Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Photochemistry and Photobiology A: Chemistry 177 (2006) 170–176
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Studies on photochromic benzimidazol[1,2*a*]pyrrolidin-2-ones from the condensation of 2-methyl-3-benzothienylethylidene-(isopropylidene)succinic anhydride with 1,2-diaminobenzenes

Mahmut Kose *, Ersin Orhan

Department of Chemistry, Faculty of Art and Science, Zonguldak Karaelmas University, 67100 Zonguldak, Turkey

Received 15 April 2005; received in revised form 16 May 2005; accepted 20 May 2005
Available online 24 June 2005

Abstract

Novel photochromic benzimidazol[1,2*a*]pyrrolidin-2-ones, which give thermally stable highly coloured photochromes, have been synthesised by condensation of 2-methyl-3-benzothienylethylidene(isopropylidene)succinic anhydride with 1,2-diaminobenzene and its 4,5-dimethyl and 4,5-dimethoxy derivatives. The photochromic properties are reported.

Keywords: Photochromism; Fulgide; 1,2-Diaminobenzene; Benzimidazol[1,2*a*]pyrrolidin-2-one

1. Introduction

Certain derivatives of fulgides [1] and diarylethylenes [2] are known to give highly coloured thermally stable photochromes on exposure to ultraviolet light. The photochromes undergo the reverse reactions when irradiated with visible light. These photochromic compounds have attracted much attention due to their potential industrial applications, including re-writeable optical memory media [3]. For these applications, the photochromic compounds should possess fatigue resistance, particularly to hydrolysis of the anhydride group in these systems.

A useful starting point for improving fatigue resistance and enhancing the photochromic properties is to replace either of the oxygen atoms of the anhydride moiety with other functional groups.

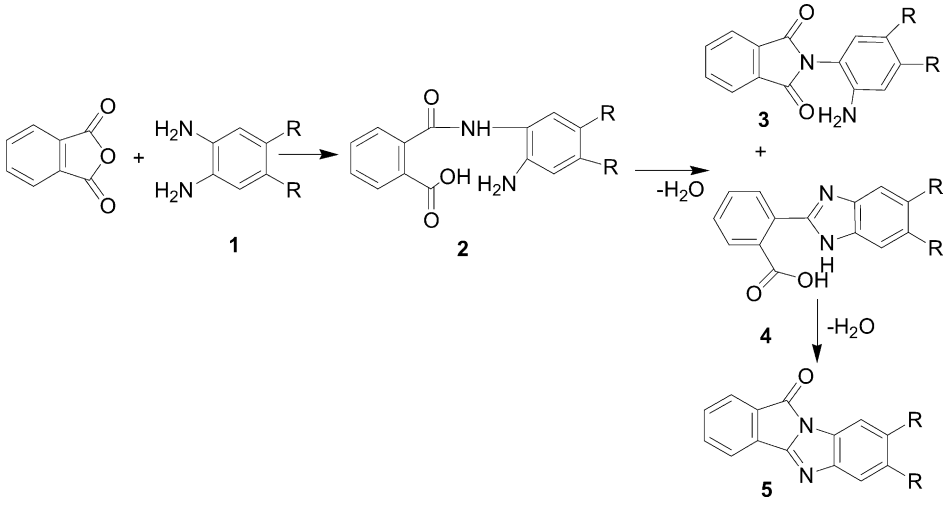
For example, Heller et al. [4] reported that replacement of one of the carbonyl groups in fulgides by a dicyanomethylene group (=C(CN)$_2$) gave a new class of thermally stable photochromic compounds which were near infrared active. Fulgides react with primary aliphatic and aromatic amines to give either fulgimides [5] or isofulgimides [6]. Fulgimides display excellent photochromic properties as well as much greater resistance to hydrolysis than their corresponding fulgides [7].

In 1972, Young [8] reported that phthalic anhydride condensed with 1,2-diaminobenzene (**1**, R = H) to give *N*-4-(*o*-aminophenyl)phthalamic acid (**2**), which eliminates water to form *N*-(*o*-aminophenylphthalimide (**3**) and 2-(*o*-carboxyphenyl)benzimidazole (**4**). At 200 °C, compounds (**3**) and (**4**) dehydrate to yield 11-*H*-isoindolo[2,1-*a*]benzimidazol-11-one (**5**) (Scheme 1).

