Photochromic Heterocyclic Fulgides. Part 7.[1] (*E*)-Adamantylidene-[1-(2,5-dimethyl-3-furyl)ethylidene]succinic Anhydride and Derivatives: Model Photochromic Compounds for Optical Recording Media

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The thermally-stable coloured form **5a**, obtained by irradiation (λ = 366 nm) of the title compound **4a**, contains a rigid inflexible spiroadamantylidene group which results in a five- to nine-fold increase in the quantum efficiency for bleaching compared to the analogous compound **2** having methyl groups in the 7-position. The quantum efficiency for bleaching decreases with increasing wavelength of irradiation and increases with increasing temperature in a linear manner, and is solvent dependent.

The development of a reversible optical information storage medium based on photochromic organic compounds, as suggested by Hirshberg,[2] became a potential commercial reality with the discovery of the first thermally-stable fatigue-resistant near-colourless photochromic fulgides, which undergo near quantitative conversion into their coloured forms on exposure to UV light.[3] For example, fulgide **1** [1-(2,5-dimethyl-3-furyl)ethylidene(isopropylidene)succinic anhydride] cyclised on irradiation at 366 nm to the deep red 7,7a-dihydrobenzofuran derivative (7,7a-DHBF) **2**. The latter, dissolved in polymethyl methacrylate (50% w/v), can be used to record 1000 lines mm^{-1} at 16 mW cm^2. The recording rate is slow because the quantum efficiency for bleaching (φ_b) is only 5.9% at 494 nm for a solution in toluene at 21 °C[4]. φ_b for the red DHBF **2** in toluene at 21 °C shows a linear dependence on wavelength (λ/nm) over the range 436–536 nm in accord with eqn. (1).

$$\varphi_b = [0.178 - 2.4 \times 10^{-4}\,\lambda] \times 100\% \qquad (1)$$

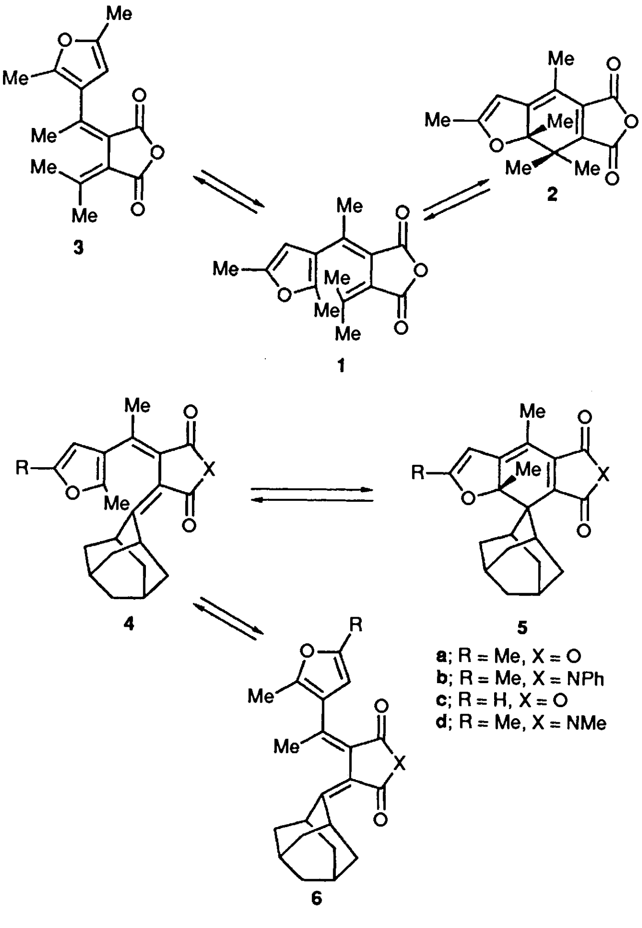
Quantum efficiencies for bleaching show a linear dependence on temperature over the range −50 to +80 °C.†

Quantum efficiencies for bleaching are also solvent dependent. For a solution of the 7,7a-DHBF **2** in hexane at 21 °C (1×10^{-4} mol dm^{-3}) (λ_{max} 473 nm, ε_{max} 8200 dm^3 mol^{-1} cm^{-1}), the quantum efficiency for bleaching φ_b at λ 500 nm is 10.9%, compared to 5.8% at the same wavelength for a solution in toluene, eqn. (2).

$$\varphi_b = [0.187 - 1.56 \times 10^{-4}\,\lambda] \times 100\% \qquad (2)$$

To improve the recording efficiency, it was necessary to increase φ_b by molecular tailoring of fulgide **1** and its corresponding 7,7a-DHBF **2** but without adversely affecting the fatigue resistance, thermal stability or other photochromic properties.

