



Solvent and ring substitution effect on the photochromic behavior of fluorescent 2-indolylfulgide derivatives

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Abstract

A new class of thermally stable and fatigue resistant fluorescent photochromic 2-indolylfulgide derivatives have been synthesized. The absorption spectra, quantum yields of the photochemical reaction and fluorescence of these fulgides were measured and the solvent polarity dependent properties were also determined. Polar solvents were found to shift the absorption spectra of colored form to the longer wavelengths. The quantum yields of both coloration and bleaching process increased in nonpolar solvents, while the fluorescence quantum yields decreased. Electron donor substituents, at the 5-position of the indole ring shift the absorption spectra to longer wavelengths of both open and closed forms. The experimental data clearly show that substitution at the 5-position of the indole ring does not affect fatigue resistance. The solvent may affect the cycle fatigue. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Photochromism, one of the most striking phenomena of photochemistry, which involves light induced reversible transformation of a molecule between two states with differential distinguishable absorption spectra, has received great attention in recent years [1,2]. One reason for that is the possibility that rewritable optical memories may use organic photochromic compounds as media for high capacity ultra fast computing storage devices [3]. The bottleneck, which restrains the practical use of such devices, is the synthesis of suitable materials. Unfortunately, no material has been found, so far, which satisfies all the requirements needed for high density information storage. Among the well known organic photochromic compounds, spiropyrans and spirooxazines have been widely studied, however, even though the efficiency of their photochromic process is acceptable, the low and unacceptable thermal stability of the colored forms, which is very pivotal requirement for long-term information storage, restrained their application. In the 1980s, photochromic heterocyclic fulgides [4,5] and heterocyclic diarylethenes [6] were developed. Those compounds show excellent thermal stability in both their colorless and colored forms, high photochemical reaction efficiency and high fatigue resistance to repeated coloration/bleaching cycles.

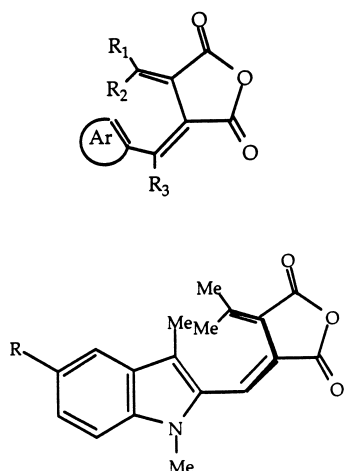
Such materials therefore could be thought as promising candidates for erasable optical memory devices. However, most 3D optical memory devices access the information stored by means of the fluorescence emitted by the written medium [7]. It is therefore mandatory that the colored form of the photochromic materials, the written form, must fluoresce strongly. This important property has not been studied previously, because no fluorescent fulgides and diarylethenes have been reported.

We report in this paper some photochromic fulgides, that we have made which have high reversible photochemical reaction efficiency, long-term thermal stability and the colored form also fluoresces when irradiated with visible light. In a previous paper we have reported the synthesis of these photochromic fluorescent 2-indolylfulgides [8], in this paper we present the effect of solvent polarity and ring substitution on the photochromic behavior and spectroscopic properties of these fulgides.

2. Results and discussion

Fulgides, first investigated by Stobbe, are derivatives of dimethylene succinic anhydride [9]. For photochromic fulgides, at least one aryl group (usually heterocyclic aryl group) attached to the methylene form a $4n+2$ system (see Scheme 1(a)). When the open-ring form (known as colorless form) of these fulgides is irradiated with UV light,

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Scheme 1. R=OCH₃(a), CH₃(b), H(c), Cl(d), F(e)

a conrotatory ring-closure reaction occurred according to the Woodward–Hoffman selection rules (see Scheme 2) [10]. This results in the formation of a cyclized structure (known as colored form or C-form) whose absorption spectrum is red shifted to the visible region.

