

Photochemistry of photochromic 2-indolylfulgides with substituents at the 1'-position of the indolylmethylene moiety

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Abstract

Substituted 2-indolyl fulgides with methyl and isopropyl groups at the 1'-position of the indolylmethylene moiety were synthesized. Steric effects on the spectroscopic and photochromic properties were measured and discussed. The methyl and isopropyl groups at the 1'-position decrease the quantum efficiency of the *E*–*Z* isomerization, while increase the coloration quantum yield. The thermal stability and fatigue resistance of these fulgides were determined. © 2001 Published by Elsevier Science B.V.

Keywords: Photochromism; Fulgides; Fluorescence; Substituent effect; Quantum yield

1. Introduction

Photochromic fulgides are derivatives of dimethylene succinic anhydrides, containing a hexatriene frame. The photochromic reaction is based on reversible light-induced hexatriene/cyclohexadiene interconversion, a concerted reaction in accordance with Woodward–Hoffmann selection rules. Usually, for aromatic heterocyclic fulgides, both, the open-ring and closed-ring forms are thermally stable and their absorption spectra are well separated from each other. These properties make fulgides potentially attractive photochromic systems for application in optical memory devices and optical switches [1,2].

Photochromic fulgides with aromatic heterocycles such as furan, thiophene, pyrrole, indole and thiazole rings have been synthesized and their spectroscopic and photochromic properties have been previously described [3–7]. In order to achieve certain properties, such as absorption of the colored form at longer wavelengths and higher fatigue resistance to coloration–bleaching cycles, improvement have been made by modifying the fulgide frame [8–11]. However, to be suitable for applications in rewritable two-photon 3D optical storage memory devices [12,13], the colored form should fluoresce. Today, only very few of the fulgides or fulgimides are known to emit fluorescence [7,14–16].

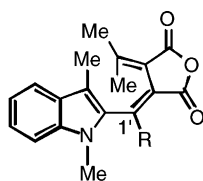
In previous papers, we have reported that 2-indolylfulgides are promising materials for use in two-photon 3D optical

memory devices [14,17]. We showed that these fulgides exhibit thermally irreversible photochromic reactions and in addition the colored forms emit fluorescence when irradiated with visible light. We have also investigated the effect of substituents at the 5-position of the indole ring on the spectroscopic and photochromic properties of 2-indolylfulgides [17]. In this paper, we will consider the effect of R substituents on the spectroscopic and photochromic properties of 2-indolylfulgides, shown in Scheme 1.

2. Results and discussion

Previous experimental results had indicated that substituents at the aromatic ring or directly connected to the hexatriene frame of the fulgide molecule could significantly affect the spectroscopic properties and photoreaction efficiency [6,17,18]. Excitation of the open-ring, *E*-form, of 2-indolylfulgide, induces the electrocyclization reaction, *E*–*Z* isomerization and other radiationless processes. Excitation of the ring-closed, *C*-form, leads to the reverse decyclization reaction and fluorescence of *C*-form accompanied by the radiationless processes. These energy relaxation processes are competing with each other and therefore increase in the efficiency of one channel would decrease the efficiency of another. Substituents at the 1'-position of the indolylmethylene moiety, which is in the middle of indole and anhydride groups, may sterically or electronically affect the absorption spectra and efficiency of the *E*–*Z* isomerization process. A steric hindrance at this position may restrict

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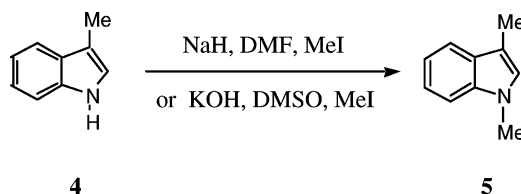
1. R = H, 2. R = Methyl (Me), 3. R = iso-Propyl (*i*-Pr)

Scheme 1.

E–*Z* isomerization and, as a result, increase the quantum yield of the ring closure reaction [4].

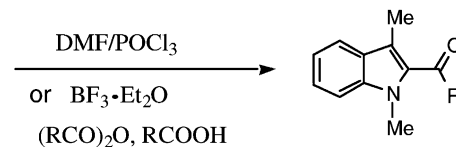
2.1. Synthesis of the materials

The indole intermediates were synthesized by the methods shown in Scheme 2. Commercially available 3-methylindole (**4**) was converted to 1,3-dimethylindole (**5**) by reacting it with iodomethane either in DMF solution, in the presence of sodium hydride, or in DMSO solution in the presence of potassium hydroxide. For both methods, the reaction yield was higher than 90% [19,20]. The intermediate, 1,3-dimethylindole-2-carbaldehyde (**6**), was synthesized by the Vilsmeier–Haack reaction with 87% yield [21]. Intermediates **7** and **8** were prepared by acylation reaction,



4

5

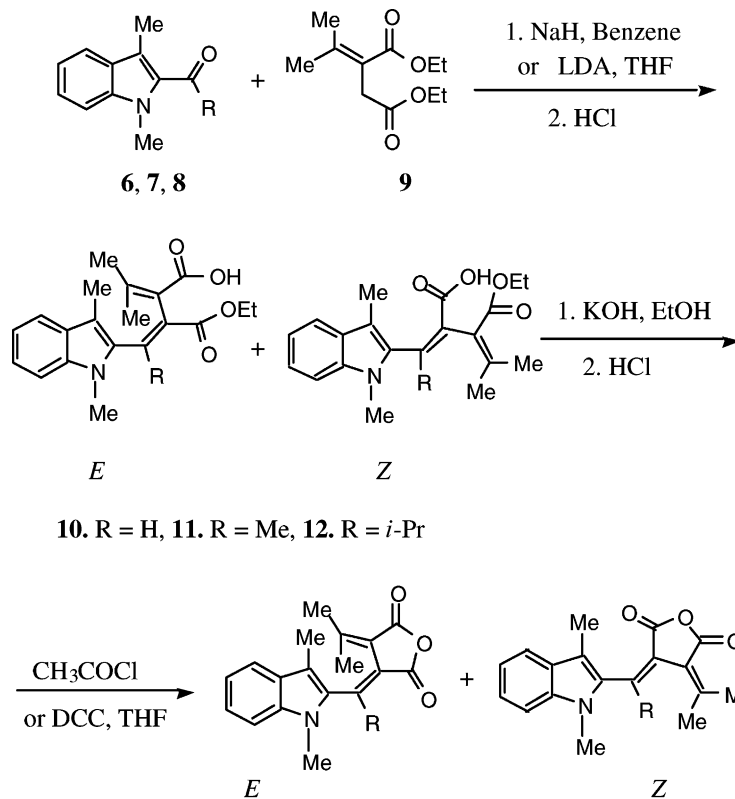


6. R = H, 7. R = Me, 8. R = *i*-Pr

Scheme 2.

catalyzed by boron trifluoride ethylether at room temperature [22]. This simple and efficient method gives almost a quantitative yield.