A major increase in the quantum efficiencies for bleaching (φ_b) in fulgides and fulgimides, illustrated by the following examples, was achieved simply by replacing the isopropylidene group by the rigid inflexible bulky adamantylidene group which weakens the 7,7a σ bond in the 7,7a-DHBF **5a–d**, presumably because of back strain and steric interactions.



3

1

2

4

5

6

a; R = Me, X = O
b; R = Me, X = NPh
c; R = H, X = O
d; R = Me, X = NMe

Photocyclisation of fulgides **4a** and **4c** gave the 7,7a-DHBFs **5a** and **5c** which have the adamantylidene group as part of a spiro system. These compounds show a marked increase in φ_b (30% and 58%, respectively) compared to DHBF **2** (5.5%) for solutions in toluene (21 °C) on irradiation at 514 nm. φ_c for fulgides **4a** and **4c** is 15% compared to 20% for fulgide **1**. Quantum efficiencies for colouring and bleaching were determined using the Heller and Langan method of chemical actinometry.[4]

On irradiation at λ 366 nm, a solution of the (*E*)- or (*Z*)-fulgides **4a** or **6a** (0.2 mol dm^{-3} in $CDCl_3$), turned deep red and gave a photostationary state (PSS) consisting of a 85:15 mixture of the 7,7a-DHBF **5a** and (*E*)-fulgide **4a** as measured by NMR spectroscopy. Unlike fulgide **1**, fulgide **4a** (1×10^{-4} mol dm^{-3} in toluene) is not converted quantitatively into the 7,7a-DHBF **5a** on irradiation at λ 366 nm. By irradiation to the PSS at two different wavelengths (344 and 366 nm) and

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† This study was carried out at the Chemistry Department, Weizmann Institute, Rehovoth, Israel, using a Cary spectrometer with a thermostatted variable-temperature cell, with irradiation at λ 366 nm *in situ*. We thank Professor E. Fischer for the use of his special facilities.

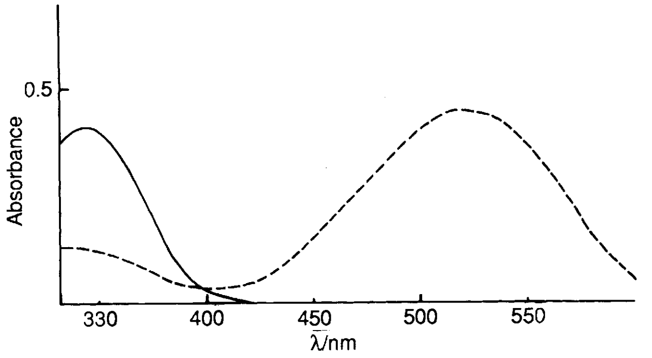


Fig. 1 Fulgide **4a** (X = O) (1 × 10^{-4} mol dm^{-3} solution in toluene) before (——) and after (·········) irradiation (λ 366 nm)

Table 1 NMR data (δ)

Compound	2-Me	R	MeC=	4-H
1	2.02	2.28	2.60	5.98
2	2.06	2.17	2.11	5.60
4a	2.07	2.28	2.53	5.60
4b	2.11	2.28	2.56	5.98
4c	2.16	7.38d[a]	2.58	6.40d[a]
4d	2.08	7.25d[a]	2.53	6.29d[a]
5a	1.47	2.10	2.04	5.98
5b	1.51	2.25	2.08	5.60
6a	2.21	2.28	2.15	5.98
6c	2.23	7.27d[a]	2.16	6.33d[a]

[a] *J* 2Hz.