2.1. UV–Vis absorption spectra of E, Z and C forms

Table 1 lists the absorption maxima of the E, Z and C isomers of fulgide a–e, in various solvents. The electronic absorption spectra of E-fulgides, at 385–408 nm, were found not to be affected strongly by solvent. Substitutions of electron donor groups at the 5-position of the indole ring were found to shift the maximum absorption to longer wavelengths, while chloro and fluoro substituents at the same position shift the maximum absorption to shorter wavelengths, compared to 5-H fulgide. The maximum absorption of

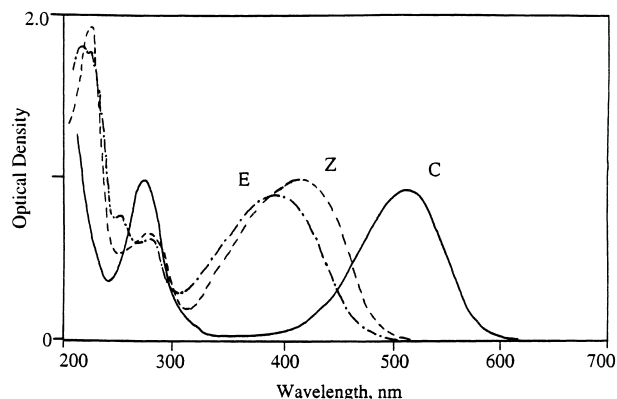
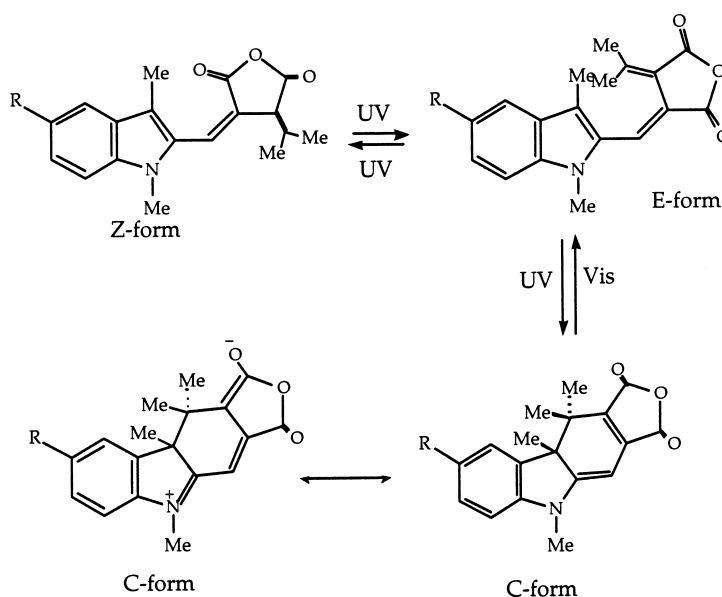


Fig. 1. Absorption spectra of 1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride in acetonitrile: (· · ·) E-form, (– – –) Z-form and (—) C-form.

the Z-forms is in the region of 405–429 nm, which is red shifted by about 20 nm compared to the corresponding E-forms. The X-ray data results show, in the open-ring fulgide form, the indole and anhydride components are not in a planar form, and consequently, absorb in the blue region (390 nm), due to low conjugation between indole and anhydride parts. Upon irradiation with UV light, a near planar closed-ring structure was formed, resulting in a longer conjugated system, which shifted the absorption to longer wavelengths. Longer wavelength shift in polar solvent and a high absorption extinction coefficient support the assignment of this E, Z and C-forms absorption to a π – π^* transition [11]. Fig. 1 shows the E-form, Z-form and C-form absorption spectra of 1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride in acetonitrile. The long wavelength absorption maxima and extinction coefficients of these fulgides in different solvents are listed in Table 1.



Scheme 2.