In this paper, we report the syntheses of new photochromic benzimidazol[1,2*a*]pyrrolidin-2-one derivatives, obtained by condensation of *Z*-fulgides, *Z*-(2-methyl-3-benzothienylethylidene(isopropylidene)succinic anhydrides) (**14**) with 1,2-diaminobenzene (**1**, R = H), 4,5-dimethyl-1,2-diaminobenzene (**1**, R = Me) and 4,5-dimethoxy-1,2-diaminobenzene (**1**, R = MeO).

* Corresponding author. Tel.: +90 3722574010; fax: +90 3722574181.
E-mail address: mahmutkose@gmail.com (M. Kose).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.05.022



Scheme 1. The reaction of phthalic anhydride with 1,2-diaminobenzene (**1**, R = H).

2. Results and discussions

A mixture of *Z*- and *E*-fulgides (**14** and **15**) were prepared by the Stobbe condensation of 2-methyl-3-acetylbenzothiophene (**8**) with diethyl isopropylidene succinate (**11**), followed by hydrolysis and cyclisation with acetyl chloride (Scheme 2). On irradiation (365 nm), *Z*-fulgide (**14**) in toluene isomerised to *E*-fulgide (**15**), which photocyclised to the thermally stable red photochrome, 4,4*a*-dihydro-1,4,4,4*a*-tetramethyldibenzo[*b*,*d*]thiophene-2, 3-dicarboxylic anhydride (**16**). Photochrome (**16**) underwent the reverse reaction to fulgide (**15**) on exposure to white light (Scheme 4). The absorption spectra of (**14**) and its photostationary states of 365-nm light irradiation are shown in Fig. 1.

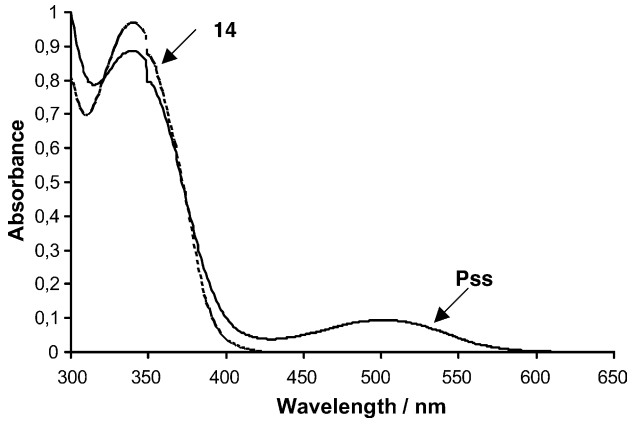


Fig. 1. Absorption spectral change of (**14**) in toluene (1×10^{-4} mol dm^{-3}) irradiated with 365 nm light.

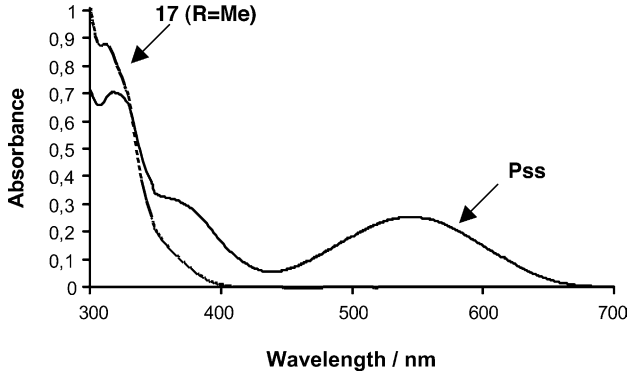
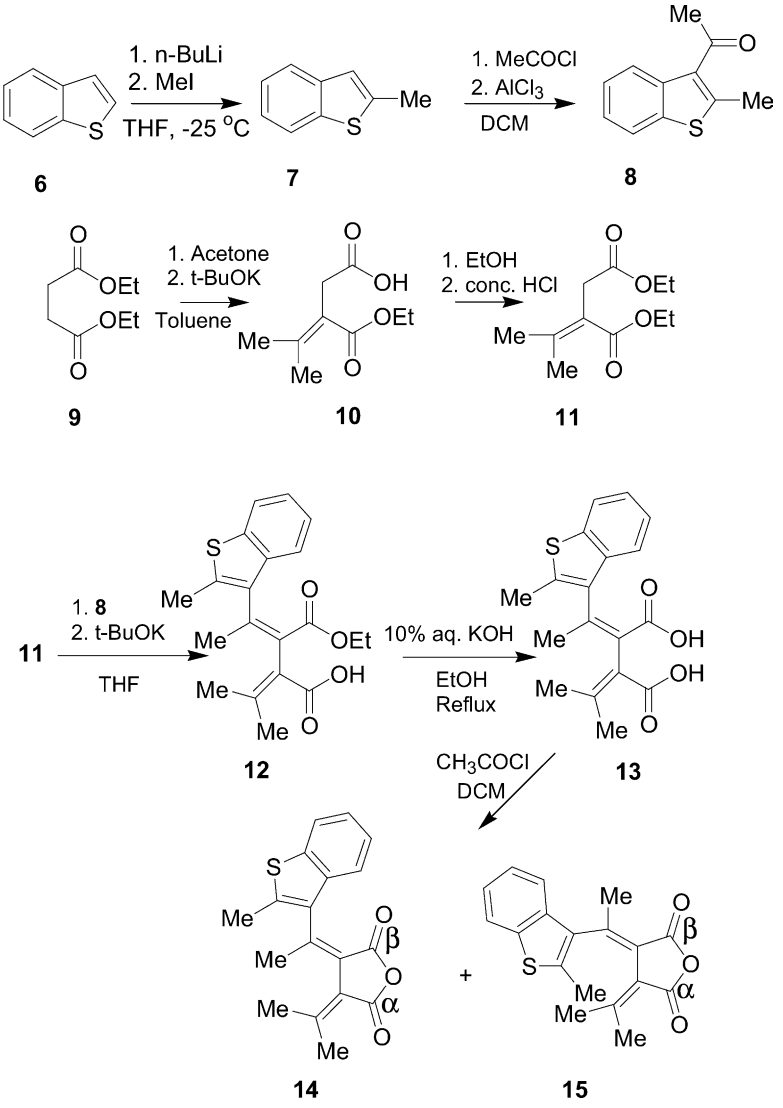


