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Synthesis and photochromism of *E*,*E*-3,4-(3,5-dimethoxybenzylidene) succinic anhydride and its infra red active 2-dicyanomethylene derivative

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Abstract

The pale yellow fulgide **7** was prepared via two successive Stobbe condensations of one molar equivalent of diethylsuccinate and two molar equivalent of 3,5-dimethoxybenzaldehyde. The pale yellow fulgide **7**, in both solid and solution, turned pink when irradiated with 366 nm light. The fulgide **7** was found to undergo a Knovenagel type reaction when condensed with malononitrile under basic condition to give, after ring closure, the dicyanomethylene derivative **14**. The later on irradiation with 366 nm gave the infrared active 1,8*a*-DHN derivative **16**. The 1,8*a*-DHN derivative of fulgide **7** (e.g. **15**) showed remarkable positive solvatochromism as the solvent polarity is increased.

Keywords: Photochromic; Photochromism; Fulgides; Dicyanomethylene; Infrared active

1. Introduction

Stobbe [1,2] first discovered the photochromism of some phenyl substituted bis-methylene succinic anhydrides (fulgides) **1** in the solid state. Later studies showed that the photochromic properties result from photocyclization of these yellow to orange compounds to give red 1,8*a*-dihydronaphthalene intermediates (1,8*a*-DHNs) **2** which undergo the reverse process on exposure to white light [3–5]. These stereo specific processes occur in accordance with Woodward–Hoffmann rule for pericyclic reaction [6] (Scheme 1).

Organic photochromic compounds, such as fulgides are potential candidates for application in erasable optical information media, attempts have been made to improve their photochromic properties [7]. Previous paper [8] reported that the color of the ring-closed form of fulgides can be altered to deep blue (e.g. λ_{max} 610 nm) by synthesis of heterocyclic fulgides from 3-pyrryl group. This system is encountered by difficulties in the synthesis of pyrryl fulgides due to the sensitivity of the pyrrole ring to the reaction conditions applied in the condensation. Recently, it has been reported that the replacement of one of the carbonyl oxygen by the more powerful electron withdrawing group, such as dicyanomethylene, to produce novel fulgides derivatives, which on exposure to UV light were ring closed to give new photocyclized forms absorbing beyond 600 nm [9–11]. In this paper, the synthesis of new symmetrical fulgide **7** and its 2-dicyanomethylene derivative **14** will be investigated.

2. Results and discussion

2.1. Synthesis of the fulgide 7

Fulgide **7** was prepared via Stobbe condensation of one mole of diethylsuccinate and one mole of 3,5-dihydroxybenzaldehyde using potassium *tert*-butoxide as a base in toluene at room temperature to form the acid ester **3**. The latter was re-esterified using methanol and acetyl chloride to give the diester **4**, which was subjected to another Stobbe condensation by using another mole of 3,5-dihydroxybenzaldehyde to give the acid ester **5** which was hydrolyzed using alcoholic potassium hydroxide to give the diacid **6**. This was dehydrated to give fulgide **7** as yellow needles (Schemes 2 and 3). The fulgide **7** was obtained exclusively as *E*,*E*-isomer as follows from its ^{1}H-NMR spectrum which showed a singlet at 3.60 ppm assigned to the four methoxy groups, two doublets, one at 6.0 ppm and the other at 6.30 ppm assigned to the aromatic hydrogens, and a two proton singlet at 7.83 ppm assigned to the olefinic protons shielded by the aromatic rings.

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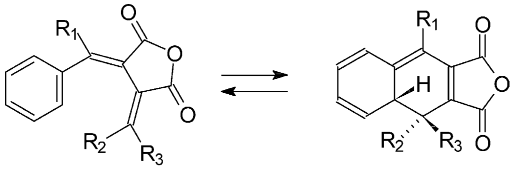