Table 1
Maximum absorption of 2-indolylfulgides in different solvents

Solvent	Isomer	5-OMe λ_{\max} (nm) (ϵ_{\max})	5-Me λ_{\max} (nm) (ϵ_{\max})	5-H λ_{\max} (nm) (ϵ_{\max})	5-Cl λ_{\max} (nm) (ϵ_{\max})	5-F λ_{\max} (nm) (ϵ_{\max})
Acetonitrile	E	406 (18100)	399 (16800)	395 (13400)	386 (15400)	386 (14700)
	Z	419 (20300)	–	419 (16000)	405 (15300)	–
	C	531 (14900)	523 (15900)	514 (14100)	510 (14400)	513 (14100)
Methanol	E	408 (18000)	403 (17100)	395 (13300)	389 (15200)	388 (14400)
	Z	426 (22300)	–	423 (17000)	409 (16400)	–
	C	530 (14500)	522 (15400)	512 (13700)	509 (13800)	512 (13600)
1,2-Dichloro ethane	E	411 (18900)	407 (17700)	403 (14100)	394 (15700)	393 (15100)
	Z	429 (21300)	–	429 (16900)	415 (16200)	–
	C	531 (15400)	524 (16100)	515 (14100)	512 (12900)	513 (14100)
Hexane	E	405 (18700)	400 (17200)	398 (13500)	387 (15800)	385 (14600)
	Z	428 (16400)	–	426 (18700)	416 (18800)	–
	C	490 (14100)	484 (14800)	475 (13300)	471 (13500)	471 (13400)

The maximum absorption of the C-form, was found to be located in the 470–530 nm region, which is red shifted by about 120 nm compared to the corresponding open-ring forms. Polar solvents strongly affect the absorption maximum of the C-form. This suggests that in the excited state, there is a large dipole molecule formed which is stabilized by polar solvents.

2.2. Photoreaction quantum yield of 2-indolylfulgide

When the synthesized a–e open-ring form fulgides, were illuminated with UV light, they undergo photoinduced electrocyclic reaction which generates the closed-ring structure C (see Scheme 2). The initially light yellow colored solutions of the a–e open-ring form became red after excitation with 360 nm light. Fig. 2 shows the absorption spectra changes, of (E)-1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride in acetonitrile, induced by

360 nm light. In parallel with the ring-closing process, photoisomerization between E- and Z-forms also takes place, which is evident by the 20 nm shift in the isobestic point (see Fig. 2). We have also observed the formation of the Z-form in the NMR spectra when pure E-form was irradiated with UV light. Because of more than 100 nm Stokes shift of the absorption spectra of E and C and very low absorption of C-form at 360 nm compared to that of E-form, we were able to convert the open form, almost quantitatively, to the cyclized colored form by 360 nm excitation of the E-form in acetonitrile solvent. The colored form can be reversed back to the open-ring, bleached form, by excitation with $\lambda > 530$ nm (with filter which cut below 530 nm). During the bleaching process only the formation of the E-form was observed (see Fig. 3), which is the favorite configuration for the cyclization process. It should be noted that, because the absorption spectra of the E- and Z-forms are only slightly different, photoexcitation in the 360 nm

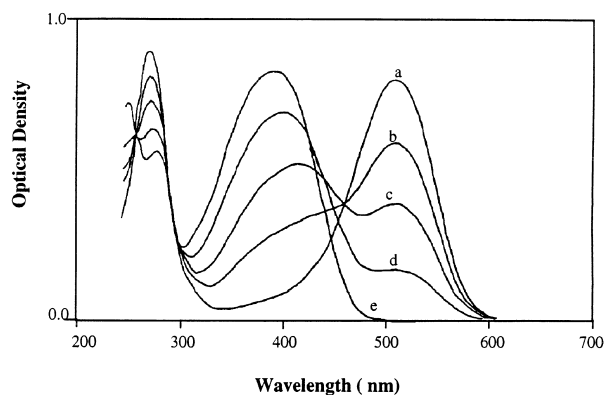


Fig. 2. Absorbance change, ΔA , vs. λ for (E)-1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride in acetonitrile, irradiation with 360 nm light: (a),(b),(c),(d), after 4.8 min, 2.8 min, 1.2 min and 25 s irradiation, respectively; (e), initial E-form.