Fig. 2. Absorption spectral change of (**17**) (R = Me) in toluene (1×10^{-4} mol dm^{-3}) irradiated with 365 nm light.

Photochrome (**16**) in toluene showed a hypsochromic shift of its long wavelength absorption band (λ_{max} 500 nm) compared to the photochrome, 7,7*a*-dihydro-2,4,7,7, 7*a*-pentamethylbenzothiophene-5,6-dicarboxylic anhydride (λ_{max} 520 nm) in toluene [9], presumably due to affect of benzannelation on the dipolar character of the coloured form.

Because the non-symmetric *Z*-fulgide (**14**) was reacted with symmetrical diaminobenzene (**1**), two products were expected, depending on which carbonyl group of the anhydride ring was involved in the reaction (Scheme 3). If condensation occurred at the α carbonyl, an α-isomer would be formed and if the β carbonyl was involved, a β-isomer was formed. When *Z*-fulgide (**14**) and 1,2-diaminobenzene (**1**, R = H, Me or MeO) were boiled in toluene, three new spots were observed on TLC.[i] The upper two spots were photochromic. The component of the lowest spot could not be isolated or identified.

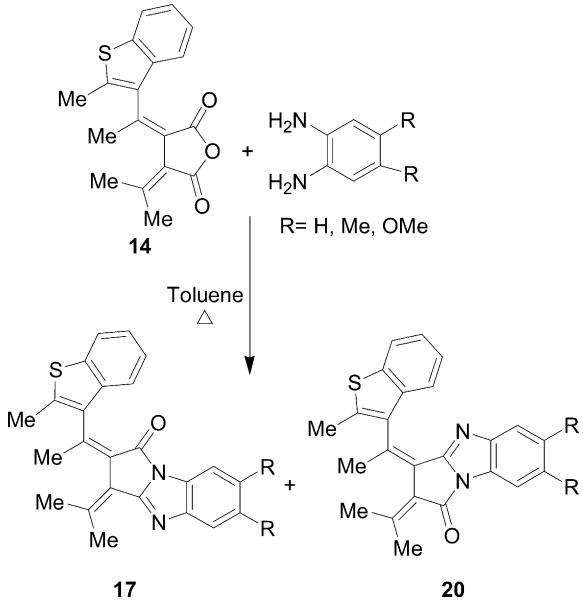
[i] The reaction of *Z*-fulgide (**14**) with 1,2-diaminobenzene (**1**) gave three new spots on TLC (in ethyl acetate (50%) and hexane). α-*Z*-Benzimidazol[1,2*a*]pyrrolidin-2-one (**17**, R = H) Rf 0.60; β-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**20**, R = H) Rf 0.73 and unidentified non-photochromic component Rf 0.18; α-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**17**, R = Me) Rf 0.66; β-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one(**20**, R = H) Rf 0.74 and unidentified photochromic component Rf 0.5; α-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**17**, R = MeO) Rf 0.47; β-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**20**, R = MeO) Rf 0.58; and unidentified photochromic component Rf 0.3.