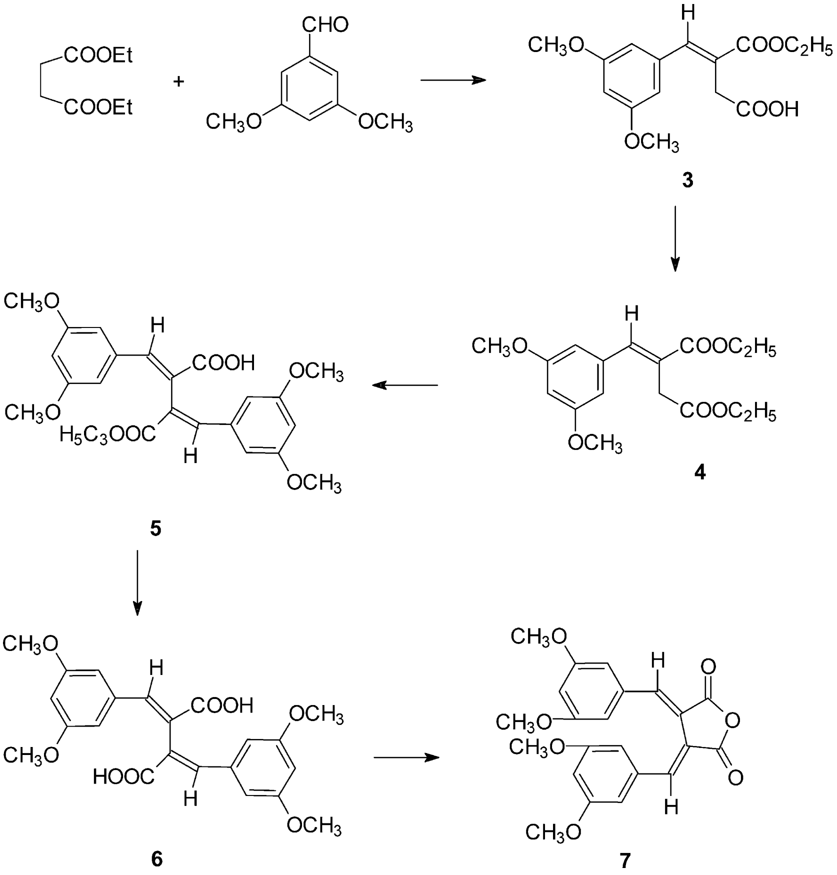
1 **2**

Scheme 1.

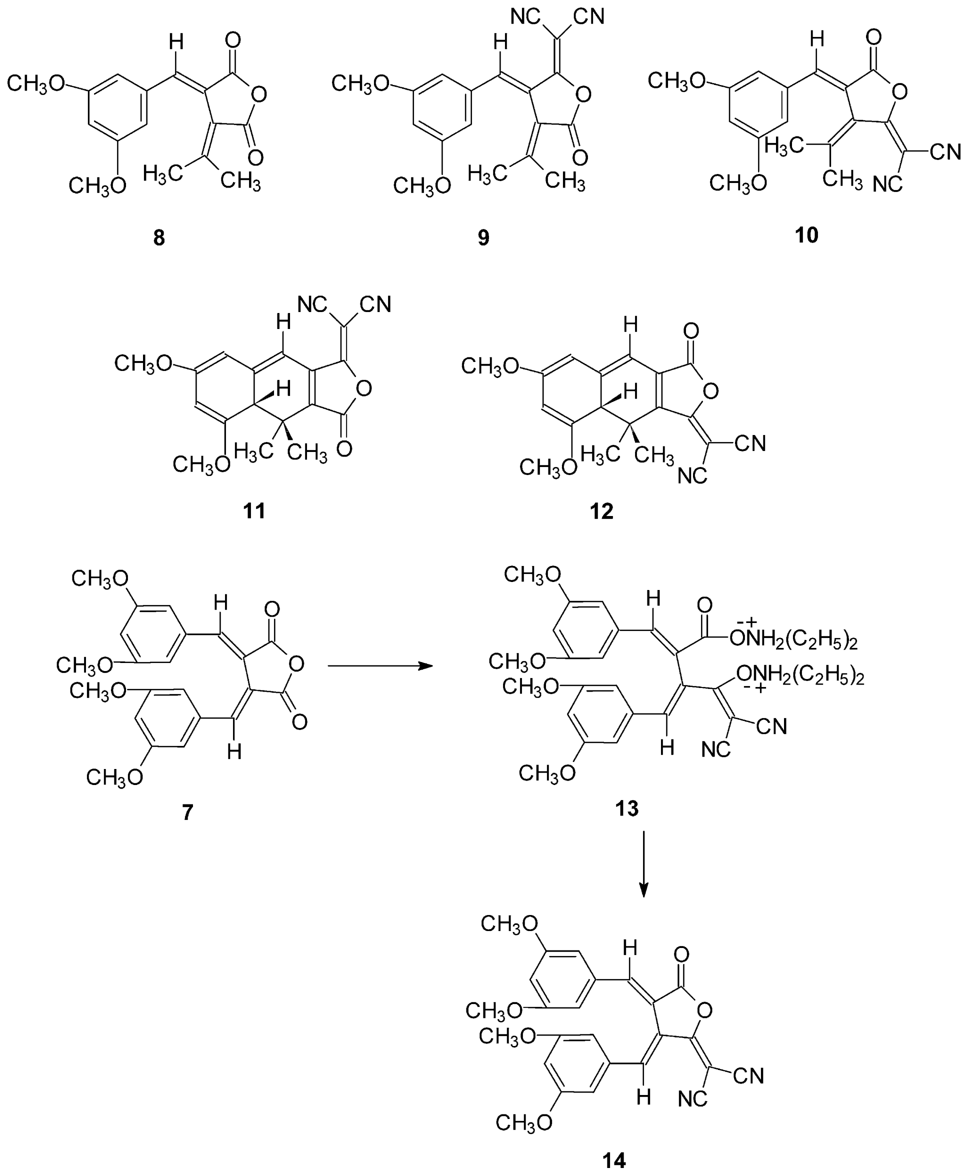
2.2. Synthesis of dicyanomethylene derivative **14**

