Comparison of photochromic properties and thermal stabilities of fulgide, fulgimide, and benzimidazole[1,2-a]pyrrolidine-2-one derivatives

Mahmut KÖSE*, **Ersin ORHAN**

Department of Chemistry, Faculty of Arts and Science, Zonguldak Karaelmas University,
Zonguldak, 67100, TURKEY
e-mail: mahmutkose@gmail.com

New thermally stable photochromic fulgimides and benzimidazole[1,2-a]pyrrolidin-2-one derivatives of furylfulgide and thienylfulgide were prepared and their photochromic properties were investigated. Thermal stabilities of some of the new isomers in an alcoholic solution and in PMMA (poly(methyl methacrylate)) polymer films, and pyrolytic behaviors in inert atmosphere with TGA were compared.

The colored form of fulgimide and that of benzimidazole[1,2-a]pyrrolidin-2-one derivatives showed large bathochromic shifts for visible absorption maximum compared with the colored form of corresponding fulgides. The imides and benzimidazole[1,2-a]pyrrolidin-2-one derivatives of fulgide displayed better thermal stability than corresponding fulgides.

Key Words: Photochromism, fulgide, fulgimide, benzimidazole[1,2-a]pyrrolidin-2-one, thermal stability, quantum yield.

Introduction

Photochromic compounds that undergo reversible color change by photoirradiation attract much attention because of their potential applications for optical devices. Among the photochromic compounds, fulgides[1,2] and diarylethenes[3,4] are regarded as the best candidates, because of their thermal stabilities and fatigue resistance. Fulgimides,[5−8] which are imide derivatives of fulgides, exhibit excellent photochromic properties as well as their highly resistant property to solvolytic degradation compared to the fulgides. Although there are many

---

*Corresponding author

experimental studies on the preparation of new fulgides and investigations of their photochromic properties, relatively few studies have focused on their thermal stabilities.

In a previous paper,[9] we reported photochromic benzimidazole[1,2-a]pyrrolidine-2-one derivatives obtained by condensation of Z-fulgide with 1,2-diaminobenzenes. In the present paper, the preparation of new thermally stable photochromic fulgimides and benzimidazole[1,2-a]pyrrolidine-2-one derivatives of fulgide and their photochromic properties are presented. Thermal stabilities for some of the new compounds in an alcoholic solution and in PMMA (poly(methyl methacrylate)) and pyrolytic behaviors in inert atmosphere are also compared.

Experimental

General methods

All commercially available materials were used without further purification. The ^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer for samples in $CDCl_3$. The signals are expressed as parts per million downfield from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; 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 over CaH_2 immediately before use. Solutions were dried over anhydrous sodium sulfate. Flash column chromatographic separation was carried out on Merck Kieselgel 60 (230-400 mesh) using ethyl acetate and hexane as the eluents. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25-mm thick TLC plates.

PMMA (poly(methyl methacrylate)) films

A mixture of photochromic isomer (20% w/w) and PMMA polymer (80% w/w) was dissolved in THF and the mixture were placed in a 5 cm diameter glass petri dish and the solvent was evaporated overnight at room temperature. The film thickness was measured by a digital caliper and found to be 0.12 mm.

Thermogravimetric analyses (TGA)

The TGA analyses were carried out using a PL 1500 TGA apparatus under a nitrogen flow (50 mL/min) at temperatures ranging from 25 to 900 °C. The heating rate was 10 °C/min and the initial sample weights were approximately 1 mg for **2c-E** and 6 mg for **4-E**.

Synthesis

Fulgide **1-E** and **3-E** were prepared according to the reported method.[10,11]

(E)-3-(dicyclopropylmethylene)-4-(1-(2,5-dimethylfuran-3-yl)ethylidene)-1-(thiazol-2-yl)pyrrolidine-2,5-dione (2a-E)

A mixture of fulgide (0.5 g, 1.60 mmol), 2-aminothiazole (0.17 g, 1.76 mmol), and hexamethyldisilazane (HMDS) (0.33 mL, 1.60 mmol) in dry toluene (35 mL) was refluxed under nitrogen with a Dean-Stark adaptor for 11 h. The progress of the reaction was monitored by TLC. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using hexane and ethyl acetate as eluents. Pure fulgimide was obtained by re-crystallization. Yield 0.37 g (58%), mp 131-134 °C (AcOEt/hexane). ^{1}H-NMR (400 MHz, CDCl$_3$) (δ_H ppm) 7.62 (1H, d, J=3.5 Hz, thiazole-H), 6.59 (1H, d, J=3.5 Hz, thiazole-H), 5.88 (1 H, s, furyl-H), 2.18 (3H, s), 2.19 (3H, s), 1.84, (3H, s), 2.76 (2H, m), 0.91-0.38 (8 H, m). IR (KBr) v_{max} (cm^{-1}) 2924, 1708 (C=O), 1617 (C=O), 1504, 1439, 1331, 1263, 1182, 1094, 922, 804, 724, 617. MS (EI, 70 eV) m/z (rel intensity), 394 (M$^+$, 78), 351 (78), 337 (30), 294 (38), 251 (42), 237 (48), 223 (44), 195 (32), 152 (44), 127 (70), 95 (78), 81 (100). Found: m/z 394.0435. Calculated: C$_{22}$H$_{22}$N$_2$O$_3$S: M, 394.1351.

