

Photochromic thiophenefulgides. Photokinetics of two isopropyl derivatives

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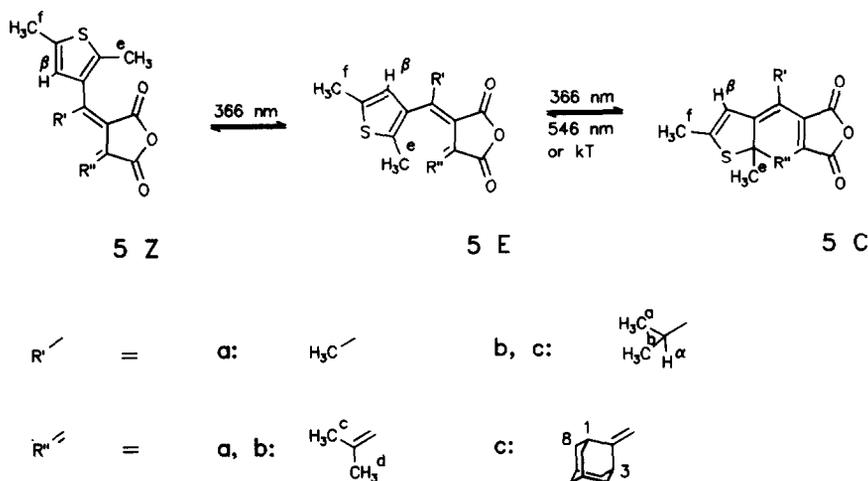
For two photochromic isopropyl-thiophenefulgides a complete photokinetic analysis is given. For one compound (**5b**), the partial quantum yield for the colouring process ($\Phi_{EC} = 54\%$) is the highest value found for thiophenefulgides. EZ-isomerisations do not play an important role. The colouring quantum yield is temperature independent down to 20 K, whereas bleaching requires little thermal activation. In case of an adamantylidene substituted isopropyl-thiophenefulgide (**5c**), the bleaching efficiency ($\Phi_{CE} = 31\%$) is very high. Upon heating of the cyclic products, thermal bleaching occurs with an activation energy of 1 eV.

1. Introduction

Arylfulgides are capable of two different types of reversible photoreactions: EZ-isomerisations and ring closure reactions [1–3,8,9,11,15–17]. Whereas the former ones are accompanied by only a slight colour change, the colour is altered dramatically during the latter ones. Therefore, the reversible cyclisation reactions are referred to as photochromism of fulgides. In most cases, ring closure and ring opening reactions follow the Woodward–Hoffmann rules [1–9,13]. Heller and his group [3–6] found that alkyl-substituted heterocyclic fulgides show high reversibility (“fatigue resistance”) along with thermal stability.

As far as any practical application of photochromic materials is concerned, high efficiencies of the photochromic processes are desirable. Some years ago, predictions (based on semiempirical PPP-calculations) were made how to optimize the quantum yield for the colouring process [19]. According to these results, bulky substituents R' (increasing sterical hindrance and constraints of the exocyclic double bond) should increase the colouring quantum yield and lower the efficiencies for EZ-isomerisations and radiationless deactivations. On the other hand, it has been shown [3,9] that bleaching efficiency of some furanfulgides is enhanced by introduction of the adamantylidene group R". (see scheme 1).

Applying these concepts, isopropyl- and adamantylidene substituted thiophenefulgides were synthesized. We report here a complete photokinetic analysis of the different isomerisations of these compounds. Furthermore, we studied the temperature dependence of the photochromic behaviour including thermal bleaching.



Scheme 1.

2. Experimental

The synthesis of isopropyl-thiophenefulgide **5b** (= 2-[1-(2,5-dimethyl-3-thienyl)isobutylidene]-3-isopropylidene succinic anhydride) and of the adamantylidene derivative **5c** (= 2-adamantylidene-3-[1-(2,5)-dimethyl-3-thienyl] isobutylidene] succinic anhydride) are sketched in the appendix.

NMR experiments (Bruker WP 80, AC 250 F, CXP 300) were carried out in deuterated chloroform with tetramethylsilan (TMS) as internal standard. The photokinetic analysis was done for toluene solutions. Doped polystyrene platelets were prepared by dissolving polystyrene and the fulgide in dichloromethane and evaporating the solvent.

We used double beam UV/VIS spectrophotometers (Pye Unicam SP8-250 and Zeiss M 400, resp.) to measure the absorption spectra. The low temperature experiments were performed using a continuous flow helium cryostat (Oxford CF 204). High temperature experiments (thermal bleaching) were done in a home made optical thermostat. Irradiation of the samples was effected by using an HBO 200 W (Osram) and a monochromator (Jarrell-Ash, 0.25 m, and Zeiss B 400, resp.). In order to determine quantum yields, we used a calibrated photodiode UV-100 BG (Polytech) to measure the excitation light intensity.

3. Results

In sections 3.1 through 3.4 we give a detailed analysis of the photochromic behaviour of isopropyl-thiophenefulgide **5b** including the temperature dependence of photoinduced colouring and bleaching (3.3) and thermal bleaching (3.4). Section 3.5 summarizes the results obtained for the adamantylidene derivative **5c**.

