Photochromism, Dft Study, and Synthesis of 4-Methoxy Chalcone Fulgide and Fulgimide

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***Abstract*—Stobbe condensation is a significant reaction for forming carbon-carbon bonds, where aldehydes or ketones are condensed with dimethyl succinate to produce a corresponding acid-ester product. After the Stobbe condensation, the product undergoes a reaction called ammonolysis to form fulgimide. Substituted chalcone was synthesized using a convenient method to allow further Stobbe condensation reactions. When chalcone, such as (E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one, is reacted with dimethyl succinate in the presence of a strong base at room temperature, the corresponding acid-ester product is formed, which is (3Z,5E)-3-(methoxycarbonyl)-4-(4-methoxyphenyl)-6-phenylhexa-3,5-dienoic acid. The esterification of this product, followed by another Stobbe condensation with Acetone, gives the acid-ester product (3Z,5E)-3-(methoxycarbonyl)-4-(4-methoxyphenyl)-6-phenyl-2-(propan-2-ylidene) hexa-3,5-dienoic acid. This acid ester product was saponified to give the corresponding diacid, known as fulgenic acid, which is (Z)-2-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-3-(propan-2-ylidene) succinic acid. Acetylation of the fulgenic acid results in the formation of fulgide, which is (Z)-3-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-4-(propan-2-ylidene) dihydrofuran-2,5-dione. Further ammonolysis of the fulgide with aniline produces the corresponding fulgimide, (Z)-3-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-1-phenyl-4-(propan-2-ylidene) pyrrolidine-2,5-dione. Photochromism is the reversible change of color in a material when exposed to light of a certain frequency or intensity. This property makes these materials useful in applications such as optical memory devices, ophthalmic lenses, novelty printing sensors, and more. The fulgide was irradiated at 254 nm wavelength in an immersion-well photochemical reactor to study its photochromic properties. Properties such as bond length, bond angle, dipole moment, HOMO-LUMO gap, and vibrational frequencies were analyzed using Density Functional Theory (DFT) at the B3LYP level with 6- 311+ G** basis set.**

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

I. INTRODUCTION

A simple chemical compound called chalcone, which has the name 1,3-diphenyl-2-propene-1-one, has two aromatic rings connected by groups that have double bonds and a carbonyl group. Chalcones are made when aromatic aldehydes and acetophenones join together with the help of a catalyst [1]. Chalcone helps in making useful medicines. They have been extensively studied due to their numerous health-related effects and their straightforward structures [2-3]. People still make chalcones and their modified versions for these reasons. Many scientists around the world have described ways to make these chemical. Among the methods used, aldol condensation and Claisen-Schmidt condensation are the most common ones.

Fulgide and Fulgimide were made through a process called Stobbe condensation, followed by acetylation and ammonolysis [4-8]. These compounds have drawn interest from scientists because of their ability to change color or shade when exposed to light, a property known as photochromism. A lot of studies have been done on Stobbe products to explore their photochromic features [9-12]. Photochromic materials can switch between different colors or shades in response to specific wavelengths of light, and this reversible change makes them useful in a variety of applications, such as optical memory devices, eyewear lenses, novelty printing, and sensors. One key use is as the active component in erasable and rewritable optical storage systems [13-15].

Density Functional Theory is a powerful method for determining key properties of a system in its lowest energy state, such as electron density and total energy. It is popular because it can deal with complex systems and offers a good balance between accuracy and the cost of computation. DFT helps in finding the lowest possible value of the Hamiltonian related to electron density [16]. This study uses DFT to analyze the vibrational spectra of a photo-heterocyclic compound in its ground state. The calculation also gives other important information about the molecule, like its bond length, energy, and dipole moment, using the DFT/B3LYP method, with a 6-311+G** basis set [17-18].