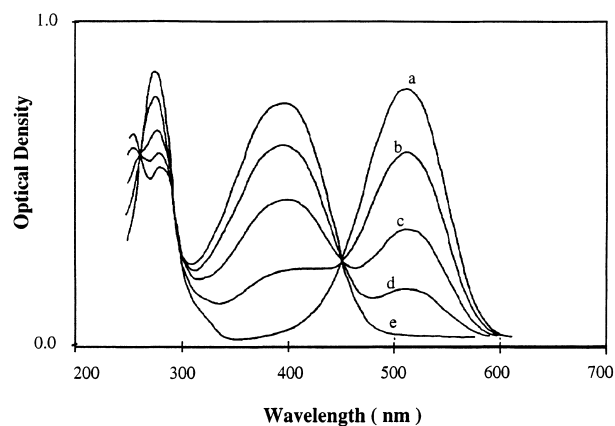


Fig. 3. Change in optical density, ΔA , vs. wavelength, λ , for (C)-1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride in acetonitrile irradiation with $\lambda > 530$ nm light: (a) initial colored form; (b), (c), (d), and (e), after 0.5, 1.3, 2.5 and 6 min irradiation, respectively.

Table 2
Quantum yield of photocoloration and photobleaching of 2-indolylfulgides in different solvents

Substituent	ϕ_{E-C} ($\lambda_{EX}=350$ nm)			ϕ_{C-E} ($\lambda_{EX}=495$ nm)		
	Acetonitrile	Dichloroethane	Hexane	Acetonitrile	Dichloroethane	Hexane
5-H	0.12	0.11	0.26	0.018	0.16	0.32
5-OMe	0.093	0.063	0.16	0.00007	0.003	0.33
5-Me	0.11	0.091	0.22	0.0011	0.015	0.29
5-Cl	0.12	0.11	0.24	0.040	0.19	0.30
5-F	0.13	0.11	0.24	0.022	0.15	0.33

region, where both forms have strong absorption, leads to the formation of a photoequilibrium mixture between these two forms. This causes spectral broadening, therefore when a solution of the pure Z-form is excited with 360 nm light, it also generates the colored form but with a low quantum efficiency. Most probably this Z to colored form reaction proceeds via the formation of E-form, as intermediate which in turn decays into the colored form.

Table 2 lists the quantum yields of ring-closing (coloration) and ring-opening (bleaching) of 2-indolylfulgides in various solvents. These data show that, in polar solvents, such as acetonitrile, the quantum yield of E to C is about 0.1, while in nonpolar, hexane solvents, the quantum yield is increased by a factor of two compared to polar solvents. The quantum yield for the coloration processes is about the same as that of furylfulgide [12,13] and thienyl fulgide [14] but higher than that of 3-indolylfulgide [15]. According to our experimental results, the quantum yield of the bleaching process C to E, strongly depends on the polarity of the solvents. The fact that low quantum yield were observed in polar solvents may be explained by the existence of strong interaction between the charge separated excited state of the fulgide molecule and the polar solvents, which may have raised the reaction activation energy and therefore lower the transformation rate of the process. Electron donor substituent groups, such as methoxyl group, were found to stabilize strongly the colored form, and consequently reduce the bleaching quantum yield. This phenomenon was also observed with 3-indolylfulgides [15]. However, no photochromic reactions were detected when 2-indolylfulgide crystals were used instead of solution.