3.1. Photochromism

The synthesis (cf. appendix) yields E- and Z-isomers of isopropyl-thiophenefulgide **5b** which could be separated by chromatographic means. Table 1 gives ¹H-NMR data of these two isomers. In the E-isomer the isopropyl proton H- α (4.20 ppm) is deshielded by the adjacent carbonyl group, and the methyl group c-CH₃ (1.30 ppm) is shielded by the thiophene ring. In the case of the Z-isomer H- α (2.84 ppm) and c-CH₃ (2.13 ppm)

Table 1

¹H-NMR data (CDCl₃) of the three isomers Z, E, C of isopropyl-thiophenfulgide **5b** and adamantylidene-isopropyl-thiophenfulgide **5c**, respectively (indication according to scheme 1, $\delta = [\text{ppm}]$ ($|J| = [\text{Hz}]$))

	isopropyl-thiophenfulgide 5b (300 MHz)			isopropyl-adamantylidene-thiophenfulgide 5c (250 MHz)		
	Z	E	C ^{a)}	Z	E	C ^{b)}
a(d, ³ J)	0.97 (6.6)	0.81 (6.8)	1.20 (7.1)	0.92 (6.6)	0.72 (6.8)	1.23 (7.1)
b(d, ³ J)	1.15 (6.9)	1.35 (7.1)	1.25 (7.2)	1.14 (6.8)	1.29 (7.1)	1.26 (7.3)
c/ad 1	2.13	1.30	1.35	2.79	2.43	2.56
d/ad 3	2.41	2.24	1.54	4.25	4.14	2.84
e	2.22	2.01	1.57	2.19	2.07	1.52
f	2.43	2.43	2.23	2.43	2.43	2.20
α (sept., ³ J)	2.84 (6.7)	4.20 (7.0)	3.31 (7.2)	2.82 (6.8)	4.18 (6.9)	3.20 (7.2)
β	6.35	6.56	6.18	6.36	6.52	6.11
ad 8a(d, ² J)	-	-	-	-	0.29 (12.6)	-
adamantyl-H	-	-	-	1.82–2.16	1.39–2.01	1.5–1.9 2.53–2.65 2.73–2.89

^{a)} Photostationary equilibrium 7% E, 93% C. ^{b)} Photostationary equilibrium 12% Z, 21% E, 67% C.

are outside the deshielding zone of the adjacent carbonyl and outside the shielding zone of the thiophene ring, respectively.

Irradiation of the E-isomer in deuterated chloroform solution ($\lambda' = 366$ nm, 2 hours) leads to a photostationary equilibrium containing 93% of the cyclic product C. The ¹H-NMR data of C are given in table 1. In the C-isomer, only the methyl group f-CH₃ is allylic with an absorption at 2.23 ppm. The absorption of H- β (6.18 ppm) is at high field compared to E- and Z-isomers.

Scheme 1 shows the different photochemical reactions (and the thermal reaction) under study. Ring closure reaction E→C and ring opening C→E could be observed in different liquid solutions (toluene, chloroform, hexane, dichloromethane, propylene carbonate), in polymer matrix (polystyrene), and in the solid state (thin film). Thermal reactions did not occur at ordinary temperatures. The thermal bleaching reaction was studied at temperatures beyond 100°C (see section 3.4).

A detailed photokinetic analysis was performed for toluene solutions. The extinction coefficients of the different isomers at the wavelengths used to analyze the photochromic behaviour ($\lambda_1 = 524$ nm, $\lambda_2 = 330$ nm) and at the irradiation wavelengths ($\lambda' = 366$ nm, $\lambda'' = 546$ nm) are given in table 2. The data for the cyclic isomer C

Table 2

Extinction coefficients [$1 \text{ mol}^{-1} \text{ cm}^{-1}$] of the three isomers (Z, E, and C) of isopropyl-thiophenfulgide **5b** and isopropyl-adamantylidene-thiophenfulgide **5c** in toluene at wavelengths of analysis and irradiation

λ (nm)	isopropyl-thiophenfulgide 5b			isopropyl-adamantylidene-thiophenfulgide 5c		
	Z	E	C	Z	E	C
330	2050	4000	1910			
340				2410	3580	1360
366	1180	1160	490	1510	1120	480
524	0	0	8250			
546	0	0	7320	0	0	5970
560				0	0	6140

could be obtained by an extrapolation method described in section 3.2.

Fig. 1a shows the optical colouring of the E-isomer ($\lambda' = 366$ nm). A broad featureless absorption band in the visible range (extending from 400 nm through 600 nm, maximum at 524 nm) and a UV band at 310 nm are coming up during irradiation. Simultaneously, the absorption around 330 nm decreases. Clear-cut isosbestic points occur at 384 nm and 322 nm, respectively. The absorbances ($\lambda_1 = 524$ nm, $\lambda_2 = 330$ nm, and $\lambda' = 366$ nm) of this series are used in the extinction diagram (fig. 2, upper and lower curves).

The effect of irradiation of the Z-isomer ($\lambda' = 366$ nm) is shown in fig. 1b. As indicated by the increasing absorptions at 524 nm and 310 nm, respectively, photoproduct C is being formed. The absorption mainly decreases at 350 nm. Isosbestic points occur at 395 nm and 324 nm, the latter being less pronounced. These data are analyzed at the extinction diagram (fig. 2, middle curve).

Bleaching of the C-isomer upon irradiation at $\lambda'' = 546$ nm is depicted in fig. 1c. The visible absorption band disappears, the absorption at 310 nm decreases whereas the absorption at 330 nm increases. Isosbestic points occur at 384 nm and 322 nm, respectively.