II. EXPERIMENTAL DETAIL

1. General Procedures and Materials

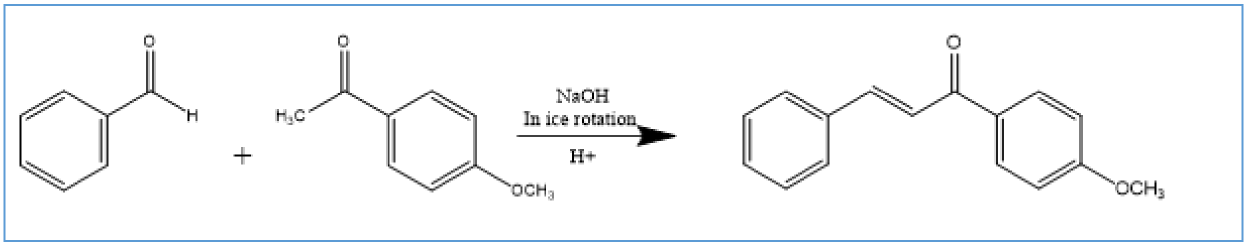
Pure chemicals and solvents of the highest quality (A.R.) were used. The compound was purified using silica gel column chromatography. A photochromic test was performed using an immersion well photochemical reactor (SAIC-model IQW-I) along with a UV lamp that emits 254nm light. For spectral analysis, a UV/VIS/NIR spectrometer called lambda-750 was employed. A DFT calculation was conducted using the Gaussian 09 software, and calculations were based on B3LYP and 6-311+G** basis set.

2. Chalcone synthesis

Chalcone was made using a method that is already described in scientific papers [1]. This method involves a chemical reaction called Claisen-Schmidt condensation, which is catalyzed by a base. The reaction uses Acetophenone and benzaldehyde that have been modified with the right groups, namely a base-catalyzed Claisen-Schmidt condensation reaction of appropriately substituted Acetophenone and benzaldehyde [2,3].

Synthesis of (E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (1)

In a round-bottom flask with a magnetic stirrer, 100 cm^3 of rectified spirit was used to dissolve 10.7 g (0.1 mol) of benzaldehyde. The reaction flask was kept in a bath of crushed ice to keep the temperature right. Then, 4-methoxyacetophenone (14.2 g, 0.1 mol) was added drop by drop while the mixture was stirred hard for four to five hours. A 0.02M hydrochloric acid solution was added to neutralize the reaction mixture until a solid started to form. After filtering under vacuum, the product (E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (1) was recrystallized in ethanol (see Scheme 01). The purified substance was then separated using column chromatography with silica gel and 10% ethyl acetate in hexane. Found: Yield 18.1 g (79%), Melting point:108°C, UV: λ_{max} (EtOH): 248 nm; FTIR cm^{-1}: 1664 (C=O), 1610 (C=C), 2959 (-CH), 972 (C=C-H); ^{1}H-Nmr $CDCl_3$: δ 7.82 (2H, d, Aromatic CH), 7.61 (1H, d, Olefinic CH), 7.53 (1H, d, Olefinic CH), 3.57 (3H, s, $-OCH_3$).



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

3: Synthesis of (3Z,5E)-3-(methoxycarbonyl)-4-(4-methoxyphenyl)-6-phenylhexa-3,5-dienoic acid (3)

A mixture of (E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (1) (17.7 g, 0.08 mol) and dimethyl succinate (2) (12.6 mL, 0.08 mol) was dissolved in a 50 mL of tert-butyl alcohol and slowly added to a solution of anhydrous potassium tertiary butoxide (13.5 g, 0.15 mol) in 500 mL round-bottomed flask. The reaction mixture was heated to reflux for 30 minutes at room temperature and then let stand for another 10 minutes. Then alcohol was removed by distillation under reduced pressure, and the mixture was made acidic using 3M hydrochloric acid. The acidic substances were separated using 10% sodium carbonate. Further acidification produced an orange semi-solid ester, (3Z,5E)-3-(methoxycarbonyl)-4-(4-methoxyphenyl)-6-phenylhexa-3,5-dienoic acid (3) (see Scheme 02), which was recrystallized with n-hexane/Benzene petroleum ether, giving pure acid ester (3). Found :Yield: 18.7 g (65%), Melting point: 181°C, eq. wt. 352.20 required for $C_{21}H_{20}O_5$ (353.60), UV: λ_{max} (EtOH): 278 nm, FTIR (cm^{-1}): 1735 (C=O, ester), 1708 (C=O, acid), 1632 (C=C); ^{1}H-Nmr ($CDCl_3$): δ(ppm): 3.52 (3H, s, -OCH_3), 7.15 (5H, Ar-H), 6.78 (1H, =CH) 6.52 (1H, =CH), 3.37 (2H, s, -CH_2).