Scheme 2. The synthesis of *Z*- and *E*-fulgides (**14**) and (**15**).

Table 1
Ultraviolet and visible spectral data for *E*- and *Z*-fulgides (**14** and **15**), their benzimidazol[1,2*a*]pyrrolidin-2-one derivatives (**17** and **20**) and photochromes (**16**, **19** and **22**)

Compounds	λ_{max}, O-form (nm)	ε_{max}, O-form ($mol^{-1}dm^3\ cm^{-1}$)	λ_{max}, at Pss (nm)	Absorbance (at Pss)
14	341	9490	–	–
15	340	9700	–	–
16	–	–	500	0.119
17 (R = H)	304	8830	–	–
19 (R = H)	–	–	538	0.188
20 (R = H)	310	9330	–	–
22 (R = H)	–	–	532	0.138
17 (R = Me)	314	4060	–	–
19 (R = Me)	–	–	545	0.253
20 (R = Me)	315	3750	–	–
22 (R = Me)	–	–	516	0.183
17 (R = MeO)	332	9700	–	–
19 (R = MeO)	–	–	567	0.305
20 (R = MeO)	351	6070	–	–
22 (R = MeO)	–	–	475	0.550



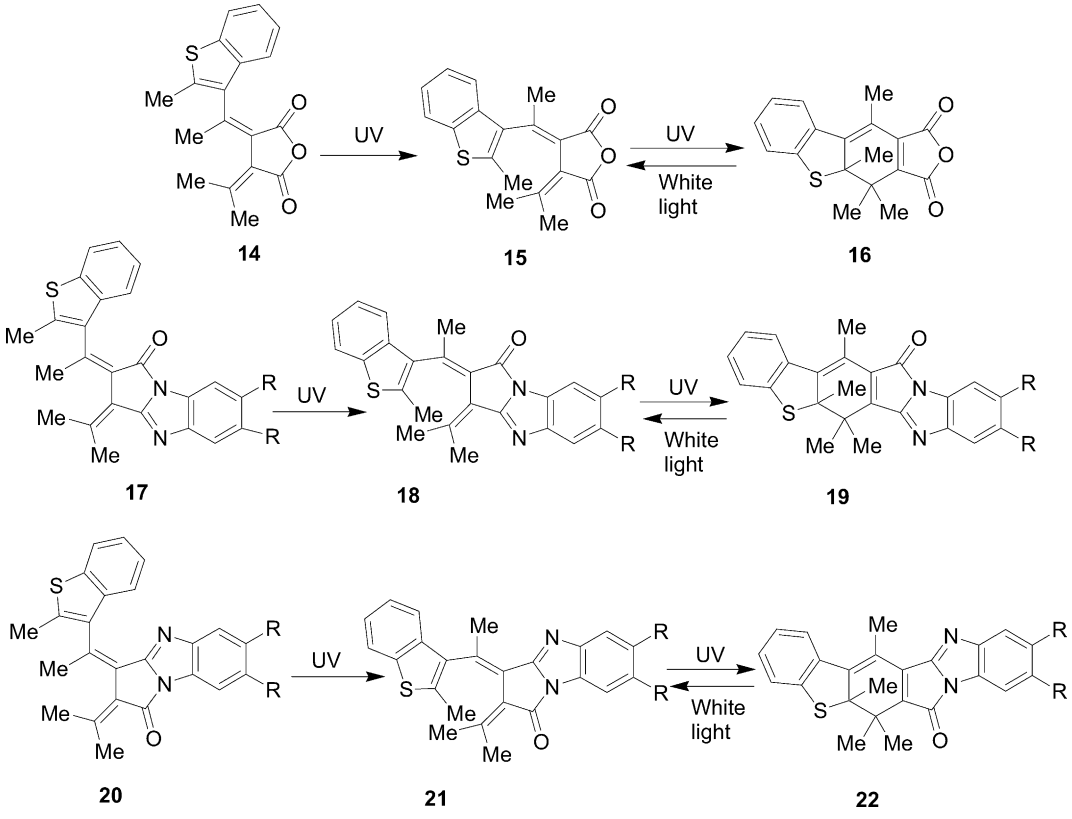
Scheme 3. Synthesis of novel photochromic benzo[*d*]pyrrolo[1,2-*a*]imidazol-1-one derivatives.