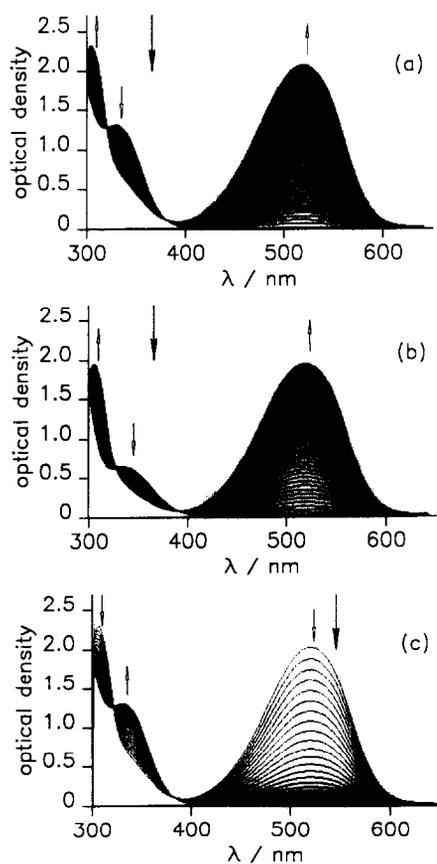


Fig. 1. Photochromism of isopropyl-thiophenfulgide **5b** in toluene solution at room temperature (bold arrows indicate the irradiation wavelengths, faint arrows indicate change of optical absorption): (a) colouring of E-isomer with $\lambda' = 366$ nm, $\Delta t = 3$ s; $c_0 = 3.24 \times 10^{-4}$ mol/l; $I_0 = 4.76 \times 10^{-6}$ mol/l; (b) colouring of Z-isomer with $\lambda' = 366$ nm, $\Delta t = 20$ s; $c_0 = 3.01 \times 10^{-4}$ mol/l; $I_0 = 1.97 \times 10^{-5}$ mol/l; (c) bleaching of C-isomer with $\lambda' = 546$ nm, $\Delta t = 20$ s; $c_0 = 3.24 \times 10^{-4}$ mol/l; $I_0 = 2.37 \times 10^{-5}$ mol/l.

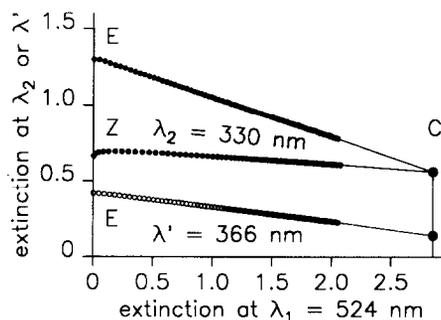


Fig. 2. Extinction diagram for the colouring of isopropyl-thiophenfulgide **5b** in toluene ($\lambda' = 366$ nm), upper curve: colouring of E, data from 1 (a); middle curve: colouring of Z, data from 1 (b); concentration of Z normalized to that of E; lower curve: extinction at $\lambda' = 366$ nm versus $\lambda_1 = 524$ nm; extrapolation of linear reach to determine the extinction coefficients of the C-isomer at λ_1 , λ_2 , and λ' .

3.2. Photokinetic analysis

Photokinetics of a mixture of three components is a rather complex matter [20]. Generally, there are no isosbestic points and extinction diagrams show complicated curves.

Fortunately, the photochromic behaviour of isopropyl-thiophenfulgide **5b** reveals two distinct simplifications. There are different isosbestic points (fig. 1) and the extinction diagram shows linear dependence (fig. 2).

This means that the number of independent reactions is reduced to one. Observation of a single reaction leads to isosbestic points and linear extinction diagrams.

In the case of colouring the E-isomer, it follows that the quantum yield for cyclisation must dominate, $\Phi_{EC} \gg \Phi_{EZ}$, in order to guarantee the simplifications mentioned above. It follows that the concentration of Z must be small.

Even in case of the Z-isomer, colouring leads to a linear extinction diagram (after an induction period). Thus it must be concluded that $\Phi_{EC} \gg \Phi_{ZE}$ and the concentration of E is very small throughout the experiment.

Finally, the extrapolations of the linear courses of E→C (upper curve) and Z→E→C (middle curve) intersect at the extinctions of the C-isomer, thus providing all relevant extinction coefficients (see table 2).

Making use of the extinction coefficients of all isomers (Z, E, C) at two different wavelengths (λ_1, λ_2) allows determining the partial concentrations ($[Z] + [E] + [C] = c_0$) because eq. (1) holds

$$OD = (\epsilon^Z[Z] + \epsilon^E[E] + \epsilon^C[C])d. \quad (1)$$

Fig. 3 shows the time dependence of the partial concentrations of Z, E, and C calculated by means of eq. (1) for colouring of E. As anticipated above, the concentration of Z ($[Z] < 10^{-5}$ mol/l) is negligible, therefore colouring of E can be analyzed within the simple scheme $E \rightleftharpoons C$. According to this reaction equation, the kinetics is governed by rate equation (2):

$$\frac{d[E]}{dt} = (-\Phi_{EC}\epsilon^E[E] + \Phi_{CE}\epsilon^C[C])F', \quad (2)$$

where $F' = I_0(1 - 10^{-OD'})/OD'$. The photokinetic factor F' must be evaluated at the irradiation wavelength $\lambda' = 366$ nm.

“Formal integration” [21] of eq. (2) leads to eq. (3):

$$\frac{\int d[E]}{\int [E]F' dt} = -\Phi_{EC}\epsilon^E + \Phi_{CE}\epsilon^C \frac{\int [C]F' dt}{\int [E]F' dt}, \quad (3)$$

$$Y = a + bX$$

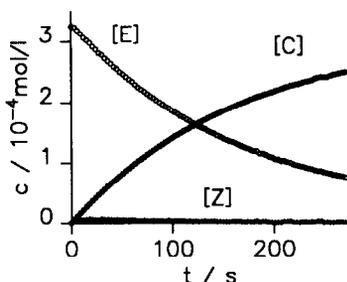


Fig. 3. Time evolution of the concentrations of E(\circ), Z($*$), and C(\bullet) during irradiation of the E-isomer of **5b** at $\lambda' = 366$ nm. The concentrations are obtained from the extinction diagram (fig. 2, upper curve) using the extinction coefficients (table 2) and eq. (1).