4. Synthesis of dimethyl (Z)-2-((E)-1-(4-methoxyphenyl)-3-phenylallylidene) succinate (4)
Acid ester (3) (18.5 g, 0.06 mol) was dissolved in 200 mL of methanol, and acetyl chloride (45 mL, 0.06 mol) was added while using argon gas. The mixture was stirred for 24 hours, then the solution was evaporated under reduced pressure. The remaining solid was treated with 100 mL of saturated aqueous sodium bicarbonate and then separated using diethyl ether. The combined organic layer was dried with magnesium sulfate, filtered, and evaporated under reduced pressure. The product formed is dimethyl (Z)-2-((E)-1-(4-methoxyphenyl)-3-phenylallylidene) succinate (4) as an orange semi-solid (see Scheme 02). Found: Yield: 10.8 g (58%), Melting point: 192°C, UV: λ_{max} (EtOH): 260 nm, FTIR (cm^{-1}): 1730 (C=O, ester), 1721 (C=O, ester), 1628 (C=C); ^{1}H-Nmr ($CDCl_3$): δ (ppm): 3.54 (3H, s, -OCH_3), 3.3 (3H, s, OCH_3-(C=O)), 3.5 (3H, s, OCH_3-(C=O)), 7.17 (5H, Ar-H), 6.80 (1H, =CH), 3.14 (2H, s, -CH_2).
5. Synthesis of (3Z,5E)-3-(methoxycarbonyl)-4-(4-methoxyphenyl)-6-phenyl-2-(propan-2-ylidene) hexa-3,5-dienoic acid (6)