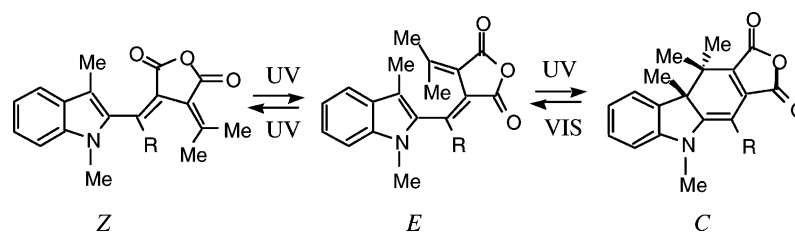
The Stobbe condensation of **6** (R = H) and **7** (R = Me) with diethyl isopropylidene succinate (**9**) can be conducted in the presence of sodium hydride in anhydrous benzene solution [23]. However, condensation of **8** (R = *i*-Pr) with **9** proved to be unsuccessful. The use of lithium diisopropylamide (LDA) instead of sodium hydride as a base leads



10. R = H, 11. R = Me, 12. R = *i*-Pr

1. R = H (*E* and *Z*), 2. R = Me (*E* and *Z*), 3. R = *i*-Pr (*E*),

Scheme 3.



Scheme 4.

to the formation of condensation products. Hydrolysis of half-ester **10**, **11** and **12** yields corresponding diacids, see Scheme 3. The diacids undergo intramolecular anhydride formation, that yields fulgides. The products were purified by flash silica gel column chromatography that resulted in light yellow fulgide crystals. When R is hydrogen, both the Z and E isomers were formed with the E-form the main product. In contrast, when R is methyl, both the Z and E isomers were obtained, however, the Z-form was the main product. Furthermore, when R is isopropyl, only the E isomer was formed without any Z-form produced.

2.2. UV–VIS absorption spectra

The absorption spectra of the open-ring, colorless form of fulgides, are located in the UV region. In contrast, the closed-ring form, has its absorption band in the visible region. The open-ring form contains a fundamental hexatriene frame. Upon irradiation with UV light, a conrotatory electrocyclization reaction occurs, see Scheme 4. This results in the formation of a cyclic, ring-closure structure, often referred as the colored C-form, because its absorption spectrum is red shifted to the visible region. Conversely, when the colored form was excited with visible light, it reversed back to the pale yellow or colorless fulgide form. This light induced ring-closing and ring-opening reaction is referred to as its photochromic cycle.

Table 1 lists the absorption spectra maxima of the E, Z and C isomers of the fulgides **1–3**, in various solvents. The absorption spectra of the E-fulgides have their maximum at 395 nm, and are not affected, strongly, by solvents. Fulgides with methyl (**2**) and isopropyl (**3**) substituents at 1'-position of the indolylmethylene moiety have the same absorption maximum, as the non-substituted fulgide with R = H. The absorption maximum of **1**, Z-form, is red shifted by 20 nm compared with **1**, E-form. However, the absorption maximum of **2** Z-form is almost the same as the corresponding E-form, but its absorption band exhibits different shape. The indole and the anhydride moieties of both E and Z open-ring forms of fulgide molecule are not in the same plane, but are twisted out of plane. Such a structure forces the conjugation system to break and as a result, the absorption spectra of the E- and Z-forms are blue shifted to 395 nm. Irradiation of the E-form with UV light induces ring-closure, which is the near planar structure C-form that allows the formation of a larger conjugated system. The absorption spectra of the C-forms are consequently red shifted by about 150 nm. High extinction coefficient values and shift to longer wavelength in polar solvents support the assignment of the E-, Z- and C-form absorption bands to a π - π^* transition [24].

We observed also, that the absorption maxima of the **2** and **3** C-forms are strongly affected by solvent polarity. In polar acetonitrile solvent, the absorption maximum is red shifted by 42 nm compared to the spectra in nonpolar

Table 1
UV–VIS maximum absorption and extinction coefficients of E-, Z- and C-forms of 2-indolylfulgide, **1–3**, in various solvents

Solvent	Isomer	λ_{\max} (nm), ϵ_{\max} ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)		
		R = H (1)	R = Me (2)	R = <i>i</i> -Pr (3)
Acetonitrile	E	395 (13400)	390 (7080)	394 (3800)
	Z	419 (16000)	381 (6608)	–
	C	514 (14100)	550 (11012)	550 (9800)
1,2-Dichloroethane	E	403 (14100)	398 (7320)	402 (4044)
	Z	429 (16900)	393 (7071)	–
	C	515 (14100)	549 (11028)	549 (9422)
Toluene	E	404 (13400)	395 (8922)	399 (3889)
	Z	–	398 (7181)	–
	C	500 (13600)	530 (11156)	530 (8911)
Hexane	E	398 (13500)	391 (7290)	396 (4200)
	Z	426 (18700)	398 (7490)	–
	C	475 (13300)	509 (10044)	508 (9022)

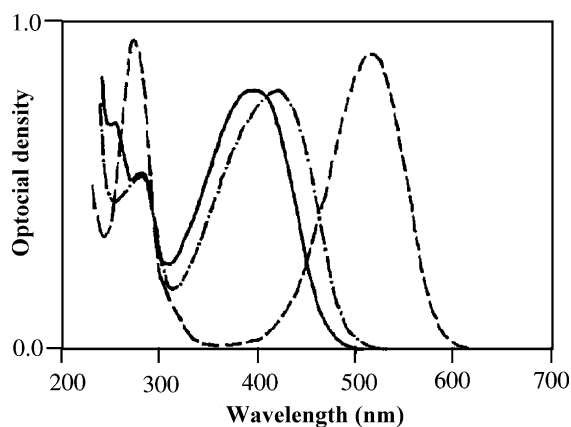


Fig. 1. Absorption spectra of **1** in acetonitrile: *E* (—), *Z* (---), and *C* (- · -) form.

hexane. The same spectral behavior was observed earlier for fulgides **1** [17]. This data suggest that the excited state of the *C*-form has a large dipole moment and therefore is stabilized by polar solvents. Figs. 1 and 2 show the *E*-, *Z*- and *C*-form absorption spectra of **1** and **2** in acetonitrile.