It was not possible to distinguish between α-*Z*- and β-*Z*-isomers (**17** and **20**) by ^{1}H NMR or FT-IR spectroscopy. The assignment was based on the different absorption maxima in the visible region of the α- and β-coloured forms (**19**) and (**22**). The UV–visible electronic transitions were calculated with ZINDO using INDO/S parameters [10] after optimizing geometry and predicted that the α-coloured form (**19**) should show a bathochromic shift of about 15 nm compared to the β-coloured form (**22**). On this basis, the photochrome with the higher absorption maximum in the visible region is tentatively assigned as the α-isomer.

Upon irradiation at 365 nm, the α-*Z*- and β-*Z*-isomers (**17**) and (**20**) in toluene isomerised to the *E*-α- and *E*-β-isomers (**18**) and (**21**), which cyclised to the thermally stable purple and orange α- and β-photochromes (**19**) and (**22**), respectively. On exposure to white light, α- and β-photochromes (**19**) and (**22**) ring opened to the *E*-α- and *E*-β-benzimidazol[1,2*a*]pyrrolidin-2-ones, respectively (Scheme 4). The absorption spectra of (**17**) (R = Me) and its photostationary states of 365-nm light irradiation are shown in Fig. 2. Ultraviolet and visible spectral data for E- and Z-fulgides (**14** and **15**), their benzimidazol[1,2a]pyrrolidin-2-one derivatives (**17** and **20**) and photochromes (**16**, **19** and **22**) are listed in Table 1.

The α-isomers of photochromes (**19**, R = H, Me or MeO) showed a 38–67 nm bathochromic shift of the absorption maxima in the visible region compared to the corresponding photochrome (**16**) of fulgide (**15**).

The quantum yields of the ring closure ($\Phi_{O\rightarrow C}$) by 365 nm light for *E*- and *Z*-fulgide (**14** and **15**) and their benzimidazol[1,2*a*]pyrrolidin-2-one derivatives (**17** and **20**)



Scheme 4. Photoreactions of fulgide (**14**) and benzo[*d*]pyrrolo[1,2-*a*]imidazol-1-one derivatives (**17**) and (**20**).

Table 2
Quantum yields for *E*- and *Z*-fulgide (**14** and **15**) and their benzimidazol[1,2*a*]pyrrolidin-2-one derivatives (**17** and **20**)

Compounds	($\Phi_{O \rightarrow C}$) at 365 nm
Z-fulgide (**14**)	0.32
E-fulgide (**15**)	0.39
α-*Z*-imidazole (**17**, R = H)	0.23
β-*Z*-imidazole (**20**, R = H)	0.35
α-*Z*-imidazole (**17**, R = Me)	0.16
β-*Z*-imidazole (**20**, R = Me)	0.20
α-*Z*-imidazole (**17**, R = MeO)	0.25
β-*Z*-imidazole (**20**, R = MeO)	0.38

were determined using the chemical actinometer Aberchrome 540 as described by Heller and Langan [11]. The quantum yields for colouring are listed in Table 2.

3. Experimental

3.1. General

The ^{1}H NMR spectra were recorded on Brucker 400 MHz spectrometers for samples in $CDCl_3$. The signals are expressed as parts per million down fields from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were measured using a Jasco FT-IR-300E spectrometer. Mass spectra were taken with a Thermo Finnigan mass spectrometer. Melting points were not corrected. UV–vis spectra were recorded on a UNicam UV2-100 spectrophotometer or a Varian Cary 100 Bio UV–vis spectrophotometer. Photochemical reactions at 365 nm in toluene were carried out in a 10 mm path length quartz cell using 8 W three-way UV lamp (Cole-Parmer). During the photoreaction, solutions in the cell were stirred. Chemical reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl and dichloromethane was distilled from CaH_2 immediately before use. Solutions were dried over anhydrous sodium sulphate. Flash column chromatographic separation was carried out on Merck Kieselgel 60 (230–400 mesh) using ethyl acetate and hexane as the eluent. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25 mm thick TLC plates.

3.2. Synthesis

3.2.1. 2-Methylbenzothiophene (*7*)

A hexane solution of butyl lithium (27.7 ml, 15% in hexane, 44.78 mmol) was added to a stirring solution of benzo[*b*]thiophene (**6**) (5 g, 37.25 mmol) in dry THF (100 ml) at −25 °C under a nitrogen. The resulting mixture was allowed to warm to 0 °C and then recooled to −25 °C. MeI (3.03 ml, 48.42 mmol) was added and the mixture was allowed to warm up to room temperature. After overnight stirring, the reaction was quenched by adding water; the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated aq. NaCl solution, dried with anhydrous Na_2SO_4 and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using ethyl acetate/hexane (10–20%) as the eluent, to give (**7**) (5.2 g, 94%).