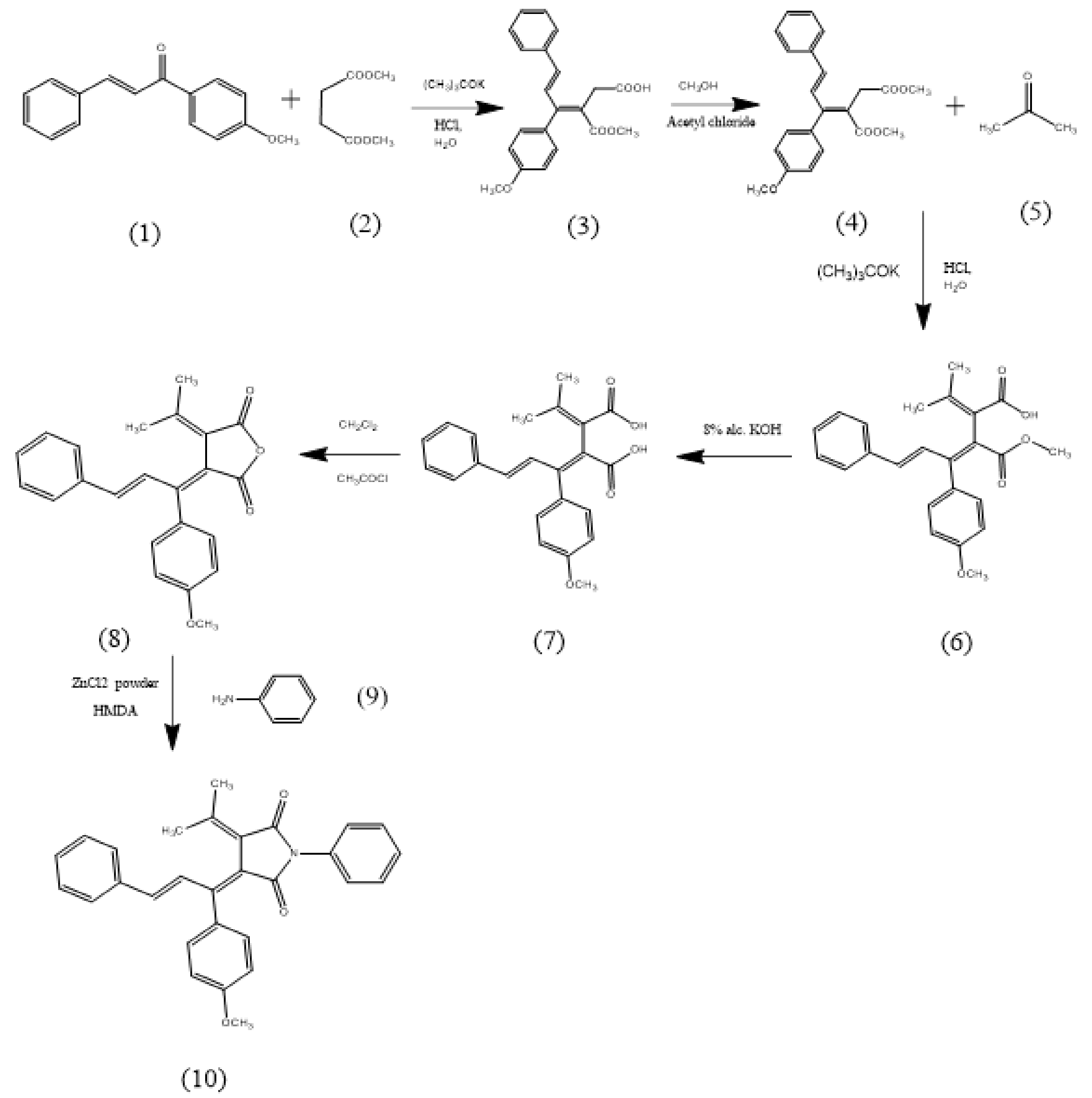
A mixture of diester (4) (10.5 g, 0.03 mol) and acetone (5) (1.8 g, 0.03mol) was slowly added to a solution of anhydrous potassium tertiary butoxide (4.6 g, 0.05 mol) in a 250 mL round-bottomed flask. The reaction mixture was heated and kept at the same temperature for 30 minutes, then left to sit for another 10 minutes. Alcohol was then removed by distilling under lower pressure. Next, the mixture was slowly made more acidic using 3M hydrochloric acid. Further acid treatment produced the acid ester (3Z,5E)-3-(methoxycarbonyl)-4-(4-methoxyphenyl)-6-phenyl-2-(propan-2-ylidene) hexa-3,5-dienoic acid (see Scheme 02), which has again recrystallized with n-hexane/benzene-pet ether. Found: Yield: 7.6 g (59%), Melting Point: 212°C, eq. wt. 392.20 required for $C_{24}H_{24}O_5$ (393.40), UV: λ_{max} (EtOH): 292 nm, IR (cm^{-1}): 3087 (O-H, acid), 1745 (C=O, ester), 1712 (C=O, acid), 1629 (C=C), 1465 (aliphatic CH_2); ^{1}H-Nmr ($CDCl_3$): δ (ppm): 3.52 (3H, s, -OCH_3), 3.41 (3H, s, O-(C=O)), 3.45 (aliphatic CH_2), 7.05 (5H, Ar-H), 6.72 (1H, =CH), 2.12 (3H, d, -CH_3).