In comparison with fulgide **1** ($R = H$), which has the *C*-form absorption maximum at 513 nm in acetonitrile solution, the absorption maxima of **2** ($R = \text{methyl}$) and **3** ($R = i\text{-Pr}$) *C*-forms are shifted to 550 nm. This large shift may be explained by the steric strain between the *N*-methyl and the methyl or isopropyl groups at the 1'-position of the indolylmethylene moiety. In the ground state, the cyclized, *C*-form, has a planar structure, which is destabilized by this steric strain, while in the excited state the steric strain can be significantly relieved by the twisting of the formal double bonds. Therefore, the energy gap between the ground state and the first excited state is lowered (see Scheme 5). Similar examples are found in the literature [25].

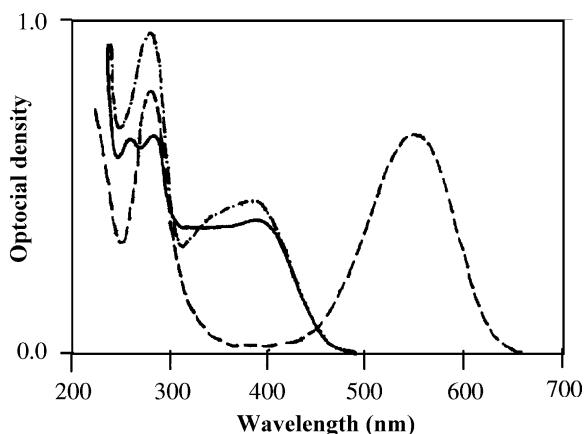
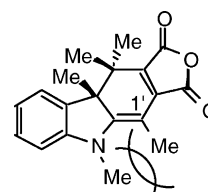


Fig. 2. Absorption spectra of **2** in acetonitrile: *E* (—), *Z* (---), and *C* (- · -) form.



Scheme 5.

2.3. Quantum yields of photochromic reactions

Irradiation of the open-ring, *E*-forms of the synthesized fulgides **1**, **2** and **3**, with UV light induces an electrocyclic reaction that yields the closed-ring isomer structure, *C*-form (see Scheme 4). This is evident by the shift of the initially light yellow colored acetonitrile solutions to red.

Fig. 3 shows the absorption spectra changes for **1** *E*-form in acetonitrile solution, excited at 360 nm. The photoisomerization between *E*- and *Z*-forms also takes place in parallel with the ring-closing process, been evidenced by the shift of the isosbestic point and the proton NMR spectra (see Figs. 3 and 4). In acetonitrile solution the long wavelength absorption band of **1** *C*-form is red shifted by more than 120 nm in comparison to **1** *E*-form, but it exhibits a much smaller absorption intensity at 360 nm. This difference in absorption spectra allows for conversion of the open-ring *E*-form to the closed-ring *C*-form, almost quantitatively, when excited with 360 nm light. It should be noted, however, that the absorption spectra of the **1** *E*- and **1** *Z*-forms vary only slightly. Therefore, photoexcitation with 360 nm light, where both forms have strong absorption, leads initially to the formation of a photo equilibrium mixture between these two forms. The colored, *C*-form can revert back to the open-ring, bleached form, by excitation with $\lambda > 530$ nm light. During the ring-opening process the formation of only the *E*-form was observed (see Fig. 5), which is the favored configuration for the cyclization process.

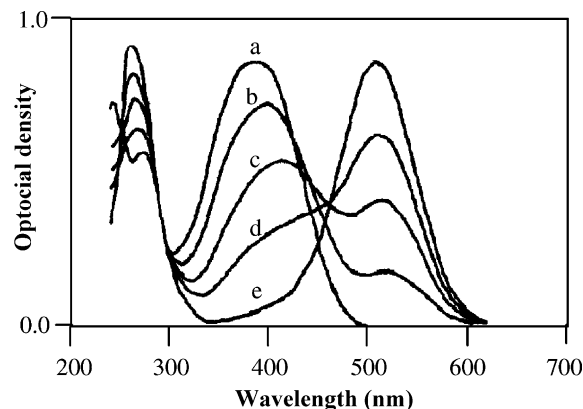


Fig. 3. Absorption spectra change of **1** *E*-form in acetonitrile under irradiation with 360 nm light: (a) initial *E*-form; (b–e) after 25 s, 1.2, 2.8, and 4.8 min irradiation, respectively.

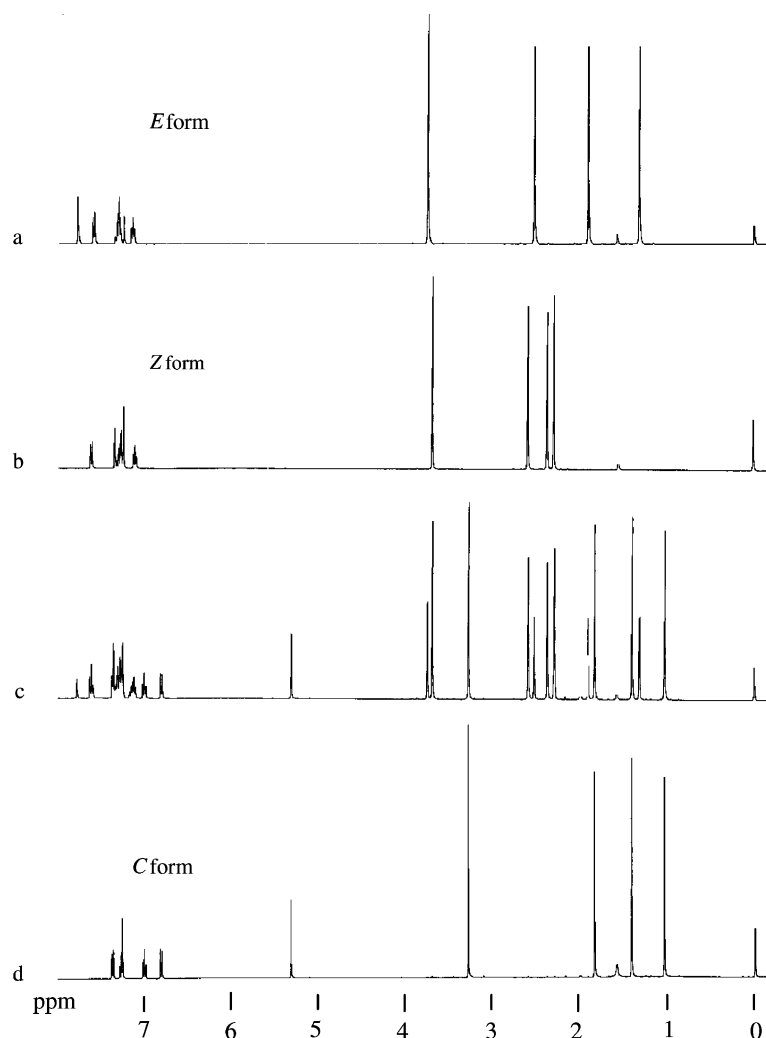


Fig. 4. The proton NMR spectra of **1**: pure *E*-form (a); pure *Z*-form (b); the mixture of *E*-, *Z*- and *C*-forms obtained by irradiating the *E*-form with 360 nm light for 30 min (c); and pure *C*-form (d) obtained by irradiating the *E*-form with 360 nm light for 3 h.