applying the Fischer method,[5] the extent of conversion into the coloured form can be calculated. The only assumption of this method is that the ratio of the quantum yields for colouring and bleaching at the two activating wavelengths are the same. The conversion of the fulgide **4a** into the 7,7a-DHBF **5a** on irradiation at λ 366 nm was calculated (93%) and hence the spectrum of the 7,7a-DHBF **5a** could be determined (λ_{max} 520 nm, ε_{max} 5400 dm^3 mol^{-1} cm^{-1}) (Fig. 1) (*cf.* 7,7a-DHBF **2**, λ_{max}, 496 nm, ε_{max} 8200 dm^3 mol^{-1} cm^{-1}). The remarkable wavelength dependence of the quantum efficiency for bleaching (φ_b) of the DHBF **4a** in toluene at 21 °C is in accord with eqn. (3) (correlation coefficient 0.999 98).

$$\varphi_b = [0.467 - 3.29 \times 10^{-4}\,\lambda] \times 100\% \qquad (3)$$

The temperature dependence of the quantum yields for bleaching of the DHBF **4a** in toluene over the temperature range 22–81.5 °C, measured at λ 514.5 nm, is in accord with eqn. (4),

$$\varphi_b = [0.262 + 1.64T \times 10^{-3}] \times 100\% \qquad (4)$$

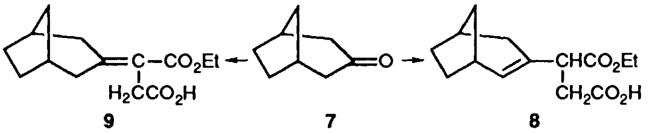
where T is the temperature in °C. Combination of eqns. (3) and (4) gives eqn. (5).

$$\varphi_b = \{0.4326 - [(3.285\,\lambda - 16.4T) \times 10^{-4}]\} \times 100\% \qquad (5)$$

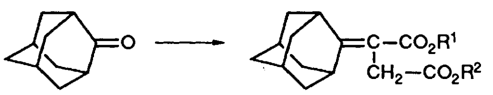
The excellent correlation between the experimental values for quantum efficiencies (φ_b) for 7,7a-DHBF **5a** in toluene with wavelength and temperature compared to the values calculated by using eqn. (5) can be seen in Table 2. Maximum efficiency for optical recording is achieved at the shortest acceptable wavelength and the highest practical temperature.

A solution of fulgide **4c** or **6c** (0.2 mol dm^{-3} solution in $CDCl_3$) was irradiated (λ 366 nm) to the PSS giving a 65:35 mixture of DHBF **5c** and (*E*)-fulgide **4c** as measured by NMR spectroscopy. The (*E*)-fulgide **4c** (1 × 10^{-4} mol dm^{-3} solution in toluene) was converted into the PSS by irradiation at λ 366 and 313 nm and the spectra measured before and after irradiation. Application of the Fischer method[5] gave a 92% conversion into the DHBF **5c** at λ 366 nm and hence the spectrum of the coloured form was determined (λ_{max} 505 nm, ε_{max} 4500 dm^3 mol^{-1} cm^{-1}).

A solution of the (*E*)-fulgimide **4b** (0.2 mol dm^{-3} in $CDCl_3$) on irradiation (λ 366 nm) turned deep purple and gave a 55:45 mixture of the 7,7a-DHBF **5b** and fulgimide **4b** at the PSS, as measured by NMR spectroscopy. Similarly, a solution of (*E*)-fulgimide **4d** (0.2 mol dm^{-3} in $CDCl_3$) on irradiation (λ 366 nm) at the PSS gave a 30:70 mixture of DHBF **5d** and (*E*)-fulgimide **4d**.



9 **7** **8**



10 **11**

Unlike bicyclo[3.2.1]octan-3-one (**7**), which undergoes a Stobbe condensation with diethyl succinate to give the bicyclo[3.2.1]oct-2-en-3-yl succinic half ester **8**, and not the bicyclo[3.2.1]octan-3-ylidenesuccinic half ester **9**[6], 2-adamantanone **10** reacts with dimethyl succinate to give exclusively methyl adamantylidenesuccinate **11** (R^1 = Me, R^2 = H). In this case, the formation of an endocyclic double bond cannot occur because of the resulting ring strain (Bredt's rule). A Stobbe condensation between dimethyl adamantylidenesuccinate **11** (R^1 = R^2 = Me) and 3-acetyl-2,5-dimethylfuran, followed by hydrolysis and cyclisation of the resulting diacids gives the (*E*)- and (*Z*)-fulgides **4a** and **6a** in high yield.