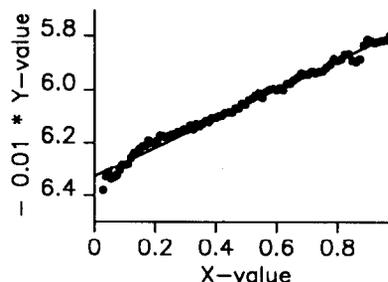


Fig. 4. Result of the “formal integration” of eq. (3) for colouring the E-**5b**. The slope of the straight line yields $\Phi_{CE} = 10\%$, from the ordinate one gets $\Phi_{EC} = 54\%$. The correlation of the experimental values to the straight line is 98.8%.

Table 3
 Partial quantum yields for different thiophenefulgides in percent (toluene solution, $\lambda' = 366$ nm, $T = 300$ K)

	EC	CE	EZ	ZE
ordinary thiophenefulgide 5a	(13 ± 5)	(8 ± 3)		
isopropyl-thiophenefulgide 5b	(54 ± 2)	(10 ± 1)	(1.5 ± 1.0)	(3.0 ± 2.0)
isopropyl-adamant.-thiophenefulgide 5c	(28 ± 2)	(31 ± 2)	(5.8 ± 0.9)	(3.1 ± 0.5)

which can be treated numerically. Plotting the integrals (Y versus X) for colouring of E apparently shows linear dependence (see fig. 4). Slope and intersect provide the quantum yields Φ_{CE} and Φ_{EC} , respectively. We got $\Phi_{EC} = (54 \pm 2)\%$ for the cyclisation reaction and $\Phi_{CE} = (10 \pm 1)\%$ for ring opening.

Irradiation of a coloured sample with $\lambda'' = 546$ nm leads to a simple bleaching reaction. The photokinetic analysis of which is straight forward. Determination of the quantum yield for ring opening verifies the above value ($\Phi_{CE} = 10\%$).

We were not able to determine quantum yields for the E → Z and Z → E isomerisations from analysis of the three component system due to the fact that the concentration of the third component (Z if E is irradiated, E if Z is irradiated) is too erroneous.

To overcome this problem, a toluene solution of isopropyl-thiophene-fulgide was irradiated with $\lambda' = 366$ nm ($I'_0 = 0.01 \mu\text{W}$) and $\lambda'' = 546$ nm ($I''_0 = 5.5 \mu\text{W}$) simultaneously. The highly intense visible light (compared to the UV light intensity) causes the C-concentration to be negligible. The photostationary equilibrium between E and Z turns out to be $[E(\infty)]/[Z(\infty)] = 2.0$ and taking into account equal extinction coefficients of E and Z, the relation $\Phi_{EZ}/\Phi_{ZE} = 0.5$ must hold. A closer inspection of the experimental results upon irradiating Z with $\lambda' = 366$ nm allows estimating $\Phi_{EZ} = (1.5 \pm 1.0)\%$ and thus $\Phi_{ZE} = (3.0 \pm 2.0)\%$.

3.3. Temperature dependence

In order to get more insight in the mechanism of the photoreactions, we studied the temperature dependence of colouring and bleaching of polystyrene platelets doped with isopropyl-thiophenefulgide 5b. Fig. 5 gives difference spectra (obtained by subtracting the first spectrum) for the colouring (upper part) and bleaching (lower part). These spectra fit well into the scheme outlined in section 3.1 for toluene solutions. Ignoring minute spectral shifts – isosbestic points at 388 nm and 324 nm, maximum of visible absorption at 527 nm, UV bands at 313 nm (increasing) and 342 nm (decreasing) – we conclude that irradiation of doped polystyrene with $\lambda' = 366$ nm causes mainly cyclisation and attribute bleaching to the ring opening reaction. These assumptions are further confirmed by the mirror symmetry of the difference spectra of colouring versus bleaching.

The concentration of the C-isomer is determined by integration of the visible absorption band (fig. 5). Fig. 6 shows the evaluation of the C-concentration versus the irradiation time for temperatures down to 20 K. It turns out that colouring of the sample is temperature independent whereas bleaching needs very weak thermal activation (activation energy about 2.5 meV).

3.4. Thermal bleaching

Thermal reactions of fulgides have been scarcely discussed in the literature [11]. Heller [3] reported on thermal EZ-isomerizations at boiling toluene solutions of a thiophenefulgide. In some cases [6], thermal cyclisation occurred. Thermal bleaching (ring opening) was not discussed at all.

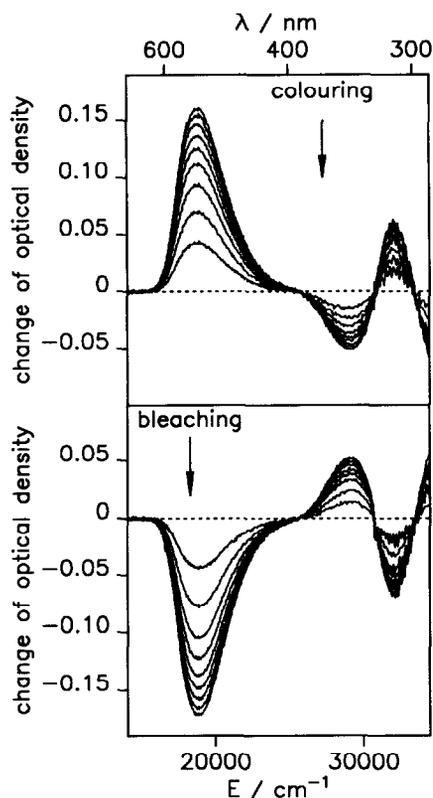


Fig. 5. Difference spectra obtained upon colouring and bleaching of a polystyrene platelet ($d=1$ mm) doped with 2.5×10^{-4} mol/l of isopropyl-thiophenfulgide **5b** (at room temperature): upper part: colouring E→C with 366 nm, $\Delta t=10$ s; lower part: bleaching C→E with 546 nm, $\Delta t=10$ s.