6: Synthesis of (Z)-2-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-3-(propan-2-ylidene) succinic acid (7)
Acid ester (6) (7.4 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-(4-methoxyphenyl)-3-phenylallylidene)-3-(propan-2-ylidene)succinic acid (7) (see Scheme 02), Yield: 4.1 g (52.8%), Melting point: 192°C, eq. wt. 189.20 required for $C_{23}H_{22}O_5$ (378.60), UV: λ_{max} (EtOH): 269 nm, IR (cm^{-1}): 1712,1730 (C=O, acid) stretch, 1324,1579 (C=C); ^{1}H-Nmr ($CDCl_3$): δ (ppm): 7.52 (1H,s, vinylic), 6.7-7.5 (Ar-H, m), 3.44 (3H, s, -OCH_3), 2.15 (3H, d, -CH_3).

7. Synthesis of (Z)-3-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-4-(propan-2-ylidene) dihydrofuran-2,5-dione (8)
The diacid (7) (3.9 g, 0.02 mol) was dissolved in dichloromethane (100 mL), and acetyl chloride (110 mL) was added drop by drop to the solution. The mixture was then heated under reflux for 21 hours. After that, the extra acetyl chloride was removed using a vacuum. The resulting crude product was then recrystallized with n-hexane/Benzene-pet ether to give the corresponding Fulgide (Z)-3-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-4-(propan-2-ylidene) dihydrofuran-2,5-dione (8) (see Scheme 02). Found: Yield: 2.2 g (62%), Melting point: 229°C, UV: λ_{max} (EtOH): 288 nm, IR (cm^{-1}): 1745 (CO-O-CO anhydride), 1740 (Conjugate anhydride), 1462 (C-H, d-2H), 738 (C=C benzene), 2918 (C-H, d-2H), ^{1}H-NMR ($CDCl_3$): δ (ppm): 7.52 (1H,s, vinylic), 6.70-7.45 (Ar-H, m), 3.40 (3H, s, -OCH_3), 2.15 (3H, d, -CH_3).

8. Synthesis of (Z)-3-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-1-phenyl-4-(propan-2-ylidene) pyrrolidine-2,5-dione (10)
A Flask was filled with a solution of Fulgide (8) (2.1 g, 0.96 mmol) in benzene (20 mL). Using a dropping funnel, a solution of aniline (9) (0.9 g, 0.96 mmol) in benzene (10 mL) was added drop by drop, and the reaction mixture was stirred for one hour at room

temperature. Zinc chloride powder (0.45 g, 0.1 mmol) was then added all at once to the reaction mixture. The temperature of the reaction mixture was increased to its boiling point, and then Hexamethyl disilazane (HMDA) (0.34 g, 0.1mmol) in benzene was added through a dropping funnel over 10 minutes. The reaction mixture was then boiled for 20 hours. The benzene was removed using a rotary evaporator. The crude product was purified using a flash silica gel chromatography column with a 9:1 mixture of hexane and ethyl acetate as the eluent, resulting in bright yellow crystals of (Z)-3-((E)-1-(4-methoxyphenyl)-3-phenylallylidene)-1-phenyl-4-(propan-2-ylidene) pyrrolidine-2,5-dione (10) (see Scheme 02). Found: Yield: 1.4 g (48%), Melting Point: 274℃, UV: λ_{max} (EtOH): 315 nm, IR (cm^{-1}): 1761 (C=O), 1710 (C=O), 1632 (-CH=C-C=O), 1611 (-C=C-$(CH_3)_2$), 1102 (N-C=O), ^{1}H-NMR ($CDCl_3$): 7.48 (1H,s, vinylic), 6.7-7.5 (Ar-H, m), 3.48 (3H, s, -OCH_3), 2.10 (3H, d, -CH_3).



Scheme 02.

Scheme 02.

III. PHOTOCHROMISM

A molecule can switch back and forth between two different states, and each state has its own way of absorbing light, which makes the color change noticeable. This is called photochromism. Usually, the change happens in one direction when there is light, like UV light, and the other way can be triggered by heat or by turning off or changing the light source. Santiago and Becker studied how these chemical changes work.