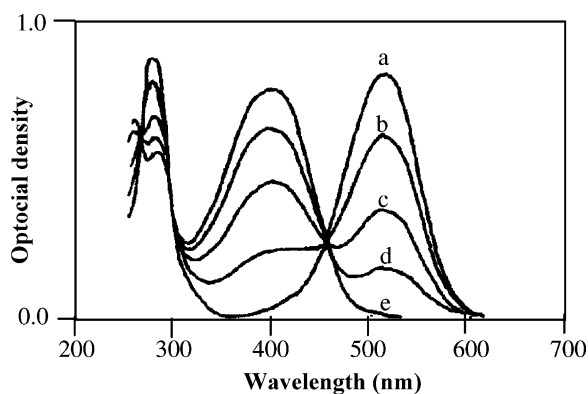


Fig. 5. Absorption spectra change of **1** *C*-form in acetonitrile under irradiation with $\lambda > 530$ nm light: (a) initial *C*-form; (b–e) after 0.5, 1.3, 2.5, and 6 min irradiation, respectively.

Fig. 6 shows the absorption spectra changes, induced in **2** *E*-form in acetonitrile solution by 390 nm excitation. In parallel with the ring-closure process, photoisomerization between *E*- and *Z*-forms may also take place. However, the introduction of a methyl group significantly decreases the efficiency of *E*–*Z* isomerization, that does not compete with the ring-closure reaction. The observation of the isosbestic points in Fig. 6 supports this assumption. Unfortunately, the introduction of methyl group does not block the *E*–*Z* isomerization completely. After a careful investigation of the coloration process, we have found that about 90% of the original colorless form could be transferred very easily to the colored form, but it requires a very long time, 3 h, to transfer the remained 10%, to the *C*-form. We evaporated the solvent and subsequently measured the proton NMR spectra at this stage of the reaction (see Fig. 7). The NMR spectra show only the presence of the *C*-form and 10% of the *Z*-form in the mixture. Since the transformation of *E* to *Z* is not efficient, we may assume that the reverse process, *Z* to

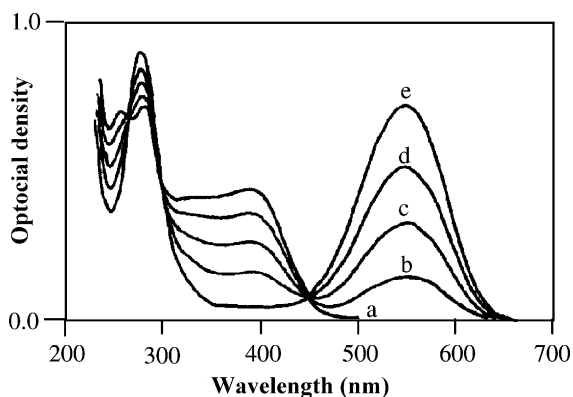


Fig. 6. Absorption spectra change of **2** *E*-form in acetonitrile under irradiation with 390 nm light: (a) initial *E*-form; (b–e) after 25, 40 s, 1.0, and 6.0 min irradiation, respectively.

E has also low efficiency. Therefore, in the coloration process, a small amount of *Z*-form, which is generated from the *E*-form, was accumulated. It should be mentioned here, that similar to **1** *Z*-form, excitation with 390 nm light of the solution of pure **2** *Z*-form also generates the colored form

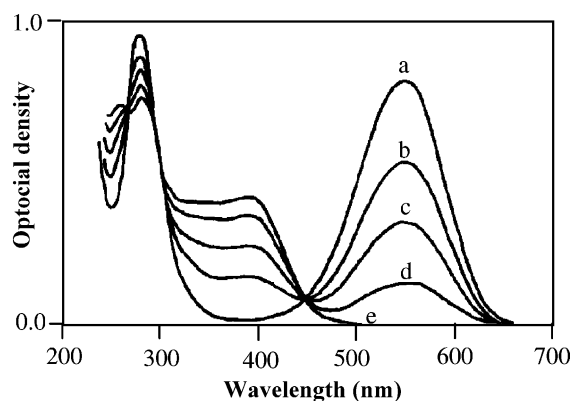


Fig. 8. Absorption spectra change of **2** *C*-form in acetonitrile under irradiation with $\lambda = 550$ nm light: (a) initial *C*-form; (b–e) after 1.3, 2.7, 4.7, and 10 min irradiation respectively.

via formation of *E*-form as an intermediate, however with very low quantum efficiency. The colored form of **2** can revert back to the open-ring, bleached form, by excitation with $\lambda = 550$ nm. During the bleaching process only formation of the *E*-form was observed (see Fig. 8), which is the