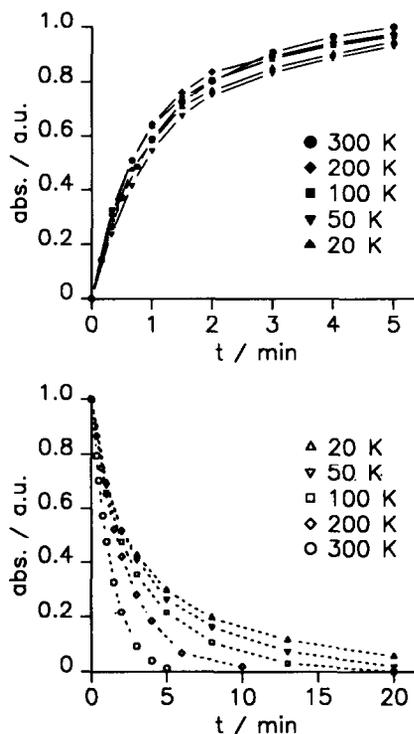


Fig. 6. Temperature dependence of photochemical colouring E→C (upper part) and photochemical bleaching C→E (lower part) of isopropyl-thiophenfulgide **5b** in polystyrene matrix.

Upon heating of a propylene carbonate solution of C-isomer (**5b**) to temperatures above 100°C, thermal bleaching occurs. The visible absorption band decreases and the UV band increases similarly to bleaching with 546 nm.

We investigated thermal bleaching of the C-isomer of isopropyl-thiophenfulgide **5b** by means of non-isothermal reaction analysis. Due to the fact that thermal bleaching fits well to a monoexponential decay, we suppose the reaction under study being of first order

$$\dot{c} = -kc \quad (4)$$

Furthermore, we take the Arrhenius law for being valid

$$k(T) = k_{\infty} \exp(-E_a/RT) \quad (5)$$

The heating rate α of the thermostat was held constant by means of a PID controller, thus

$$T = \alpha t \quad (6)$$

one can evaluate the time evolution of the concentration c by solving the following differential equation

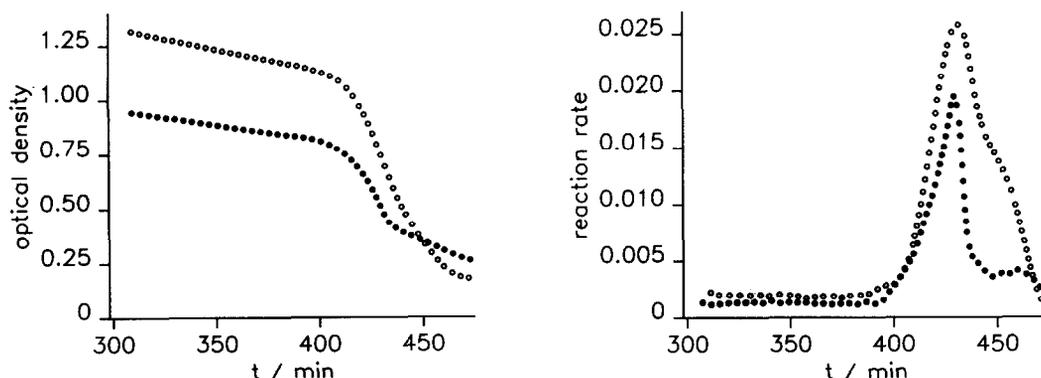


Fig. 7. Thermal bleaching of the cyclic isomers C→E in propylene carbonate solutions, heating rate $\alpha = 1$ K/min; (●) isopropyl-thiophenfulgide **5b** ($\lambda_{\text{det}} = 530$ nm) and (○) isopropyl-adamantylidene-thiophenfulgide **5c** ($\lambda_{\text{det}} = 575$ nm), left part: time evolution of the optical density ($\approx [C(t)]$); right part: time evolution of the reaction rates; from the maxima of the reaction rates one gets activation energy and frequency factor.

$$\dot{c} = -k_{\infty} \exp(-E_a/\alpha Rt) c \quad (7)$$

Its time derivative (the reaction rate) shows a maximum after a certain time t_{max} value \dot{c}_{max} . Applying common approximations [22] finally the parameters E_a and k_{∞} are obtained

$$E_a = -e\alpha Rt_{\text{max}}^2 \dot{c}_{\text{max}}/c_0 \quad (8)$$

and

$$k_{\infty} = -e\dot{c}_{\text{max}} \exp(-et_{\text{max}} \dot{c}_{\text{max}}/c_0) \quad (9)$$

Fig. 7 gives the experimental data for the procedure just described. The concentration of the cyclic isomer was detected at $\lambda = 530$ nm. The sample was heated at a rate of 1 K/min and the abscissa is readjusted to corresponding to the absolute temperature. The linear decrease of the optical density during heating is due to the decreasing specific gravity of the propylene carbonate solution. This causes an offset of the time derivative which was taken into account analysing the maximum. From the maximum of the reaction rate we found by using eq. (8) an activation energy of $E_a = 0.97$ eV and by applying eq. (9) a frequency factor of $k_{\infty} = 1.4 \times 10^9 \text{ s}^{-1}$ for the thermal bleaching (ring opening) reaction.