Experimental

A planar photovoltaic silicon cell, circular sensitive diameter 11.3 mm, type 100–5 (manufactured by Centronic Ltd, Croydon) was mounted in a metal case and connected to a specially constructed amplifier. The detector system was calibrated at the National Physical Laboratory by comparison with a NPL standard detector for selected narrow wavelengths over the range 400–700 nm for 17 discrete wavelengths at *ca.* 20 nm intervals. The relative responsivity at 1 nm intervals was calculated. The standard error was <0.1%. The voltage output of the amplifier was checked using an Electroplan (Royston) 2472 Digital Panel meter supplied with a manufacturer's certificate of conformance and found to be inerrant in the 10 V DC calibration.

A 1 cm pathlength quartz cell was used in the actinometry experiments. It showed 13% reflectance when empty and 7% reflectance at λ 546 nm when filled with toluene. A quartz plate taken from a similar cell, which gave 7% reflectance under similar conditions, was placed in front of the photodiode when estimating incident radiation from a slightly divergent beam orthogonal to the surface. The beam was focused to 7 mm diameter so that it entered the cell without touching the sides. The cell was employed in a thermostatted housing which could be maintained between −10 and 85 °C. The solution in the cell was stirred by means of a Temtron microstirrer. A high radiance monochromator having a Czerny–Turner f 3.4 optical system was used (model 7300, Applied Photophysics, London). The wavelength and absorbance accuracy of the Pye Unicam SP8-200 spectrophotometer were checked at regular intervals. Since the photon flux (*I*/photons s^{-1}) was measured, the volume of solution (*V*/dm^3) and the molar extinction coefficient of the

Table 2 Quantum efficiencies for bleaching (φ_b) for 7,7a-DHBF **5a** in toluene

λ/nm	T/°C	φ_b(%) Observed	φ_b(%) Calculated from eqn. (5)
436	21	3.24	3.24
514.5	21	2.98	2.98
514.5	40.5	3.29	3.30
514.5	57.5	3.55	3.58
514.5	81.5	3.96	3.98
570	21	2.80	2.80

coloured form (ε/dm^3 mol^{-1} cm^{-1}) known, and the change in absorbance (ΔA) after irradiation with monochromatic light (λ nm) for a time interval (t s) determined, it was possible to calculate the quantum yield (φ_b) from eqn. (6) where N is 6.023×10^{23} mol^{-1}, provided that all the incident light was absorbed.

$$\varphi_b = \frac{VN\Delta A}{I\varepsilon t} \qquad (6)$$

In cases when all the incident light is not absorbed, eqn. (7) was used.

$$\varphi_b = \frac{VN}{I\varepsilon} \times \frac{[\log T_0/1 - T_0) - \log T_t/(1 - T_t)]}{t} \qquad (7)$$

where T = [antilog $-A$], A_0 is the initial absorbance at λ_{max} and A_t is the absorbance at λ_{max} after irradiation.

The quantum efficiency for bleaching of 7,7a-DHBF **2** in toluene at 500 nm (5.8%) has already been determined by Heller and Langan[4] using the Schaffner method[7]. Using the procedure outlined above, the quantum efficiencies in toluene at 21 °C at 436, 460, 477, 488, 494, 520 and 546 nm were determined. The correlation coefficients for eqns. (1) and (2) are 0.9930 and 0.9997, respectively.