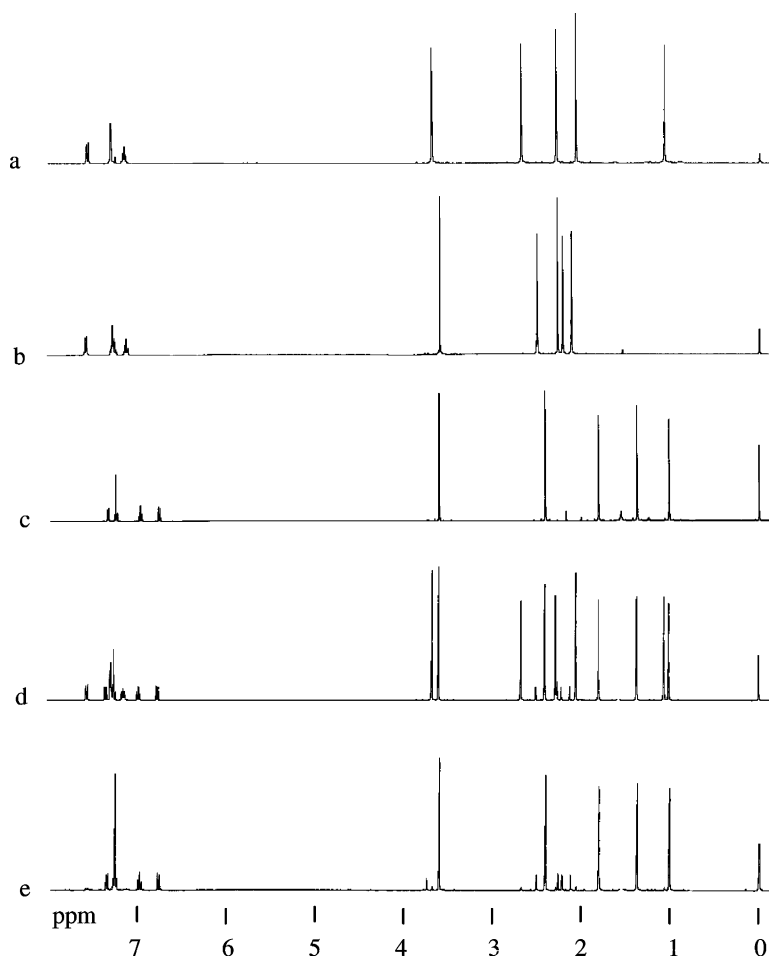


Fig. 7. The NMR spectra of **2**: (a) pure *E*-form, (b) pure *Z*-form, (c) pure *C*-form, (d) mixture of isomers obtained by irradiation of the *E*-form with 390 nm light for 100 s, and (e) photostationary state isomers obtained from the irradiation the *E*-form with 390 nm light for 16 min.

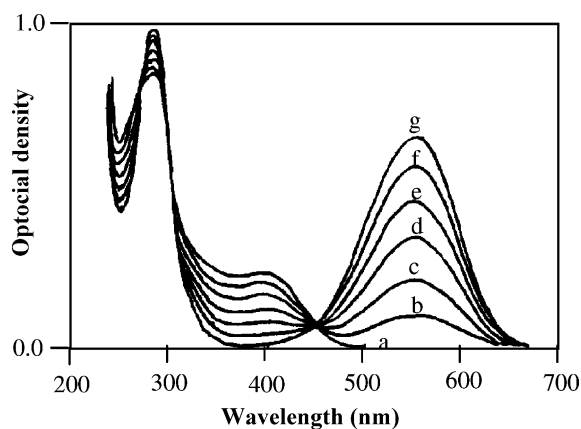


Fig. 9. Absorption spectra change of **3** *E*-form in acetonitrile under irradiation with 390 nm light: (a) initial *E*-form; (b–g) after 20 and 45 s, 1.4, 2.2, 3.3, and 6.5 min irradiation, respectively.

favorite configuration for the ring-closure and ring-opening processes.

Fig. 9 shows the absorption spectra changes, induced by 390 nm light excitation of **3** *E*-form in acetonitrile solution. The isosbestic points indicate that there is only one product

formed in the photoreaction. Unlike **2**, the *E*-form of **3** could be transferred to the colored *C*-form almost quantitatively (98%) by excitation with 390 nm light. This suggests that the introduction of highly steric isopropyl group blocks the *E*–*Z* isomerization more efficiently than the methyl group. Fig. 10 shows the changes in the proton NMR spectra of **3** during UV irradiation. The pure *E*-form of **3** was irradiated with 390 nm light for 100 s. Unlike **2**, for this irradiation time the NMR spectra do not show any significant peaks of the *Z*-form, but only the initial *E*-form and the photo-product *C*-form. When the irradiation time was extended to 16 min and the photostationary state was reached, nearly pure *C*-form was produced. This result confirms that the isopropyl group at the 1'-position of the indolylmethene moiety can efficiently block the undesired *E*–*Z* isomerization.

The bleaching process of **3** *C*-form, is similar to the one for **1** and **2** that is shown in Fig. 11. The **3** *E*-form was collected quantitatively when the colored **3** *C*-form was irradiated with 550 nm light, where the *E*-form does not absorb. Table 2 lists the quantum yields for the ring-closure (coloration) and ring-opening (bleaching) processes of **1**–**3**, in polar acetonitrile and nonpolar hexane, solutions. These data show that in polar acetonitrile the quantum yield of *E*

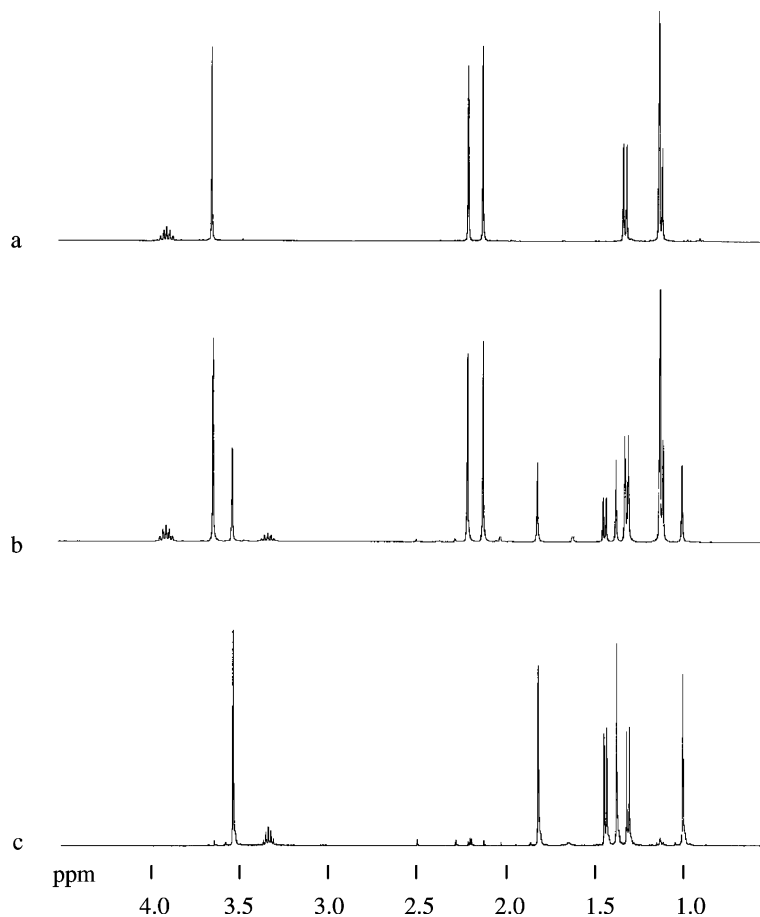


Fig. 10. The NMR spectra of **3**: (a) pure *E*-form, (b) mixture of isomers obtained by irradiation of the *E* form with 390 nm light for 100 s, and (c) photostationary state isomers obtained after irradiation of the *E*-form with 390 nm light for 16 min.