3.5. Adamantylidene derivative **5c**

The synthesis of isopropyl-adamantylidene-thiophenfulgide **5c** and the separation and identification of the different isomers (Z, E, and C) were done following the procedure described for isopropyl-thiophenfulgide **5b** (cf. appendix and section 3.1). The NMR data for the isopropyl-protons α , β , and the thiophene-protons ϵ , δ , and γ are almost at the same values as in the corresponding isomers of isopropyl-thiophenfulgide **5b**. The adamantyl-H-8a (0.29 ppm) in the E-isomer is extremely shifted to high field due to the thiophene ring. See table 1 for NMR data. In deuterated chloroform, the photostationary equilibrium ($\lambda' = 366$ nm) comprises 12% Z-, 21% E-, and 67% C-isomer.

For toluene solutions, colouring (with $\lambda' = 366$ nm) and bleaching (with $\lambda'' = 546$ nm) monitored at the detection wavelengths $\lambda_1 = 560$ nm and $\lambda_2 = 340$ nm. See table 2 for extinction coefficients for the three isomers at the different wavelengths. Analogous to the procedure described in section 3.2, partial quantum yields for the different reactions were determined by means of photokinetic analysis.

All partial quantum yields can be determined by carefully analysing a sequence of spectra obtained from irradiation of the E-isomer with $\lambda' = 366$ nm. Due to the fact that the colouring quantum yield ($\Phi_{\text{EC}} = 28 \pm 2\%$) and the efficiency of the EZ-isomerisation ($\Phi_{\text{EZ}} = 5.8 \pm 0.9\%$) are of the same order of magnitude, the analysis of the three component system is straight forward. (Simultaneously irradiating with $\lambda' = 366$ nm and $\lambda'' = 546$ nm is not necessary in this case.) The quantum yield for ZE-isomerisation ($\Phi_{\text{ZE}} = 3.1 \pm 0.5\%$) is close to the value for isopropyl-thiophenfulgide **5b** whereas the quantum yield for ring opening ($\Phi_{\text{CE}} = 31 \pm 2\%$) is enhanced by a factor of three. Bleaching of the C-isomer with $\lambda'' = 546$ nm verifies the quantum yield ($\Phi_{\text{CE}} \approx 30\%$) being independent of the excitation wavelength.

Prolonged UV irradiation of the sample leads to decomposition of the photoproduct C: the visible absorption band around 560 nm decreases, a broad band with maximum at 460 nm rises up. The decomposition product has not been identified.

Thermal bleaching of the C-isomer of isopropyl-adamantylidene-thiophenfulgide **5c** was investigated following the same procedure described in section 3.4 for isopropyl-thiophenfulgide **5b**. While heating a propylene carbonate solution at a rate of 1 K/min, the cyclic isomer was detected at $\lambda = 575$ nm (see fig. 7). From the maximum of the reaction rate, one calculates $E_a = 1.00$ eV and $K_\infty = 1.4 \times 10^9$ s⁻¹.

4. Discussion

Our study on thiophenfulgides reveals that their photochromic behaviour is mainly a molecular phenomenon. Environmental effects and even temperature do not play an important role.

The isopropyl derivative **5b** improves the colouring efficiency compared to the ordinary thiophenfulgide **5a** (= 2-[1-(2,5-dimethyl-3-thienyl)ethylidene]-3-isopropylidene succinic anhydride) [6,8]. The quantum yield for colouring is fairly promoted by the extreme sterical hindrance caused by the isopropyl substituent. Similar results were achieved on furanfulgides [9] and phenylfulgides [19]. So it seems to be a general rule that the cyclisation tendency increases in the order -H, -methyl, -isopropyl in accordance with theoretical models [19].

The thermal bleaching experiment clearly demonstrates that, in our case, the cyclic isomer is metastable against ring opening. For furanfulgides, theoretical estimations [23] and qualitative energy level diagrams suggested recently [18] predict the cyclic isomer being the most stable one.

Another very distinct feature is the weak temperature dependence of the photochromic behaviour. The temperature independence of colouring (cyclisation) is in correspondence with the results on different fulgides [8,10,14]. Temperature dependence of bleaching (ring opening) is even weaker in the isopropyl case **5b** (activation energy of 2.5 meV) than for the ordinary thiophenfulgide **5a** (activation energy of 6 meV) [8].

Concerning the adamantylidene derivative **5c**, attention must be paid to three distinct features. First, the quantum yields are altered dramatically. The bleaching efficiency is enhanced by a factor of four compared to the ordinary thiophenfulgide **5a** and by a factor of three relative to the isopropyl-thiophenfulgide **5b** (table 3). This effect is similar to results published on furanfulgides [3]. At the same time, the colouring quantum yield is half the value found for isopropyl-thiophenfulgide **5b** (table 3) whereas for the furanfulgide case [9], this quantum yield is not reduced.

Second, for the first time, we deal with a less "fatigue-resistant" fulgide. Our adamantylidene derivative **5c** shows poor photostability. Finally, it should be pointed out that the activation energy for thermal bleaching of the cyclic isomer of the adamantylidene derivative is the same as for the isopropyl-thiophenfulgide **5b**. Obviously, in the ground state of the cyclic isomer, the endo-cyclic σ -bond is not traceably weakened due to the adamantylidene substituent. This is in contrast to arguments found in the literature [3,9] to explain the higher bleaching quantum yields of adamantylidene substituted fulgides.