3.2.2. 3-Acetyl-2-methylbenzothiophene (*8*)

A mixture of 2-methylbenzothiophene (**7**) (5 g, 33.78 mol), acetyl chloride (3.13 ml, 43.91 mol) and anhydrous aluminum chloride (5.40 g, 40.53 mol) in dry DCM (120 ml) was stirred overnight. After removing the DCM, equal amount of water and ethyl acetate was added. The organic layer was separated and washed with saturated aq. NaCl, dried with anhydrous Na_2SO_4 and the drying agent filtered off. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel using ethyl acetate/hexane (10–30%) as the eluent, to give (**8**) as a colourless solid (5.3 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (3H, s), 2.7 (3H, s), 7.21–7.25 (2H, m), 7.37 (1H, d, *J*/Hz = 2), 7.38 (1H, d, *J*/Hz = 3). LRMS (EI, 70 eV) *m*/*z* (rel intensity), 190 (M^+, 7), 175 (12), 152 (18), 149 (38), 135 (34), 121 (42), 109 (35), 95 (62), 81 (100), 67 (79). Found: *m*/*z* 190.1604. $C_{11}H_{10}OS$: M, 190.26.

3.2.3. Diethyl isopropylidenesuccinate (*11*) [12]

A mixture of acetone (12.65 ml, 172 mmol), diethyl succinate (32 g, 189 mol) and potassium *tert*-butoxide (21.2 g, 189 mol) in toluene was stirred overnight. After work up, ethyl isopropylidenesuccinic half ester was obtained as red oil. Esterification was carried out using concentrated hydrochloric acid (10 ml) and ethanol (125 ml) to give diethyl isopropylidenesuccinate as a colourless oil (19.5 g, 76%), after purification by flash chromatography using ethyl acetate/hexane as a eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.1 (6H, t, *J*/Hz = 8), 1.7 (3H, s), 1.98 (3H, s), 3.19 (2H, s), 4.02 and 3.96 (4H, two q, *J*/Hz = 8).

3.2.4. Z- and E-2-methyl-3-benzothienylethylidene-(isopropylidene)succinic anhydride (*14*) and (*15*)

A mixture of 3-acetyl-2-methylbenzothiophene (**8**) (1 g, 5.25 mmol), diethyl isopropylidenesuccinate (**11**) (1.12 g, 5.3 mmol) and potassium *tert*-butoxide (0.70 g, 6.3 mmol) in THF (40 ml) was stirred overnight. After work up, half ester (**12**) was obtained. It was hydrolyzed to the diacids (**13**) and cyclised to give (**14**) and (**15**) which were separated and purified by column chromatography using ethyl acetate/hexane as a eluent.

Z-Fulgide (**14**) (0.26 g, 19%, overall yield from 11), pale yellow crystals, mp 173–176 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (3H, s), 2.16 (3H, s), 2.46 (3H, s), 2.5 (3H, s), 7.28–7.36 (3H, m), 7.9 (1H, dd, *J*/Hz = 5.9, 1.3). LRMS (EI, 70 eV) *m*/*z* (rel intensity), 312 (M^+, 22), 223 (56), 198 (56), 165 (100), 138 (11), 97 (22). Found: *m*/*z* 312.2451. Calcd for $C_{18}H_{16}O_3S$: M, 312.082. IR (KBr) ν/cm^{-1} 2924, 1763, 1621, 1435, 1372, 1218, 1130, 1009, 918, 740, 620.

E-Fulgide (**15**) (0.19 g, 12%, overall yield from **11**), pale yellow crystals, mp 121–124 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (3H, s), 2.15 (3H, s), 2.37 (3H, s), 2.42 (3H, s), 7.19–7.28 (3H, m), 7.69 (1H, dd, *J*/Hz = 10.5, 3). LRMS (EI, 70 eV) *m*/*z* (rel intensity), 312 (M^+, 80), 286 (41), 265 (82), 240 (40), 226 (20), 188 (66), 165 (80), 152 (100), 131 (20). Found: *m*/*z* 312.1360. $C_{18}H_{16}O_3S$: M, 312.082. IR (KBr) ν/cm^{-1} 2927, 1757, 1614, 1435, 1227, 926.