Table 3 shows the experimental quantum yields of the E-Z isomerization for three 2-indolylfulgides in polar acetonitrile and nonpolar hexane solvents. It is evident from the

Table 3
Quantum yield of 2-indolylfulgides E-Z isomerization

Substituent	ϕ_{E-Z} ($\lambda_{EX}=350$ nm)		ϕ_{Z-E} ($\lambda_{EX}=350$ nm)	
	Acetonitrile	Hexane	Acetonitrile	Hexane
5-H	0.208	0.204	0.107	0.190
5-OMe	0.348	0.639	0.275	0.889
5-Cl	0.283	0.697	0.179	0.328

data that the quantum yield of the E-Z isomerization process, which competes with the coloration, has practically the same value as that of the coloration. We believe that decreasing the rate of the E-Z isomerization will increase the coloration quantum yield.

2.3. Thermal stability and fatigue resistance

Thermal stability of the media plays an important role in long-term information storage and electronic switching devices. Because of the possibility that these materials may be potential candidates as storage media, we measured the thermal stability of E, Z and C-forms of these fulgides. Our data show that all the isomeric forms of fulgides, a–e, have excellent long term, room temperature, thermal stability. No changes, owing to temperature, were detected by means of NMR and UV–Vis absorption spectroscopy, when pure E-, Z- and C-forms were dissolved in chloroform-d₃, hexane and acetonitrile solvents separately and kept in dark at room temperature for over one month. This data suggests, strongly, that no thermal decomposition or other thermal reactions occurred at room temperature during this long test-period. We also investigated the fatigue resistance of our fulgides as a function of coloration/bleaching cycles. These data are shown in Table 4 and Fig. 4. Table 4 shows the ratio of the nondecomposed fulgides to original forms after 100 complete coloration/bleaching cycles in acetonitrile, MMA, 1,2-dichloroethane and hexane. The experimental data clearly show that substitution at the 5-position of the indole ring does not affect fatigue resistance. The solvent may affect the cycle fatigue, but not to a great extent.

Table 4
The ratio of the nondecomposed fulgides to original forms after 100 complete coloration/bleaching cycles in various solvents

Substituent	C/C ₀ (%)			
	Acetonitrile	Dichloroethane	MMA	Hexane
5-OMe	–	–	91	–
5-Me	–	–	91	–
5-H	90	93	92	87
5-Cl	90	–	91	–
5-F	95	–	92	–

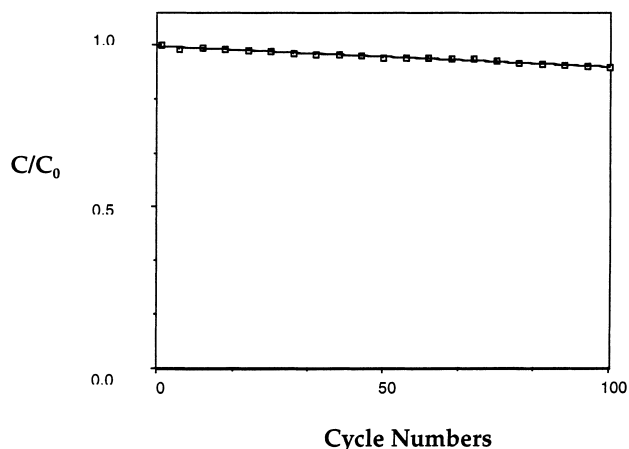


Fig. 4. Fatigue, defined as ratio of fulgide after 100 cycles to original, of 1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride in 1,2-dichloroethane, as a function of coloration/bleaching cycles.

