3 g, 0.1 mmol) in benzene through a dropping funnel, over 10 minutes. This reaction mixture was then refluxed for 20 hours. The benzene was removed by rotary evaporation. The crude product was purified by flash silica gel chromatography column (9:1 hexane-ethylacetate as eluent), giving bright yellow crystals of (Z)-1-phenyl-3-((E)-1-phenyl-3-(p-tolyl) allylidene)-4-(propan-2-ylidene) pyrrolidine-2,5-dione (10) (see Scheme 02). Yield: 1.2 g (49%), Melting Point: 262℃, UV: λ_{max} (EtOH): 321 nm, IR (cm^{-1}): 1764 (C=O), 1706 (C=O), 1628 (-CH=C-C=O), 1608 (-C=C-$(CH_3)_2$), 1105 (N-C=O), ^{1}H-NMR ($CDCl_3$): 7.50 (1H,s, vinylic), 6.7-7.49 (Ar-H, m), 2.42 (3H, s, -CH_3), 2.10 (3H, d, -CH_3).



Scheme 02.

9. PHOTOCHROMISM

A molecule can reversibly change between two different states, each with its own absorption spectrum, causing an evident color shift. This phenomenon is known as photochromism. This transformation usually takes place in one direction when electromagnetic radiation, like UV light, is present, and the opposite change can be made by thermal processes or by eliminating or altering the light source. Santiago and Becker have analyzed the mechanism of photochemical changes.

The UV irradiation at 254 nm in an inert atmosphere of 1 x 10^{-5} mol dm^{-3} solution of chalcone substituted fulgide (8) and fulgimide (10) was carried out in an immersion well reactor (model IQW-1). The samples were scanned between (200-400 nm) by using an instrument type UV/VIS/NIR Spectrometer, Lambda 750 nm.

The structural changes that resulted from irradiating a 1 x 10^{-5} mol dm^{-3} solution of compounds (8) and (10) at 254 nm for 5, 10, 15, 20, 25, and 30 minutes in a photochromic investigation. Usually, the reaction's progress can be observed by looking for the disappearance of the distinctive absorption band in the starting material's UV spectrum.

Following 5, 10, and 15 minutes of irradiation, the absorption peak of compound (8) was seen at 296 nm. However, when the exposure time was extended to 20, 25, and 30 minutes, the absorption peak shifted from 296 nm to 315 nm (Table 1, Fig. 01). For compound (10), the absorption peak shifted to 321 nm from 346 nm, when irradiated by UV lamp at 254 nm in an immersion well reactor for 30 minutes (Table 1, Fig. 01).

Table 1. Main peaks before and after irradiation at 254 nm

Time in Minutes	Main peak Before Irradiation in nm	Main peak Before Irradiation in nm	Main peak After Irradiation in nm	Main peak After Irradiation in nm
	Fulgide compound (8)		Fulgimide compound (10)	
5	296.0	296.0	321.0	321.0
10	296.0	296.0	321.0	321.0
15	296.0	296.0	321.0	321.0
20	296.0	315.0	321.0	346.0
25	296.0	315.0	321.0	346.0
30	296.0	315.0	321.0	346.0

10. COMPUTATIONAL METHOD:

All calculations were performed at Gaussian 09 software, and calculations were based on B3LYP and 6-311+G** basis set, invoking geometry optimization. The geometries of Chalcone anhydride in the ground state are fully optimized as shown in Fig.1. The input geometry of chalcone anhydride has been first optimized without imposing any external constraint in the potential energy surfaces at DFT/B3LYP utilizing 6-311+G** basis set for C, O, and H atoms. The resultant optimized geometries have been used as input for vibrational frequency calculation at DFT/B3LYP utilizing a 6-311+G** basis set. The polarization function has been added for better treatment of polar bonds of C=O, C=C, C-O, C-C, and C-H groups.