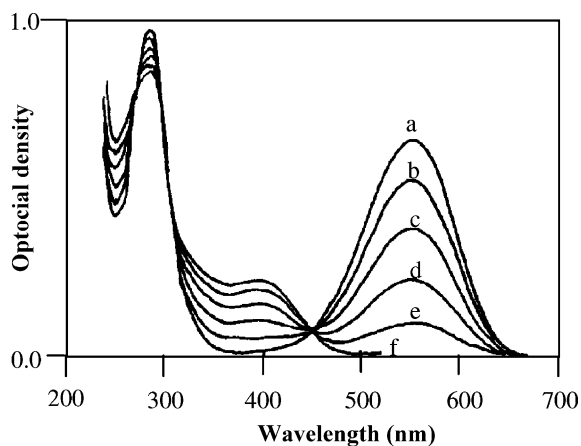


Fig. 11. Absorption spectra change of **3** C-form in acetonitrile under irradiation with 550 nm light: (a) initial C-form; (b–f) after 30 s, 1.2, 2.3, 3.9, and 9 min irradiation, respectively.

to C conversion is increased from 0.12 ($R = H$) to 0.28 ($R = i\text{-Pr}$). The steric groups at the 1'-position of the indolylmethylene moiety prevent the $E\text{-}Z$ isomerization and therefore increase the efficiency of the cyclization reaction. In nonpolar hexane, the coloration quantum yield for **3** is slightly higher than for **2**, which corresponds to an increase in the substituent group R steric effect. However, we find that the quantum yield of **1** in hexane is higher than **2** and **3**.

We have also investigated the photoreaction of **1–3** in nonpolar hexane solution by means of proton NMR. The same amount of **1–3**, E -forms, were dissolved in hexane and irradiated with 390 nm light for 1.6 min under the same conditions. The proton NMR spectra were measured after removing of the solvent. The proton integration data indicate that after irradiation of the E forms the ratio of $E:Z:C$ isomers is 42:28:30 for **1**, 64:11:25 for **2** and 66:3:34 for **3**. These results are in agreement with the data measured in acetonitrile solution and support our assumption that the steric hindrance decreases the $E\text{-}Z$ isomerization.

2.4. Fluorescence quantum yields

The closed-ring forms of fulgides **1–3** emit red fluorescence when excited with visible light. To confirm that fluorescence is emitted by the colored forms of fulgides

Table 2
Quantum yields of photocoloration and photobleaching of **1–3** in various solvents^a

R	$\phi_{E\text{-}C}$		$\phi_{C\text{-}E}$	
	Acetonitrile	Hexane	Acetonitrile	Hexane
H (1)	0.12	0.26	0.018	0.32
Me (2)	0.21	0.17	0.061	0.19
<i>i</i> -Pr (3)	0.28	0.23	0.053	0.20

^a $\phi_{E\text{-}C}$: quantum yield of coloration process; $\phi_{C\text{-}E}$: quantum yield of bleaching process.

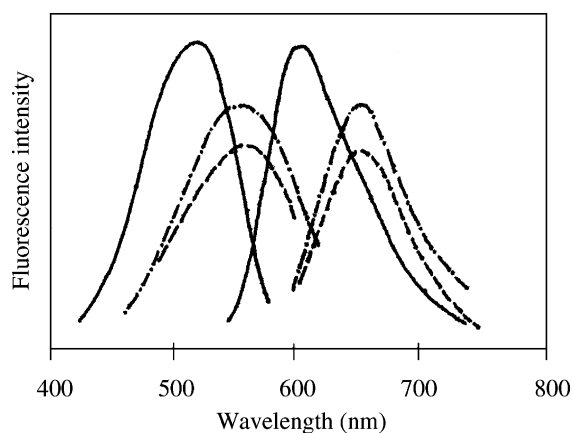


Fig. 12. Fluorescence and fluorescence excitation spectra of fulgides C-form in dichloroethane: **1** (—); **2** (---); **3** (- -).

rather than impurities or other species, we have measured the fluorescence intensity change during continuous bleaching/coloration cycles. The data show that the fluorescence intensity decreases proportionally with the bleaching of the colored form of the fulgides. When the solution was completely bleached with light, $\lambda = 550$ nm, i.e. the absorption band of the C-form completely disappeared and no fluorescence was detected. The fluorescence appeared again and increased at the same rate as the rate of the growth of the C-form. These data verify that the observed fluorescence is emitted by the colored form of fulgides, and not by impurities or decomposition products. Fig. 12 shows the fluorescence and fluorescence excitation spectra of fulgides **1–3** colored forms in dichloroethane.

Table 3, shows the fluorescence maxima and quantum yields for the colored forms of fulgides **1–3**. The data indicate that the fluorescence maxima and quantum yields depend on substituents and solvent polarity. Methyl and isopropyl groups at the 1'-position of the indolylmethylene moiety, we found to decrease the fluorescence quantum yields. This may be due to the increase of radiationless process efficiency caused by changes brought by the vibrational level density of substituted molecules.

In nonpolar hexane, the fluorescence of **2** and **3** was not detected. The decrease of fluorescence quantum yields in nonpolar hexane may be attributed to the increase in efficiencies of the competing processes such as photochemical reaction and radiationless deactivation.

2.5. Thermal stability and fatigue resistance

Thermal stability of both isomeric forms is a required property for any photochromic material that is to be used in information storage, optical electronic switching or other optical devices. We have measured the thermal stability of the E - and C -forms of the synthesized fulgides **1–3**. We found that all of the isomeric forms of these fulgides have excellent long-term thermal stability at room temperature. Pure

Table 3
Fluorescence quantum yield of **1–3** C-form in various solvents

R	Acetonitrile		1,2-Dichloroethane		Hexane	
	λ_{max} (nm) (FL)	ϕ FL	λ_{max} (nm) (FL)	ϕ FL	λ_{max} (nm) (FL)	ϕ FL
H (1 C)	618	3.3×10^{-2}	604	7.4×10^{-2}	536 nm	3×10^{-4}
Me (2 C)	662	0.4×10^{-2}	653	0.4×10^{-2}	–	0
<i>i</i> -Pr (3 C)	668	0.1×10^{-2}	655	0.1×10^{-2}	–	0

E-, and *C*-forms were dissolved in chloroform-*d*, hexane and acetonitrile and kept in the dark at room temperature for over 1 month. The NMR and UV–VIS spectra, measured before and after this testing time period, were the same and show the presence of only the original molecules in solutions, and no thermal reaction products were detected.