Dimethyl Adamantylidenesuccinate (**11**; $R^1 = R^2$ = Me).—A mixture of adamantanone (**10**) (300 g, 2 mol) and dimethyl succinate (320 g, 2.2 mol) in toluene (2.5 dm^3) was added dropwise to a stirred suspension of sodium hydride (as a 60% dispersion in oil; 90 g, 2.2 mol) in toluene (1.5 dm^3). If the mildly exothermic reaction had not occurred before 10% of the reagents had been added, the reaction was initiated by the addition of methanol (0.5 cm^3). The addition of reagents was continued with external cooling so as to maintain a brisk reaction and to keep the temperature of the reaction mixture between 45 and 50 °C. When the addition was complete, the reaction mixture was stirred overnight and then poured onto crushed ice (1 kg). The organic layer was separated and washed with water (200 cm^3). The combined aqueous solution was acidified with conc. HCl and the liberated half ester (**11**; R^1 = H, R^2 = Me) was filtered off, washed with water, dried and recrystallised from acetone, giving colourless crystals (420 g), colourless prisms m.p. 138–139 °C (Found: C, 68.2; H, 7.6. $C_{15}H_{20}O_4$ requires C, 68.18; H, 7.58%); ν_{max}/cm^{-1} 1712 (s) and 1710 (s); δ_H 3.78 (s, 3 H, OMe); 3.40 (s, 2 H, CH_2) and 2.84 and 2.0–1.76 (m, 14 H, adamantylidene). The half ester (**11**; R^1 = H, R^2 = Me) (246 g, 1 mol) was dissolved in dichloromethane (1 dm^3) and methanol (64 g, 2 mol) was added.

Dicyclohexylcarbodiimide (216 g, 1.05 mol) was melted and poured slowly with vigorous mechanical stirring, into the solution. Dicyclohexylurea separated to form a thick slurry. The reaction mixture was stirred for 3 h and dicyclohexylurea was filtered off. Dichloromethane was removed from the filtrate under reduced pressure. Diethyl ether (250 cm^3) was added and the second crop of dicyclohexylurea was filtered off. Ether was removed leaving the dimethyl ester which was distilled rapidly under vacuum (b.p. 145–195 °C/1 mm Hg) and then fractionally distilled (b.p. 152–154 °C/1 mm Hg). The dimethyl ester (**11**; $R^1 = R^2$ = Me) solidified on standing to a low melting, waxy solid, yield 220 g (overall yield 64%) (Found: C, 69.0; H, 7.95%; M$^+$, 278. $C_{16}H_{22}O_4$ requires C, 69.0; H, 7.97%; M, 278); ν_{max}/cm^{-1} 1742 (s) and 1722 (s); δ 3.70 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.38 (s, 2 H, CH_2) and 2.88 and 2.0–1.78 (m, 14 H, adamantylidene).

(E)- and (Z)-*Adamantylidene*[1-(2,5-*dimethyl*-3-*furyl*)*ethylidene*]*succinic Anhydride* (**4a** *and* **6a**).—A mixture of 3-acetyl-2,5-dimethylfuran (152 g, 1.1 mol) and dimethyl adamantylidenesuccinate (**11**; $R^1 = R^2$ = Me) (278 g, 1 mol) in toluene (2.5 dm^3) was added dropwise to a stirred solution of sodium hydride (60% dispersion in oil; 65 g, 1.5 mol) suspended in toluene (1 dm^3). Work-up, as described above, gave a mixture of the (*E*)- and (*Z*)-half esters which partially solidified on standing.

The crude half esters were hydrolysed by boiling (4 h) with 10% ethanolic KOH (1.6 dm^3). On cooling, the dipotassium salt of the diacid was filtered off and washed with a small amount of cold ethanol. Half the solvent was removed from the filtrate under reduced pressure using a rotatory evaporator and left to cool. On standing a second crop of crystals of the dipotassium salt of the diacid separated and this was filtered off and washed with a small quantity of cold ethanol. The dark brown filtrate was abandoned. The combined potassium salts were suspended in water (500 cm^3) and acidified with conc. HCl. The liberated acids were extracted into ether, the combined ether extracts were dried ($MgSO_4$), filtered and ether removed. The residual diacids were treated with a solution of acetyl chloride (350 cm^3) in dichloromethane (350 cm^3) and left for 3 h. Solvent was removed and the (9:1) mixture of (*E*)- and (*Z*)-fulgides **4a** and **6a** (210 g) was crystallised from hot acetone (2.1 dm^3; 10 cm^3 g^{-1}). The first crop of crystals was the (*E*)-fulgide **4a** (100 g), m.p. 180 °C. The volume of the filtrate was reduced to a third giving further crops of crystals, including the (*Z*)-fulgide **6a**.