Recently, it has been reported that one carbonyl group of the succinic anhydride moiety can be substituted by the more powerful electron withdrawing group such as the dicyanomethylene group [9–11].

In unsymmetrical fulgides, such as **8**, the carbonyl group in conjugation with the aryl group is more susceptible to nucleophilic attack by nucleophile such as dicyanomethane anion, and only compound **9** was obtained, as confirmed by X-ray single crystal analysis (A.M. Asiri, unpublished results). This process is governed by two factors, the electronic factor versus the steric factor. The electronic factor favors the attack to take place on the carbonyl group in conjugation with the aromatic ring to form, for example, compound **9**. On the other hand, the steric factor favors the attack to be on the less hindered carbonyl which is the carbonyl adjacent to the isopropylidene group to form compound such as **10**. This indicates that the aromatic group is more likely to be planar with the anhydride moiety so the electronic density can be migrated more easily to the carbonyl group adjacent to it. When compound **9** was irradiated with UV light, an electrocyclization took place and compound **11** was formed. The cyclized form **11** did not show large bathochromic shift, because the powerful dicyanomethylene group is in cross conjugation with the conjugation system in the 1,8*a*-DHN derivative **11**. On the other hand, if the dicyanomethane anion would attack the other carbonyl group of fulgide **8** to give the dicyanomethylene **10**, then on irradiation with UV light the cyclized form **12** would expect to show large bathochromic shift compared to the corresponding cyclized form of the orignal fulgide **8**. To overcome the problem of preferential attack, a symmetrical fulgide was required and for this reason, the fulgide **7** was prepared. The dicyanomethylene derivative **14** was prepared by condensation of fulgide **7** and dicyanomethane anion generated in situ by adding diethylamine to malononitrile in THF at room temperature, then the fulgide solution was added and the salt **13** formed was cyclized to give the dicyanomethylene derivative **14** as pale yellow crystals.



Scheme 2.



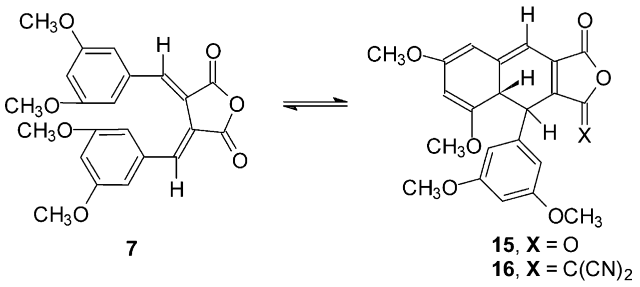
Scheme 3.

The later was obtained as *E*,*E*-isomer as established by its ^{1}H-NMR spectrum, which showed two singlets at 8.33 and 7.82 ppm attributed to the olefinic protons in conjugation with dicyanomethylene and carbonyl, respectively. The introduction of the dicyanomethylene group causes low field shift of the adjacent olefinic protons and left the other proton chemical shift unchanged.

2.3. Photochromism of fulgide **7** and its dicyanomethylene derivative **14**

On irradiation at 366 nm of fulgide **7**, both as solid or in solutions, a yellow to red coloration was observed. The red color formed is attributed to the formation of the dihydronaphthalene (DHN) derivative (**15**, X = O). The cyclization took place without any preference between the two aromatic groups as shown in Scheme 4. The original color of fulgide **7** can be restored on exposure to white light.

Likewise, the dicyanomethylene derivative **14** on irradiation at 366 nm, similar cyclization to form the infrared



Scheme 4.