As far as the mechanism of the photochromism of fulgides is concerned [1-7,12,13], it seems to be clear that in most cases cyclisation takes place in accordance with the Woodward-Hoffmann rules. Furthermore, cyclisation is an ultrafast process [17,18]. The question remains open whether the excited state of the photoproduct is

passed on the reaction pathway during the cyclisation process. On the other hand, it is not clear what determines the nature of the barrier for the optically induced ring opening reaction.

Generally, the EZ-isomerisation of fulgides competes with the colouring process (E→C). High efficiency of the EZ-isomerisation lowers the quantum yield for cyclisation. In order to reduce the tendency for EZ-isomerisations, there are two different approaches:

(1) investigation of single crystals where the constraints of the lattice prevent EZ-isomerisations due to the lack of free volume necessary for these reactions to take place [14],

(2) ingenious tailoring of the molecular structure, where the interactions of the different moieties make EZ-isomerisations inefficient. The validity of the last alternative has been proven in the case of our isopropylthiophenefulgide **5b**: Quantum yields for EZ-isomerisations are very low and can be neglected compared to the colouring quantum yield of E.

5. Conclusions

The photochromism of two new isopropyl substituted thiophenefulgides has been characterized in various media and as a function of temperature (20–300 K). In this paper, complete photokinetic analyses could be provided for toluene solutions at room temperature.

According to predictions made in the literature, the bulky isopropyl-substituent R' (**5b**) is found to enhance the colouring efficiency to above 50%, i.e. four-fold as compared to ordinary thiophenefulgide **5a**.

As for the unsubstituted compound **5a**, the colouring reaction does not require thermal activation even at low temperature (20 K), but for the bleaching reaction a small thermal activation barrier exists.

The adamantylidene substituent R'' (**5c**) increases three-fold the bleaching efficiency as compared to ordinary thiophenefulgide **5a**.

Only at high temperatures ($T > 400$ K) thermal bleaching of the cyclic photoproducts occurs.

Acknowledgement

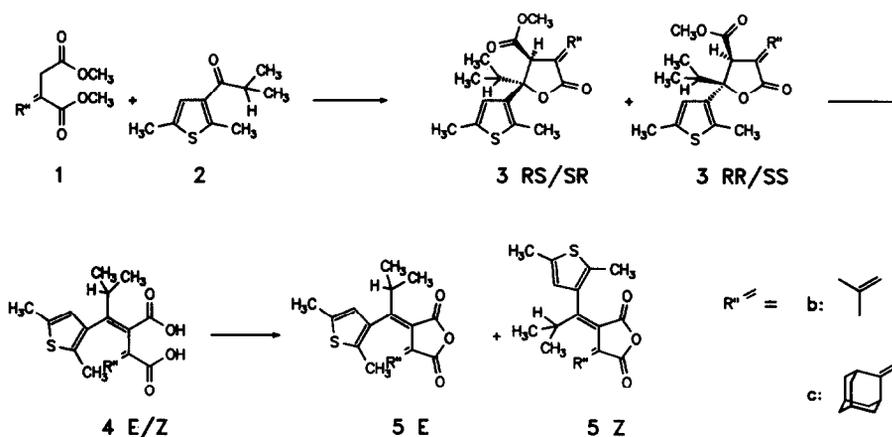
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Appendix

The thiophenefulgides were prepared analogous to the corresponding furanfulgides [9] according to the procedure for the condensation of α -ketoesters with diethylsuccinate described by Reutrakul [24] (scheme 2).

4-(2,5-Dimethyl-3-thienyl)-2-isopropylidene-3-methoxycarbonyl-5-methyl-4-hexanolide **3b**.

A solution of 1.86 g (10 mmol) dimethylisopropylidenesuccinate **1b** in 20 ml tetrahydrofuran (THF) was added over a period of 10 min to a solution of 11 mmol lithiumdiisopropylamide (LDA) in 20 ml THF at -78°C and stirred for 10 min. Then a solution of 1.82 g (10 mmol) (2,5-dimethyl-3-thienyl)isopropylketone **2** in 10 ml THF was added over a period of 20 min at -78°C . After stirring at 25°C for 2 h the reaction mixture was poured into a solution of 9 g NH_4Cl in 30 ml water, extracted twice with ether and the organic layer was dried with MgSO_4 . After removal of the ether the resulting oil was chromatographed on silica gel using dichloromethane as eluent to yield 1.36 g (4.0 mmol, 40%) of the diastereomeric mixture of lactone **3b** ($\text{C}_{18}\text{H}_{24}\text{O}_4\text{S}$ found (cal.): C 64.12 (64.26); H 7.15 (7.19); S 9.56 (9.53). $^1\text{H-NMR}$ (80 MHz, CDCl_3) $\delta =$ [ppm]: RS/SR (78%): 0.85 (d, 3 H, $J = 7.6$ Hz), 0.90 (d, 3 H, $J = 6.6$ Hz) isopropyl- CH_3 ; 1.90 (s, 3 H), 2.35 (s, 6 H), 2.42



Scheme 2.

(s, 3 H) isopropylidene-CH₃, thiophene-CH₃; isopropyl-H ^{#1}; 3.28 (s, 3H) ester-CH₃; 4.05 (s, 1H) H³; 6.50 (s, 1 H) thiophene-H; RR/SS (22%): 0.8–1.0 (m, 6 H) ^{#2} isopropyl-CH₃; 1.81 (s, 3 H), 2.22 (s, 3 H), 2.32 (s, 3H), 2.48 (s, 3 H) isopropylidene-CH₃, thiophene-CH₃); isopropyl-H ^{#1}; 3.76 (s, 3 H) ester-CH₃; 4.23 (s, 1H, H³); 6.50 (s, 1 H) thiophene-H).

2-[1-(2,5-Dimethyl-3-thienyl)isobutylidene]-3-isopropylidenesuccinic anhydride **5b**.