The thermal stability of **1–3**, *E*-forms was also measured up to the melting point temperatures. It was found that 20% of the **2** and **3** and less than 1% of **1** *E*-form were transferred to the corresponding colored *C*-forms, when crystals of the *E*-forms of these fulgides were melted and solidified. The *C*-forms appear to be stable even at the melting point temperatures and no formation of *E*-forms was detected when pure crystals of *C*-forms were melted and solidified.

To characterize the fatigue resistance of the synthesized fulgides, the decrease of the original concentration of the photochrome was measured during the sequences of ring-closing/ring-opening (coloration–bleaching) cycles. During coloration more than 80% of the *E*-form was transferred to the *C*-form by excitation with 360 nm light and then completely converted back to the *E*-form by excitation with 530 nm light. Fig. 13 shows the ratio of the *C*-form concentration to its initial concentration in acetonitrile solution, plotted as a function of number of coloration/bleaching cycles. These data show that fatigue resistance decreases in the order **1** > **2** > **3**. The detail mechanism of the photochemical decomposition of fulgides is complicated and we

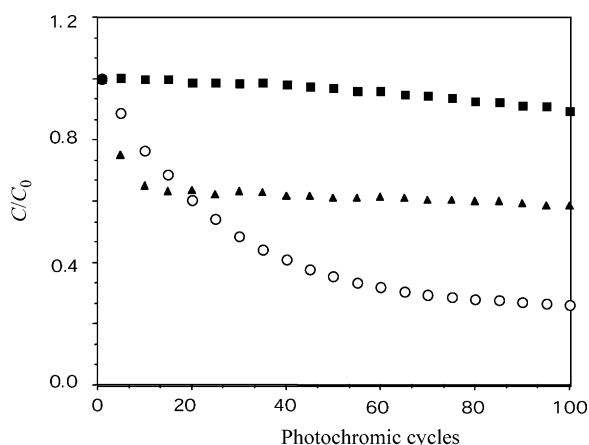


Fig. 13. Fatigue resistance of fulgide **1** (■), **2** (▲), and **3** (○) in acetonitrile solution. *C* is the concentration of the colored form after a number of coloration/bleaching cycles, *C*₀ is the initial concentration of the colored form.

were not able to separate and identify all the decomposition products. However, it has been assumed that the decomposition process may involve the hydrogen atom abstraction by the carbonyl oxygen in the excited state from the neighboring alkyl groups [26]. Our results support this assumption because the isopropyl is a hydrogen rich group and, therefore, may increase the efficiency of the intramolecular hydrogen abstraction.

3. Experimental section

3.1. General

Fulgides **1–3** were obtained directly by Stobbe condensation of the corresponding 2-acyl-1,3-dimethylindole derivatives with diethyl isopropylidene succinate. The product was the mixture of the *E* and *Z* isomers for **1**, and **2** and the pure *E* isomer for **3**. The isomers were separated and purified by column chromatography and recrystallization. The pure colored **1–3** *C*-forms of these fulgides were prepared by irradiating of acetonitrile solutions of *E*-forms with 360 nm light, followed by removing of the solvent under reduced pressure and recrystallization. The structure and purity of the obtained compounds were confirmed by NMR, MS and elemental analysis. All solvents were HPLC grade or spectral grade and were used without further purification. All spectra and quantum yields were measured in 1 cm quartz cell at room temperature. The UV–VIS absorption and fluorescence spectra were recorded by means of Shimadzu UV 160 spectrophotometer and Shimadzu RF 5000U spectrofluorophotometer. ¹H NMR spectra were obtained by means of QE 300 MHz or DRX 400 MHz NMR spectrometer (tetramethylsilane the internal standard). MS spectra were obtained using VG Analytical 7070E mass spectrometer.

Photoirradiation was carried out using a 150 W Xenon arc lamp (Oriol). Light of the appropriate wavelength was selected by using either a monochromator or a cut off optical filter (Hoya). The quantum yields of the ring-closing (coloration) and ring-opening (bleaching) photoreactions and the fluorescence quantum yields were determined as described [17].

3.2. Material synthesis

The 1,3-dimethyl-indole-2-carbaldehyde and fulgide **1** *E*- and *Z*- forms were prepared as described in [14,21,27].

3.2.1. 2-Acetyl-1,3-dimethylindole (7)

To a solution of 1,3-dimethylindole (10.2 g) in the mixture of acetic acid (40 ml) and acetic anhydride (16 ml), 3 ml of boron trifluoride ether was added dropwise in 3 min at room temperature. The mixture was stirred for 10 min, and then 150 ml of water was added. White precipitate (yield 98%) was collected after filtration, washed with water and dried. The product was recrystallized from ethanol–water solution. **7**: mp 83.5–84.5 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ : 2.59 (s, 3H), 2.60 (s, 3H), 3.94 (s, 3H), 7.11–7.67 (m, 4H); ^{13}C NMR (400 MHz, CDCl_3) δ : 11.8, 31.5, 32.5, 110.0, 119.4, 119.7, 120.8, 125.9, 127.1, 133.5, 138.8, 192.3; MS (CI) m/z : 187.

3.2.2. 1,3-Dimethyl-2-isobutyrylindole (8)

To a solution of 1,3-dimethylindole (6.0 g) in the mixture of isobutyric acid (25 ml) and isobutyric anhydride (10 ml), 4 ml of boron trifluoride ether was added dropwise at room temperature and stirred for 10 min. After that the saturated aqueous solution of sodium carbonate was slowly added to neutralize the acid and decompose the anhydride. Light yellow precipitate was collected after filtration and washing with water. The product was recrystallized from ethanol–water solution to yield white crystals (yield 95%). Here, **8**: mp 57.5–58.5 °C; ^1H NMR (300 MHz, CDCl_3 , TMS) δ : 1.22 (s, 3H), 1.23 (s, 3H), 2.56 (s, 3H), 3.83 (s, 3H), 3.44 (m, H), 7.11–7.62 (m, 4H); ^{13}C NMR (400 MHz, CDCl_3) δ : 11.1, 18.8, 32.3, 38.9, 110.0, 117.1, 119.7, 120.7, 125.4, 127.3, 133.4, 138.8, 200.4; MS (CI) m/z : 215. Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}$: C, 78.09; H, 7.97; N, 6.51. Found: C, 78.13; H, 7.87; N, 6.43.