Table 1
UV-Vis spectral data of fulgide **7** and its dicyanomethylene derivative **14** before and after irradiation at 366 nm

Compound no.	λ_{max} (nm)	ε_{max} ($l\,mol^{-1}\,cm^{-1}$)
7	353	12589
15	530	5000
14	402	18197
16	676	6500

Table 2
UV-Vis spectral data of fulgide **7** and its 1,8*a*-DHN **15** in various solvents

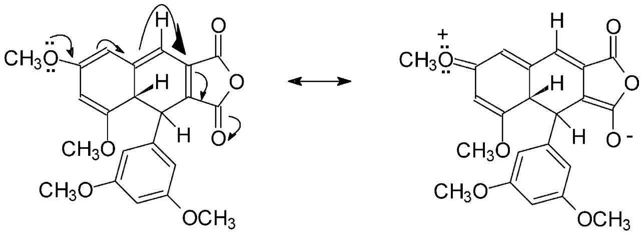
Solvent	Permittivity at 20 °C	λ_{max} (nm; **7**)	λ_{max} (nm; **15**)
Hexane	1.89	346	506
Toluene	2.38	353	530
$CHCl_3$	4.80	354	558
DCM[a]	9.08	354	564

[a] DCM denotes dichloromethane.

active 1,8*a*-dihydronaphthalen derivative (1,8*a*-DHN) **16** which has absorption maximium at 676 nm with an absorption tail going to the infrared region. The cyclization took place on the aromatic group not in conjugation with the dicyanomethylene moiety as evidenced by the large bathochromic shift of the cyclized form **16** rather than forming **17** which is expected to absorb as the cyclized form of fulgide **7**. The introduction of the dicyanomethylene group resulted in large bathochromic shift of the colored form of compound **16** compared to the cyclized form of the unsubstituted fulgide **15**. The original color of the dicyanomethylene **14** can be restored on exposure to white light. The electronic spectral properties of fulgide **7** and its dicyanomethylene **14** in toluene before and after irradiation at 366 nm are summarized in Table 1.

2.4. *Solvatochromism of fulgide **7** and its 1,8a-DHN derivative **15***

The UV-Vis spectra of fulgide **7** and its cyclized form **15** were investigated in four different solvents, and the data are summarized in Table 2. As the solvent's polarity increased, the absorption maxima of both the colored and the uncolored forms are red shifted. This may be due to the stability of the excited state of both forms as they received large contribution from the resonance hybrid **18** (Scheme 5).



15 **17**

Scheme 5.

3. Experimental

Melting points were recorded on a Thomas–Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer, ^{1}H-NMR were recorded in $CDCl_3$ on a Brucker DPX 400 MHz spectrometer using TMS as internal standard. UV-Vis spectra were recorded on a Shimadazu 260 spectrometer for solutions.

3.1. *Dimethyl 2-(E)(3,5-dimethoxybenzylidene) succinate **4***

A mixture of dimethylsuccinate (9.0 g, 0.09 mol) and 3,5-dimethoxybenzaldehyde (20 g, 0.12 mol) in dry toluene (150 ml) was added dropwise to a well stirred solution of potassium *tert*-butoxide (30 g, 0.26 mol) in dry toluene (150 ml) at 20 °C. After the addition was completed, the stirring was continued at 20 °C for further 20 h. The solvent was removed in vacuo, the residue was dissolved in water (375 ml), extracted with diethyl ether (2 × 50 ml) and the aqueous layer was acidified using aqueous hydrogen chloride (6 M, 100 ml). The residual acid ester was extracted with diethyl ether (3 × 100 ml), dried (Na_2SO_4), and filtered to give the acid ester **3** as a brown gum (16 g, 93%). The crude acid ester **3** (16 g) was dissolved in methanol (100 ml), acetyl chloride (20 ml) was added dropwise at 20 °C, the mixture was heated at reflux for 5 h, then the solvent removed in vacuo and the residual gum was distilled to give the diester **4** as deep yellow semisolid (16 g, 88%), m.p. 80 °C. Found: C, 61.02; H, 6.25%. $C_{15}H_{18}O_6$ requires C, 61.24; H, 6.12%. δ_H 7.85 (1H, s, olefinic proton), 6.4 (1H, d, *J* 2.3 Hz), 6.01 (2H, d, *J* 2.3 Hz), 4.10, 4.05 (6H, s, 2 × CH_3O), 3.64 (6H, s, 2 × CH_3O), 3.20 (2H, s, CH_2).