The UV light treatment at 254 nm was performed on a solution with a concentration of 1 × 10^ (- 5) mol dm^ (-3) of chalcone-substituted fulgide (8) and fulgimide (10). This was carried out in an immersion well reactor called Model IQW-I. After the treatment, the samples were checked using a UV/VIS/NIR Spectrometer, Lambda 750, and scanned across the wavelength range from 200 to 400 nm.

When compounds (8) and (10) were exposed to light at 254 nm for different times, 5, 10, 15,20,25, and 30 minutes, in a study about how materials change when exposed to light, structural changes happened. Typically, reaction 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 288 nm to 306 nm (Table 1, Fig. 01). For compound (10), the absorption peak shifted to 315 nm from 338 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	288.0	288.0	315.0	315.0
10	288.0	288.0	315.0	315.0
15	288.0	288.0	315.0	315.0
20	288.0	306.0	315.0	338.0
25	288.0	306.0	315.0	338.0
30	288.0	306.0	315.0	338.0

IV. COMPUTATIONAL METHOD

All calculations were done using the Gaussian 09 software. The calculations used the B3LYP method with the 6-311+G** basis set and included geometry optimization. The ground state geometry of chalcone anhydride was fully optimized, as shown in Figure 1. The initial geometry of chalcone anhydride was optimized without any external constraints on the potential energy surface using DFT/B3LYP with the 6-311+G** basis set for carbon, oxygen, and hydrogen atoms. The optimized geometries were then used for vibrational frequency calculations using the same DFT/B3LYP method and basis set. A polarization function was added to better describe the polar bonds in groups like C=O, C=C, C-O and C-H.

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)	2.250	2.251
r (C_1-C_4)	1.484	1.481
r (C_2-C_3)	1.440	1.442
r (C_3-C_4)	1.498	1.498
r (C_1-O_2)	1.212	1.215
r (C_2-O_3)	1.215	1.216
r (C_3-C_5)	1.362	1.361
r (C_4-C_6)	1.342	1.342
r (C_5-C_{13})	1.487	1.489
r (C_6-C_7)	1.467	1.465
r (C_7-C_{10})	1.400	1.399
r (C_{10}-C_{11})	1.398	1.400
r (C_8-C_{11})	1.395	1.394
r (C_8-C_{12})	1.394	1.394
r (C_{13}-C_{15})	1.401	1.405
r (C_{15}-C_{18})	1.399	1.398
r (C_{16}-C_{17})	1.401	1.398
r (C_{14}-C_{17})	1.392	1.397
r (C_{14}-C_{18})	1.399	1.401
r (C_5-C_{19})	1.470	1.476
r (C_{14}-C_{16})	1.399	1.401
r(C_1-N)	------	1.512
r(C_2-N)	------	1.513
r(C_1-O_1)	1.410	-------
r (C_2-O_1)	1.378	-------
r(C_1-O_2)	1.201	1.204
r(C_2-O_2)	1.201	1.203

Table 3: The optimized calculation of Entropy (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)	-2.93	171.66	7.35
Fulgimide (10)	-3.07	181.10	3.39

V. RESULTS AND DISCUSSION

A compound made through Stobbe condensation has the ability to change color when exposed to light. Santiago Becker's idea suggests that in a molecule called 1,3,5-hexatriene, an aromatic bond replace one of the double bonds in the triene structure. This work well with a compound called 4-Methoxy chalcone fulgide and fulgimide. Additionally, fulgimide shows a color change of 23 nm while fulgide changes by 18 nm, which means fulgimide is more light-sensitive than fulgide.

Organic compounds like fulgenic acid could be used in materials that can be erased and reused for storing information. This method also reduces the time needed for reactions and the use of harmful solvents. The compound fulgide (8) can be used to make photosensitive glasses, toys, and other devices. It's also useful for storing data on discs like compact disc, making secure inks, and creating filters that change density.

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