3.2.5. Synthesis of benzimidazol[1,2a]pyrrolidin-2-one derivatives (R = H) (17) and (20)

A solution of *Z*-fulgide (**14**) (300 mg, 96 mmol) and 1,2-diaminobenzene (190 mg, 0.99 mmol) in 30 ml toluene was refluxed for 30 h under a nitrogen atmosphere. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (5–40%) as the eluent, to give two photochromic isomers (**17**, R = H) (89 mg, 22%), (**20**, R = H) (102 mg, 26.4%) and unidentified red isomer (175 mg).

Compound (**17**, R = H): mp 168–170 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (3H, s), 2.25 (3H, s), 2.42 (3H, s), 2.59 (3H, s), 7.15–7.27 (4H, m), 7.3–7.4 (2H, m), 7.6–7.77 (2H, m,). LRMS (EI, 70 eV) *m*/*z* (rel intensity), 384 (M^+, 11), 369 (18), 355 (12), 326 (8), 283 (5), 255 (11), 213 (11), 185 (19), 149 (49), 129 (43), 97 (70), 81 (100). Found: *m*/*z* 384.1122. Calcd for $C_{24}H_{20}N_2OS$: M, 384.1296. IR (KBr) ν/cm^{-1} 2924, 1738, 1616, 1527, 1442, 1372, 1318, 1265, 1092, 1025, 805, 742, 610.

Compound (**20**, R = H): mp 144–146 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21 (3H, s), 2.27 (3H, s), 2.42 (3H, s), 2.84 (3H, s), 7.1–7.4 (4H, m), 7.68 (1H, d, *J*/Hz = 7.4), 7.72 (1H, dd, *J*/Hz = 6.9, 1.5). 7.8 (1H, dd, *J*/Hz = 7.46, 2.4). 7.92 (1H, dd, *J*/Hz = 8, 1.1). LRMS (EI, 70 eV) *m*/*z* (rel intensity), 384 (M^+, 50), 339 (30), 303 (50), 224 (6), 186 (89), 156 (100), 115 (70), 87 (20), 59 (61). Found: *m*/*z* 384.1649. Calcd for $C_{24}H_{20}N_2OS$: M, 384.1296. IR (KBr) ν/cm^{-1} 2959, 1732, 1615, 1532, 1437, 1375, 1312, 1264, 1092, 804, 745.

3.2.6. Synthesis of benzimidazol[1,2a]pyrrolidin-2-one derivatives (R = Me) (17) and (20)

A solution of *Z*-fulgide (**14**) (450 mg, 1.44 mmol) and 4,5-dimethyl-1,2-diaminobenzene (235 mg, 1.72 mmol) in 60 ml toluene was refluxed for 18 h under a nitrogen atmosphere. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (5–40%) as the eluent, to give three photochromic isomers (**17**, R = Me) (65 mg, 11%), (**20**, R = Me) (162 mg, 21%) and unidentified red isomer (63 mg).

Compound (**17**, R = Me): mp 201–203 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (3H, s), 2.19 (3H, s), 2.23 (3H, s), 2.26 (3H, s), 2.48 (3H, s), 2.56 (3H, s), 7.1–7.2 (2H, m), 7.3 (1H, dd, *J*/Hz = 5.7, 3.4), 7.43 (1H, s), 7.44 (1H, s), 7.7 (1H, dd, *J*/Hz = 6.2, 3.1) LRMS (EI, 70 eV) *m*/*z* (rel intensity), 412 (M^+, 73), 372 (64), 255 (36), 141 (37), 129 (10), 93 (100). Found: *m*/*z* 412.1644. Calcd for $C_{26}H_{24}N_2OS$: M, 412.1609. IR (KBr) ν/cm^{-1} 2959, 1740, 1614, 1528, 1446, 1362, 1262, 1090, 1025, 804.

Compound (**20**, R = Me): mp 137–139 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (3H, s), 2.22 (3H, s), 2.31 (3H, s), 2.34 (3H, s), 2.40 (3H, s), 2.47 (3H, s), 7.1–7.4 (4H, m), 7.55 (1H, d, *J*/Hz = 8), 7.7 (1H, d, *J*/Hz = 8) LRMS (EI, 70 eV) *m*/*z* (rel intensity), 412 (M^+, 46), 397 (76), 369 (100), 353 (63), 327 (50), 239 (17), 215 (8), 174 (11), 129 (13), 111 (38), 69 (21). Found: *m*/*z* 412.1873. Calcd for $C_{26}H_{24}N_2OS$: M, 412.1609. IR (KBr) ν/cm^{-1} 2960, 1730, 1625, 1538, 1443, 1367, 1262, 1090, 1029, 805, 614.