Among numerous available DFT methods, we have selected the B3LYP method, which combines Becke's three-parameter exchange functional (B3) with Lee, Yang, and Parr correlation functional (LYP). All calculations are performed by using Gaussian 09 software.

Experimental values of bond parameters like the bond length of chalcone fulgides and fulgimides are listed in Table 2. Accordingly, computational work optimized structural parameters (Enthalpy, HOMO LUMO bond gap, Total dipole moment) of chalcone fulgides and fulgimides are calculated by DFT/B3LYP levels utilizing 6-311+G** a basis set are also listed in Table 2, by atom numbering scheme as shown in Fig. 2

Photochromism is observed in this chalcone fulgides and fulgimides due to the conjugation of carbonyl groups attached to the succinic anhydride ring structure. Photochromism is done by using an immersed well photoreactor with UV-L21 of 254 nm lamp systems. Both before and after irradiated spectra are calculated by a UV-Spectrophotometer as shown in Table 1, Fig. 1

Table 2. Optimized structural parameters using B3LYP/6-311+G** Basis set for chalcone Fulgide (8) and Fulgimide (10).

Spectral parameter	Fulgide (8) (in A°)	Fulgimide (10) (in A°)
r(C_1-C_2)	2.258	2.256
r (C_1-C_4)	1.483	1.484
r (C_2-C_3)	1.447	1.445
r (C_3-C_4)	1.494	1.495
r (C_1-O_2)	1.216	1.218
r (C_2-O_3)	1.217	1.219
r (C_3-C_5)	1.360	1.361
r (C_4-C_6)	1.344	1.342
r (C_5-C_{13})	1.488	1.486
r (C_6-C_7)	1.466	1.465
r (C_7-C_{10})	1.399	1.399
r (C_{10}-C_{11})	1.396	1.399
r (C_8-C_{11})	1.394	1.394
r (C_8-C_{12})	1.394	1.395
r (C_{13}-C_{15})	1.403	1.400
r (C_{15}-C_{18})	1.396	1.398
r (C_{16}-C_{17})	1.396	1.399
r (C_{14}-C_{17})	1.394	1.395
r (C_{14}-C_{18})	1.394	1.397
r (C_5-C_{19})	1.472	1.474
r (C_{14}-C_{16})	1.396	1.399
r(C_1-N)	------	1.510
r(C_2-N)	------	1.513
r(C_1-O_1)	1.415	-------
r (C_2-O_1)	1.376	-------
r(C_1-O_2)	1.200	1.251
r(C_2-O_2)	1.201	1.253

Table 3: The optimized calculation of Enropy (cal/mol Kelvin), Homo Lumo energy (ev), total dipole moment (Debye) for chalcone fulgides and fulgimides at B3LYP/6-311+G** basis set

Parameters/ Compounds	Homo Lumo Gap (in eV)	Entropy (in Cal/mol Kelvin)	Total dipole moment (in Debye)
Fulgide (8)	-1.49	154.30	9.26
Fulgimide (10)	-3.18	165.67	4.18

11. RESULTS AND DISCUSSION:

A synthesized compound by subsequent Stobbe condensation shows photochromism. The argument of Santiago Becker is that of 1,3,5-hexatriene, in which an aromatic bond serves in place of one of the double bonds of triene holds good with chalcone substituted fulgide and fulgimide. Moreover, Fulgimide shows a shift of 25 nm, and Fulgide shows a 19 nm shift, promising that Fulgimide is more photochromic than Fulgide.

Organic photochromic compounds such as Fulgenic acids are potential candidates for application in erasable optical information media. This methodology brought down not only the reaction time but also the use of hazardous organic solvents, possibly. The prepared Fulgide (8) can also be used in the preparation of photosensitive glasses, photosensitive toys, and other instruments, Optical data recording like Compact Disc, preparation of photosensitive inks for security purposes, and variable density filters.

12. ACKNOWLEDGEMENT

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