2.4. Fluorescence quantum yield of 2-indolylfulgides

In contrast to the other previously investigated fulgides, the colored form C, of fulgides a–e, which we synthesized, emit fluorescence. The fluorescence of the C-form consists of a broad emission band with its maximum intensity in the range of 526–662 nm, which is in the sensitivity region of compact solid state detectors. We found that the wavelength maximum depends on the polarity of the solvent and substituent. To confirm, that the observed fluorescence is emitted by the colored forms of these fulgides rather than impurities or other species, we measured the fluorescence intensity change as a function of bleaching/coloration cycles. The data show that the fluorescence intensity decreases proportionally with the bleaching of the fulgides (see Fig. 5). When the solution was completely bleached, with light, $\lambda > 530$ nm, i.e. the absorption band of the C-form disappeared, 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 our statement that the fluorescence observed is due only to the colored form of fulgides, rather than any impurities or decomposition products. Table 5 shows the fluorescence quantum yield of the colored fulgides. The experimental data indicate that the quantum yield of the fluorescence depend on substituents and solvent polarity. When electron donor groups were

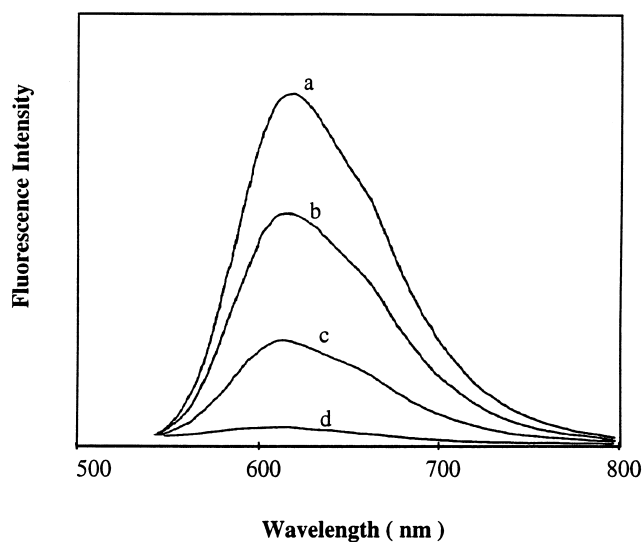


Fig. 5. Fluorescence intensity vs. λ for 1,3-dimethyl-2-indolylmethene-(isopropylidene) succinic anhydride, form C, in acetonitrile, excitation with $\lambda > 530$ nm light: (a) initial colored form; (b), (c), and (d), after 1, 2.5, and 8 min irradiation, respectively.

substituted at the 5-position of the indole ring, decrease in the fluorescence quantum efficiency was observed. In contrast, relatively high quantum yields were observed in polar solvents such as 1,2-dichloroethane as well as acetonitrile. The decrease of the quantum yields measured in nonpolar hexane may due to the increase in quantum yield of the photochemical reaction which compete with the fluorescence process. We have also investigated the possibility of the open E and Z fulgides for fluorescence, however, we were not able to detect any emission from either form. The relatively low quantum yields of both fluorescence and photoreaction of the colored 5-methoxy fulgide, are probably due to the highly efficient interconversion radiationless process.

3. Experimental

Fulgides a–e (Scheme 1(b)) E- and Z-forms were obtained directly by Stobbe condensation of the corresponding 1,3-dimethylindole-2-carboxaldehyde derivatives with diethyl isopropylidene succinate followed by column chromatogra-

Table 5
Fluorescence quantum yield of colored-2-indolylfulgides in various solvents

Substituent	Acetonitrile		Dichloroethane		Hexane	
	λ_{\max} (EM)	ϕ_{FL}	λ_{\max} (EM)	ϕ_{FL}	λ_{\max} (EM)	ϕ_{FL}
5-OMe	662 nm	0.0008	650 nm	0.0004	552 nm	–
5-Me	635 nm	–	–	–	536 nm	–
5-H	618 nm	0.033	604 nm	0.074	536 nm	0.0003
5-Cl	613 nm	0.03	602 nm	0.058	526 nm	–
5-F	616 nm	–	–	–	526 nm	–

phy purification and then recrystallization. The colored forms (C-form) of these fulgides were prepared by irradiating, with 360 nm light, the E-form fulgides in an acetonitrile solution and the subsequent removal of the solvent under reduced pressure. The structure and purity of the compounds obtained were ascertained by NMR, MS and elemental analysis. All the solvents were HPLC grade or spectral grade and were used without further purification. All spectra and quantum yields were measured in 1 cm quartz cells at room temperature. The UV–Vis absorption and fluorescence spectra were recorded on a Shimadzu UV 160 spectrophotometer and a Shimadzu RF 5000U spectrofluorophotometer, respectively.