The (*Z*)-fulgide **6a** can be isomerized to the (*E*)-fulgide by heating in toluene in the presence of a catalytic amount of 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU). In one experiment, (*Z*)-fulgide (**6a**) (70 g) in toluene (250 cm^3) containing DBU (0.3 g) was boiled (3 h). Solvent was removed and the residue crystallised from acetone (700 cm^3) giving (*E*)-fulgide **4a** (55 g) and a second crop of the *E*/*Z* mixture (12 g).

(*E*)-Fulgide **4a** was obtained as near colourless needles from ethanol, m.p. 184 °C (Found: C, 74.7, H, 6.8%; M$^+$, 352. $C_{22}H_{24}O_4$ requires C, 75.0; H, 6.86%; M, 352); ν_{max}/cm^{-1} 1807 (m) and 1767 (s). (*Z*)-Fulgide **6a** was obtained as pale yellow cubes from propan-2-ol, m.p. 168–169 °C (Found: C, 75.2; H, 6.8%; M$^+$, 352).

(E)-*Adamantylidene*[1-(2,5-*dimethyl*-3-*furyl*)*ethylidene*]-N-*phenylsuccinimide* (**4b**).—Ethyl (*Z*)-adamantylidene[1-(2,5-dimethyl-3-furyl)ethylidene]succinate (8 g, 0.02 mol) was added to a solution of anilinomagnesium bromide (0.1 mol) in tetrahydrofuran (THF) (200 cm^3). The mixture was boiled (2 h) cooled and poured into dilute hydrochloric acid. THF was removed under reduced pressure and the solid extracted with ether, dried, filtered and solvent removed, leaving the crude succinamic acid (7.3 g). The latter (1 g) was heated with acetyl chloride (25 cm^3) and the solvent removed. The residue, on recrystallisation from ethanol, gave the imide **4b** as colourless plates (0.35 g, 35% yield), m.p. 252–253 °C (Found: C, 78.8, H, 6.8. $C_{28}H_{29}NO_3$ requires C, 78.7, H, 6.84%); λ_{max} 335 nm, ε 7100 dm^3 mol^{-1} cm^{-1}.

(E)- and (Z)-*Adamantylidene*[1-(2-*methyl*-3-*furyl*)*ethylidene*]-*succinic Anhydrides* (**4c** *and* **5c**).—Treatment of diethyl adamantylidenesuccinate (27 g, 0.1 mol) with 3-acetyl-2-methylfuran (11 g, 0.1 mol) in toluene (100 cm^3) in the presence of sodium hydride (as a 60% dispersion in oil; 9 g, 0.22 mol) in toluene (100 cm^3), using the procedure described above, gave a mixture of (*E*)- and (*Z*)-fulgides which was crystallised from chloroform–light petroleum (b.p. 60–80 °C). The first crop of crystals was the pure (*E*)-fulgide **4c**, colourless needles (6.5 g, 21% yield), m.p. 197–198 °C (Found: C, 74.9, H, 6.55. $C_{21}H_{22}O_4$ requires C, 74.5; H, 6.55%). λ_{max} 330 nm, ε 6600 dm^3 mol^{-1} cm^{-1}.

The filtrates were evaporated and the residual oil was dissolved in propan-2-ol. Colourless cubes of the (*Z*)-fulgide **6c** separated on slow evaporation and these were recrystallised from propan-2-ol (0.2 g), m.p. 175–176 °C (Found: C, 74.5; H, 6.55%), λ_{max} 346 nm, ε 9550 dm^3 mol^{-1} cm^{-1}.

(E)-*Adamantylidene*[1-(2-*methyl*-3-*furyl*)*ethylidene*]-N-*methylsuccinimide* (**4d**).—(*E*)-Fulgide **4c** (1.7 g) was treated with a 25% aqueous solution of methylamine. Cyclization of the resulting succinamic acid(s) with acetyl chloride gave the (*E*)-fulgimide **4d** in 10% yield (as colourless needles from propan-2-ol), m.p. 154 °C (Found: C, 75.2, H, 7.05; N, 4.0. $C_{22}H_{25}NO_3$ requires C, 75.2; H, 7.17; N, 4.0%), λ_{max} 350 nm, ε 5750 dm^3 mol^{-1} cm^{-1}.

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