3.2.7. Synthesis of benzimidazol[1,2a]pyrrolidin-2-one derivatives (R= MeO) (17) and (20)

A solution of *Z*-fulgide (**14**) (423 mg, 1.35 mmol) and 4,5-dimethoxy-1,2-diaminobenzene (340 mg, 2.03 mmol) in 40 ml toluene was refluxed for 6 h under a nitrogen atmosphere. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (10–40%) as the eluent, to give three photochromic isomers (**17**, R = MeO) (68 mg, 12%), (**20**, R = MeO) (60 mg, 10%) and unidentified photochromic red isomer (78 mg).

Compound (**17**, R = MeO): mp 122–124 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 (3H, s), 2.32 (3H, s), 2.49 (3H, s), 2.62 (3H, s), 3.8 (3H, s), 3.9 (3H, s), 7.1–7.4 (5H, m), 7.7 (1H, m), LRMS (EI, 70 eV) *m*/*z* (rel intensity), 444 (M^+, 100), 399 (26), 353 (20), 340 (63), 297 (45), 235 (38), 225 (13), 185 (32), 147 (6), 57 (13). Found: *m*/*z* 444.1540. Calcd for $C_{26}H_{24}N_2O_3S$: M, 444.1508. IR (KBr) ν/cm^{-1} 2921, 1705, 1627, 1538, 1436, 1269, 1103, 1021, 803, 744.

Compound (**20**, R = MeO): mp 108–111 °C (AcOEt/hexane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (3H, s), 2.18 (3H, s), 2.37 (3H, s), 2.47 (3H, s), 3.7 (3H, s), 3.8 (3H, s), 6.86 (1H, s), 7.27 (1H, s), 7.15 (2H, m), 7.3 (1H, m), 7.7 (1H, dd, *J*/Hz = 6.0, 2). LRMS (EI, 70 eV) *m*/*z* (rel intensity), 444 (M^+, 51), 429 (84), 401 (100), 385 (72), 371 (33), 356 (27), 329 (22), 314 (15), 262 (8), 235 (13), 149 (9), 129 (14), 67 (18). Found: *m*/*z* 444.1460. Calcd for $C_{26}H_{24}N_2O_3S$: M, 444.1508. IR (KBr) ν/cm^{-1} 2921, 1729, 1624, 1539, 1470, 1374, 1280, 1186, 1107, 1023, 911, 835, 740.

Acknowledgements

The authors are grateful to The Scientific and Technical Research Council of Turkey (TUBITAK) for the financial support of this work (Grant No.: TBAG-2477 (104T088). The authors also thank Burak Coban for carrying out the calculations.

References

[1] (a) Y. Yokoyama, Chem. Rev. 100 (2000) 1717;
(b) Y. Yokoyama, M. Kose, J. Photochem. Photobiol. A Chem. 166 (2004) 9;

(c) Y. Yokoyama, M. Kose, in: W. Horspool, F. Lenci (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, second ed., CRC Press, 2004, pp. 1–13 (Chapter 86).
[2] (a) M. Irie, Chem. Rev. 100 (2000) 1685;
(b) M. Kose, M. Shinoura, Y. Yokoyama, Y. Yokoyama, J. Org. Chem. 69 (2004) 8403.
[3] H.G. Heller, in: W.H. Horspool, P.S. Song (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, 1994, pp. 173–183 (Chapter 13).
[4] H.G. Heller, D.S. Hughes, M.B. Hursthouse, K.V.S. Koh, J. Chem. Soc. Chem. Commun. (1994) 2713.
[5] Y. Liang, A.S. Dvornikov, P.M. Rentzepis, Tetrahedron Lett. 40 (1999) 8067.
[6] H.G. Heller, K. Koh, M. Kose, N. Rowles, Mol. Cryst. Liq. Cryst. 297 (1997) 73.
[7] R. Matsushima, H.J. Sakaguchi, Photochem. Photobiol. A Chem. 108 (1997) 239.
[8] P.R. Young, J. Heterocycl. Chem. 9 (1972) 371.
[9] H.G. Heller, D.S. Hughes, M.B. Hursthouse, N. Rowles, J. Chem. Soc. Chem. Commun. (2000) 1397.
[10] J.E. Ridley, M.Z. Zerner, Theor. Chim. Acta 32 (1973) 111 (INDO/S calculations were run on a CaChe system).
[11] H.G. Heller, R. Langan, J. Chem. Soc., Perkin Trans. II (1981) 341.
[12] C.G. Overberger, C.W. Roberts, J. Am. Chem. Soc. 71 (1949) 3618.