Photoirradiation was carried out using a 150W Xenon arc lamp (Oriel). Light of the appropriate wavelength was selected by either a monochromator or a cut off optical filter. The quantum yields of the photochromic reaction, ring-closing (coloration) and ring-opening (bleaching), were determined by comparison with the photochromic reaction yield of (E)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidene succinic anhydride (Aberchrom 540) [13] in ethyl acetate. A mini magnetic stirring bar was used to mix the solution. The fluorescence quantum yield of the samples was determined by comparing the fluorescence intensity of our sample, with that of Rhodamin B in methanol solution which has a fluorescence quantum yield of 1.0.

4. Conclusion

A new class of thermally stable and fluorescing photochromic 2-indoly fulgide derivatives have been synthesized. The absorption and fluorescence spectra, the quantum yields of fluorescence and the photochemical reactions of these fulgides were measured. The solvent polarity dependent properties were also studied. Polar solvents shift the absorption and fluorescence spectra to longer wavelengths. The quantum yields of coloration and bleaching process were found to be increased in nonpolar solvents, while the

fluorescence quantum yields were decreased. Our experiments suggest that electron donor substituents at the 5-position of the indole ring, lead to longer wavelength absorption of both open and close forms. The stability of these fulgides as function of temperature and coloration/bleaching reversible cycles has also been determined.

Acknowledgements

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References

- [1] Proceedings of the Second International Symposium on Photochromism, FL, USA, September 1996, Molecular Crystals and Liquid Crystals Section A, vol. 297 and 298, 1997.
- [2] H. Durr, H. Bouas-Laurent, Photochromism. Molecules and Systems, Elsevier, Amsterdam, 1990.
- [3] A.S. Dvornikov, I. Cokgor, M. Wang, F.B. McCormick, S.E. Esener, P.M. Rentzepis, IEEE CPMT A 20 (1997) 203.
- [4] H.G. Heller, CRC Handbook of Organic Photochemistry and Photobiology, 1995, pp. 174–183.
- [5] I.Yu. Grishin, Yu.M. Chunaev, N.M. Przhivalgovskaya, A.V. Metelitsa, Khimiya Geterotsiklicheskikh Soedinenii (1992) 422.
- [6] M. Irie, K. Uchida, Bull. Chem. Soc. Jpn. 71 (1998) 985.
- [7] A.S. Dvornikov, P.M. Rentzepis, Opt. Commun. 136 (1997) 1.
- [8] Y.C. Liang, A.S. Dvornikov, P.M. Rentzepis, Res. Chem. Intermed. 24 (1998) 905.
- [9] H. Stobbe, Ber. 37 (1904) 2236.
- [10] P.J. Darcy, R.J. Hart, H.G. Heller, J. Chem. Soc., Perkin Trans. 1 (1978) 571.
- [11] D.A. Parthenopoulos, P.M. Rentzepis, J. Mol. Struct. 224 (1990) 297.
- [12] H.G. Heller, J.R. Langan, J. Chem. Soc., Perkin Trans. 2 (1981) 341.
- [13] Y. Yokoyama, H. Hayata, H. Ito, Y. Kurita, Bull. Chem. Soc. Jpn. 63 (1990) 1607.
- [14] A. Tomoda, A. Kaneko, H. Tsuboi, R. Matsushima, Bull. Chem. Soc. Jpn. 66 (1993) 330.
- [15] Y. Yokoyama, T. Tanka, T. Yamane, Y. Kurita, Chem. Lett. (1991) 1125.