1.36 g (4.0 mmol) of lactone **3b** were treated with a solution of 5 mmol potassium t-butoxide in 25 ml refluxing t-butyl alcohol for 1 h. The resulting halfester was refluxed for 21 h in a solution of 4 g potassium hydroxide in 30 ml methanol and 10 ml water to yield after acidic work up 1.10 g (3.4 mmol, 85%) diacid **4b**. The E/Z-mixture of diacid **4b** was cyclised with 0.83 g (4.0 mmol) dicyclohexylcarbodiimide (DCCD) in 150 ml dichloromethane at 25 °C to yield after column chromatography (Nucleosil 1525 CN, Machery & Nagel, hexane/dichloromethane) 0.52 g (1.7 mmol, 50%) E- and 0.15 g (0.5 mmol, 14%) Z-fulgide **5b**, respectively (C₁₇H₂₀O₃S found for E, found for Z (cal.): C 67.24, 67.11 (67.08); H 6.70, 6.72 (6.62); S 10.48, 10.40 (10.53); mp. E-fulgide 102–3 °C, Z-fulgide 113–14 °C; see table 1 for ¹H-NMR).

Dimethyladamantylidenesuccinat **1c**.

Stobbecondensation of 58.31 g (399 mmol) dimethylsuccinate and 20.00 g (133 mmol) adamantanone with potassium t-butoxide (266 mmol) in 300 ml t-butyl alcohol and esterification of the resulting halfester with diazomethane in ether yielded 22.63 g (81 mmol, 61%) diester **1c** (bp. 106–8 °C/5 × 10⁻³ Torr; n_D²⁵ = 1.5184; C₁₆H₂₂O₄ found (cal.): C 68.87 (69.04), H 8.00 (7.97)).

2-Adamantylidene-4-(2,5-dimethyl-3-thienyl)-3-methoxycarbonyl-5-methyl-4-hexanolide **3c**.

2.78 g (10 mmol) dimethyladamantylidenesuccinat **1c** were condensed, according to the procedure described for **3b**, with 2.73 g (15 mmol) (2,5-dimethyl-3-thienyl)isopropylketone **2** and lithiumdiisopropylamide (11 mmol) in tetrahydrofuran to yield after column chromatography (silicagel, petrolether/ethylacetate) 2.93 g (6.8 mmol, 68%) RS/SR lactone **3c** and 0.69 g (1.6 mmol, 16%) RR/SS lactone **3c**, respectively. (C₂₅H₃₂O₄S found for RS/SR, found for RR/SS (cal.): C 69.93, 69.98 (70.06); H 7.64, 7.57 (7.53); S 7.23, 7.64 (7.48). ¹H-NMR (CDCl₃, 250 MHz, δ = [ppm]): RS/SR: 0.84 (d, 3 H, ³J = 6.8 Hz), 0.95 (d, 3 H, ³J = 6.7 Hz) isopropyl-CH₃; 1.55–2.05 (m, 12 H) adamantylidene-H; 2.29 (sept., 1 H, ³J = 6.9 Hz) isopropyl-H; 2.34 (s, 3 H), 2.40 (s, 3 H) thiophene-CH₃; 2.63 (s, 1 H) adamantylidene-H¹; 3.26 (s, 3 H) ester-CH₃; 4.08 (s, 1 H) lactone-H³; 4.41 (s, 1 H) adamantylidene-H³; 6.53 (s, 1 H) thiophene-H. RR/SS: 0.92 (d, 3 H, ³J = 7.0 Hz), 0.96 (d, 3 H, ³J = 6.5 Hz) isopropyl-CH₃; 1.41–2.00 (m, 12 H) adamantylidene-H; 2.33 (sept., 1 H, ³J = 6.8 Hz) isopro-

^{#1} Signals covered by the methylabsorptions from 2.2 to 2.5 ppm.

^{#2} Signals for RR/SS covered by Signals for the RS/SR-isomer.

pyl-H; 2.35 (s, 3 H), 2.48 (s, 3 H) thiophene-CH₃; 2.56 (s, 1 H) adamantylidene-H¹; 3.75 (s, 3 H) ester-CH₃; 4.13–4.18 (m, 1 H) adamantylidene-H³; 4.23 (s, 1 H) lactone-H³; 6.48 (s, 1H) thiophene-H.)

2-Adamantylidene-3-[1-(2,5)-dimethyl-3-thienyl]isobutylidene]succinic anhydride **5c**.

In two runs 2.29 g (5.3 mmol) of RS/SR and 0.59 g (1.4 mmol) of RR/SS lactone **3c** were treated with one equivalent potassium t-butoxide in refluxing t-butyl alcohol, respectively. After saponification with methanolic potassium hydroxide the resulting diacids were cyclised with dicyclohexylcarbodiimide (DCCD) in dichloromethane to yield after column chromatography (silicagel, petrolether/ethylacetate) the E- and Z-fulgides. Starting from the RS/SR lactone we got 0.87 g (2.2 mmol, 41%) E- and 0.26 g (0.7 mmol, 12%) Z-fulgide **5c**, from the RR/SS lactone we got 0.39 g (1.0 mmol, 70%) E- and 0.02 g (0.06 mmol, 4%) Z-fulgide **5c**, respectively. The two isomers were crystallised from hexane/ethylacetate. (C₂₄H₂₈O₃S found for E, found for Z (cal.): C 72.91, 72.87 (72.69); H 7.16, 7.26 (7.12); S 7.93, 8.08 (8.09); mp. E-fulgide 171–3°C, Z-fulgide 160–2°C; see table 1 for ¹H-NMR data.)

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