3.2.3. 2-[1-(1,3-Dimethyl-2-indolyl)ethylidene]-3-isopropylidene succinic anhydride (2)

A flask with a solution of diethyl isopropylidene succinate (4.5 g, 21 mmol) in anhydrous THF (15 ml) was cooled down to -78°C in a dry-ice–acetone bath, then LDA (11 ml, 2 M, 22 mmol) was added dropwise in 30 min under argon. The mixture was stirred for 1 h at this temperature and 1,3-dimethyl-2-acetylindole (4.0 g, 21 mmol) in THF (10 ml) was added dropwise. Then the mixture was warmed up to room temperature and stirred over night. The reaction mixture was quenched with water, acidified with diluted HCl (1 M), extracted with ether (3×35 ml) and extract was dried over magnesium sulfate. The solvent was then removed with a rotatory evaporator. The crude half ester was dissolved in 100 ml of 10% KOH–EtOH solution and refluxed for 16 h. The ethanol was evaporated and water (100 ml) was added. The unreacted starting material 1,3-dimethyl-2-acetylindole (2.1 g) was recovered after filtration. The solution was acidified with HCl (5 M) to pH = 1 and yellow powder of crude diacid (3.1 g) was collected. The obtained crude diacid was dissolved in anhydrous THF (80 ml), the solution was stirred with DCC (1.9 g) at room temperature for 2.5 h. After removal of the THF, the residue was purified

using flash column chromatography on silica gel (chloroform) and recrystallized (1,2-dichloroethane–hexane). Here, (*E*)-**2** (0.28 g, 4.2%, from **7**): mp 176–178.5 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ : 1.07 (s, 3H), 2.06 (s, 3H), 2.28 (s, 3H), 2.67 (s, 3H), 3.68 (s, 3H), 7.13–7.56 (m, 4H); ^{13}C NMR (400 MHz, CDCl_3) δ : 10.5, 23.2, 23.5, 26.0, 32.0, 109.5, 111.5, 120.0, 120.1, 120.7, 123.6, 123.8, 127.8, 138.1, 138.9, 143.2, 157.2, 163.2, 163.8, HRMS (CI): Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: m/z 309.1365 (M^+); Found: 309.1371; IR (KBr) 1754, 1804 cm^{-1} . Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.75; H, 6.20; N, 4.53. Found: C, 73.82; H, 6.19; N, 4.50.

Here, (*Z*)-**2** (0.82 g, 12.4%, from **7**): mp 213–215 °C (lit. [27] 212–214 °C); ^1H NMR (400 MHz, CDCl_3 , TMS) δ : 2.10 (s, 3H), 2.20 (s, 3H), 2.26 (s, 3H), 2.48 (s, 3H), 3.58 (s, 3H), 7.10–7.57 (m, 4H); ^{13}C NMR (400 MHz, CDCl_3) δ : 10.5, 23.2, 23.5, 26.0, 32.0, 109.5, 111.5, 120.0, 120.1, 120.7, 123.6, 123.8, 127.8, 138.1, 138.9, 143.2, 157.2, 163.2, 163.8; HRMS (CI): Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: m/z 309.1365 (M^+). Found: 309.1372; IR (KBr) 1767, 1813 cm^{-1} . Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.75; H, 6.20; N, 4.53. Found: C, 73.69; H, 6.23; N, 4.50.

3.2.4. 2-[1-(1,3-Dimethyl-2-indolyl)isobutylidene]-3-isopropylidene succinic anhydride (3)

A flask with a solution of diethyl isopropylidene succinate (5.0 g, 23.4 mmol) in anhydrous THF (15 ml) was cooled down to -78°C in a dry-ice–acetone bath, LDA (11.8 ml, 2 M, 23.6 mmol) was added dropwise in 30 min under argon. The mixture was stirred for 1 h, then 1,3-dimethyl-2-isobutyrylindole (5.0 g) in THF (10 ml) was added through the dropping funnel. After that the mixture was warmed up to room temperature and stirred for 24 h. The reaction mixture was quenched with water, acidified with diluted HCl (1 M), extracted with ether (3×35 ml) and extract was dried over magnesium sulfate. The solvent was then removed with a rotatory evaporator. The obtained crude half ester was dissolved in 100 ml of 10% KOH–EtOH solution and refluxed for 14 h, then ethanol was evaporated and water (100 ml) was added. The unreacted 1,3-dimethyl-2-isobutyrylindole (3.1 g) was recovered after filtration. The solution was acidified with HCl (5 M) to pH = 1 to yield yellow crude diacids (2.9 g). The obtained crude diacid was dissolved in acetyl chloride (30 ml) and stirred at room temperature for 2.5 h. After the removal of acetyl chloride, the residue was purified by flash column chromatography (silica gel, chloroform) and recrystallization (1,2-dichloroethane–hexane). (*E*)-**3** (yield, 8%, from **8**): mp 126.5–127.5 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ : 1.09 (d, 3H, $J = 7.41$ Hz), 1.29 (d, 3H, $J = 7.06$ Hz), 2.10 (s, 3H), 2.18 (s, 3H), 3.64 (s, 3H), 3.86 (dt, H, $J = 7.05$, 7.04 Hz), 7.12–7.56 (m, 4H); ^{13}C NMR (400 MHz, CDCl_3) δ : 10.5, 23.2, 23.5, 26.0, 32.0, 109.5, 111.5, 120.0, 120.1, 120.7, 123.6, 123.8, 127.8, 138.1, 138.9, 143.2, 157.2, 163.2, 163.8, HRMS (CI): Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_3$: m/z 337.1678 (M^+); Found: 337.1680; IR (KBr) 1767, 1810,

cm^{-1} . Anal. Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_3$: C, 74.74; H, 6.88; N, 4.15. Found: C, 73.73; H, 6.76; N, 4.15.

4. Conclusion

Substituted 2-indolyl fulgides with methyl and isopropyl groups at the 1'-position of the indolylmethylene moiety were synthesized. Steric effects due to the introduced groups on the spectroscopic and photochromic properties, were measured and discussed. The experimental results show that the methyl group at the 1'-position of the indolylmethylene moiety decreases the quantum efficiency of the *E-Z* isomerization to a certain degree while the introduction of the isopropyl group at the same position prevents the *E-Z* isomerization almost completely. In comparison with the non-substituted fulgide, the coloration quantum yield of the fulgides with steric bulkiness at the 1'-position of the indolylmethylene moiety increases, while the fluorescence quantum yield decreases. The thermal stability of these fulgides and their fatigue resistance were also determined. Methyl and isopropyl groups at the 1'-position of the indolylmethylene moiety were found to decrease the fatigue resistance of the fulgide.

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