3.2. *E,E-2,3-Bis(3,5-dimethoxybenzylidene)succinic acid **6***

Dimethyl 2-(*E*)(3,5-dimethoxybenzylidene)succinate **4** (16 g, 0.054 mol) and 3,5-dimethoxybenzaldehyde (9.0 g, 0.054 mol) in toluene (100 ml) was added dropwise to a suspension of potassium *tert*-butoxide (7.15 g, 0.064 mol) in toluene (150 ml) with stirring at 20 °C. After the addition was completed, the stirring was continued for 12 h at 20 °C, the solvent was evaporated in vacuo, the residue was dissolved in water (100 ml) and acidified with aqueous hydrogen chloride (6 M, 100 ml). The residual oily product **5** was extracted with diethyl ether (3 × 50 ml) and was dissolved in alcoholic KOH (100 ml, 10%) heated at reflux for 8 h, then the solvent removed in vacuo. The residue was dissolved in water (100 ml) and acidified with aqueous hydrogen chloride (6 M, 100 ml). The liberated diacid was extracted into ether (2 × 50 ml), dried (Na_2SO_4), and filtered. The solvent was removed to give the diacid **6** as dark yellow oil, which was dissolved in diethyl ether and left to crystallize. The diacid **6** was obtained as white crystals

(12.58 g, 49% overall yield), m.p. >300 °C. Found: C, 63.55; H, 5.46%. $C_{22}H_{22}O_8$ requires C, 63.78; H, 5.31%.

3.3. *E,E-Bis(3,5-dimethoxybenzylidene)succinic anhydride* ***7***

The diacid **6** (12 g, 0.029 mol) was dissolved in dichloromethane (25 ml) and to this mixture was added acetyl chloride (30 ml) dropwise with stirring at 0 °C, and the mixture was then stirred at 20 °C for 6 h. The excess acetyl chloride was removed in vacuo and the crude product was chromatographed on silica gel eluting with diethyl ether:light petrolium (1:1). The pure *E*,*E*-fulgide was crystallized from ethanol as deep yellow crystals (4.5 g, 18% overall yield), m.p. 180–182 °C. Found: C, 66.68; H, 5.58%. $C_{22}H_{20}O_7$ requires C, 66.68; H, 5.05%. H 5.32; δ_H 7.83 (1H, s, olefinic proton), 6.3 (1H, d, *J* 2.4 Hz, para aromatic protons), 6.00 (2H, d, *J* 2.4 Hz, ortho aromatic protons), 3.6 (6H, s, 2 × CH_3O); ν_{max} 1822 cm^{-1} (C=O), 1766 cm^{-1} (C=O).

3.4. *E,E-3,4-Bis(3,5-dimethoxybenzylidene)-2-dicyanomethylene-tetrahydrofuran-5-one* ***14***

Diethylamine (0.58 g, 7.94 mmol) was added dropwise with stirring to a solution of *E*,*E*-bis(3,5-dimethoxybenzylidene)succinic anhydride **7** (1.50 g, 3.79 mmol) and malononitrile (0.26 g, 3.93 mmol) in THF (20 ml) at 0 °C. The mixture was then stirred at 0 °C for 6 h, diethyl ether (15 ml) was added, the disalt **13** was not isolated. The crude product was dissolved in dichloromethane (20 ml) and cyclized by stirring with acetyl chloride (15 ml) at 20 °C for 12 h. The solvent and excess acetyl chloride were removed in vacuum, and the residual was chromatographed on silica gel eluting with a 3:7 mixture of ethyl acetate and light petroleum to give the dicyanomethylene **14** as yellow crystals (0.87 g, 52% yield), m.p. 200–201 °C from ether/light petroleum. Found: C, 67.82; H, 4.58; N, 6.33%. $C_{23}H_{20}O_4N_2$ requires C, 67.58; H, 4.50; N, 6.30%. δ_H 8.33 (1H, s, olefinic proton cis to $C(CN)_2$), 7.82 (1H, s, olefinic proton cis to C=O), 6.34 (1H, dd overlap, *J* 2.23 Hz), 6.27 (1H, dd overlap, *J* 2.23 Hz), 6.0 (2H, d, *J* 2.18 Hz), 5.98 (2H, d, *J* 2.18 Hz), 3.64 (6H, s, 2 × CH_3O), 3.62 (6H, s, 2 × CH_3O). λ_{max} 354 nm (log ε 4.26); ν_{max} 2306 cm^{-1} (CN), 1819 cm^{-1} (CO).

3.5. *Photochemical reactions of fulgide* ***7*** *and the dicyanomethylene derivative* ***14***

A toluene solution of the fulgide or the dicyanomethylene derivative (c.a. 10^{-4} M) was irradiated with 366 nm from a 250 W mercury discharge lamp (type ME/D Thorn Lighting) with a filter (type OX1 change Pilkington). The irradiation was continued while monitoring the absorption of the new visible band formed until no absorption change was observed.

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