(E)-1-(benzo[d]thiazol-2-yl)-3-(dicyclopropylmethylene)-4-(1-(2,5-dimethylfuran-3-yl)ethylidene)pyrrolidine-2,5-dione (2b-E)

A mixture of fulgide (1.5 g, 4.80 mmol), 2-aminobenzothiazole (0.8 g, 5.32 mmol), and hexamethyldisilazane (HMDS) (1.80 mL, 8.60 mmol) in dry toluene (60 mL) was refluxed under nitrogen with a Dean-Stark adaptor for 11 h. The progress of the reaction was monitored by TLC. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using hexane and ethyl acetate as eluents. Pure fulgimide was obtained by re-crystallization. Yield 0.67 g (34%), mp 164-166 °C (AcOEt/hexane). ^{1}H-NMR (400 MHz, CDCl$_3$) (δ_H ppm) 1.03 (2H, m), 0.52-0.53 (8 H, m), 2.12 (3H, s), 2.19 (3H, s), 2.24 (3H, s), 5.92 (1H, s, furyl-H), 7.28-8.0 (4H, m, benzothiazole-H). IR (KBr) v_{max} (cm^{-1}) 3003, 2903, 1709 (C=O), 1623 (C=O), 1579, 1507, 1434, 1334, 1274, 1226, 1168, 1026, 934, 761, 619. MS (EI, 70 eV) m/z (rel intensity), 444 (M+, 100), 401 (78), 373 (18), 349 (36), 323 (26), 251 (28), 223 (22), 177 (54), 151 (10), 95 (5). Found: m/z 444.1133. Calculated: C$_{26}$H$_{24}$N$_2$O$_3$S: M, 444.1508.

(4E)-1-(1H-benzimidazol-2-yl)-3-(dicyclopropylmethylene)-4-[1-(2,5-dimethyl-3-furyl)ethylidene]pyrrolidine-2,5-dione (2c-E)

A mixture of fulgide (2 g, 6.61 mmol) and 2-aminobenzimidazole (1.02 g, 7.69 mmol) in dry toluene (30 mL) was refluxed under nitrogen with a Dean-Stark adaptor for 26 h. The progress of the reaction was monitored by TLC. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using hexane and ethyl acetate as eluents. Pure fulgimide was obtained by re-crystallization. Yield 0.43 g (16%), mp 195-198 °C (AcOEt/hexane). ^{1}H-NMR (400 MHz, CDCl$_3$) (δ_H ppm) 0.2-1.1 (9H, m), 2.10 (3H, s), 2.23 (3H, s), 2.66 (3H, s), 3.18 (1H, br, s) 5.88 (1H, s, furyl-H), 7.26 (2H, br, s, Ar-H), 7.65 (2H, br, s, Ar-H). IR (KBr) v_{max} (cm^{-1}) 3007, 2919, 1752 (C=O), 1699, 1618, 1590, 1533, 1444, 1390, 1341, 1298, 1270, 1166, 1126, 1025, 929, 868. MS (EI, 70 eV) m/z (rel intensity), 427 (M+, 100), 368 (82), 332 (48), 292 (10), 255 (16), 160 (80), 134 (14), 81 (8). Found: m/z 427.1511. Calculated: C$_{26}$H$_{25}$N$_3$O$_3$: M, 427.1896.

(E)-3-(dicyclopropylmethylene)-4-(1-(2,5-dimethylfuran-3-yl)ethylidene)-1-(2-hyd-roxyphenyl)pyrrolidine-2,5-dione (2d-E)

A mixture of fulgide (1 g, 3.20 mmol) and 2-aminophenol (0.42 gr, 3.84 mmol) in dry toluene (35 mL) was refluxed under nitrogen with a Dean-Stark adaptor for 23 h. The progress of the reaction was monitored by TLC. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using hexane and ethyl acetate as eluents. Pure fulgimide was obtained by re-crystallization. Yield 0.59 g (46%), mp 102-104 $^\circ$C (AcOEt/hexane). ^{1}H-NMR (400 MHz, CDCl$_3$) (δ_H ppm) 0.2-1.2 (9H, m), 2.06 (3H, s), 2.15 (3H, s), 2.55 (3H, s), 3.11 (1H, br, s) 3.6 (1H, s, OH), 5.8 (1H, s, furyl-H). 6.85-7.3 (4H, m, Ar-H). IR (KBr) $\upsilon_{\max}$ (cm^{-1}) 3408, 3001, 2923, 1738 (C=O), 1684, 1603, 1510, 1455, 1390, 1278, 1179, 1028, 989, 926. MS (EI, 70 eV) m/z (rel intensity), 403 (M+, 86), 362 (100), 342 (26), 240 (28), 225 (34), 197 (44), 169 (18), 124 (16) 109 (8). Found: m/z 403.0938. Calculated: C$_{25}$H$_{25}$NO$_4$: M, 403.1784.

(2E)-6,7-dimethyl-3-(1-methylethylidene)-2-[1-(2-methyl-5-phenyl-3-thienyl)ethyli-dene]-2,3-dihydro-1H-pyrrolo[1,2-a]benzimidazol-1-one (4-E)

A solution of E-fulgide (**3-E**) (1 g, 2.95 mmol) and 4,5-dimethyl-1,2-diaminobenzene (0.48 g, 3.54 mmol) in 40 mL of toluene was refluxed for 28 h under a nitrogen atmosphere. The progress of the reaction was monitored by TLC. After removing the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel using ethyl acetate/hexane (5%-30%) as the eluents to give 2 photochromic isomers. Although the first photochromic isomer **4-E** (0.38 g, 29%) was obtained in pure form, we could not isolate the second one. (The C-form of unidentified photochromic isomer sowed λ: 589 nm). **4-E**: (0.38 g, 29%), mp 186-189 $^\circ$C (AcOEt/hexane). ^{1}H-NMR (400 MHz, CDCl$_3$) (δ_H ppm)= 1.38 (3H, s), 2.24 (3H, s), 2.37 (3H, s), 2.39 (3H, s), 2.44 (3H, s), 2.75 (3H, s) 7.15 (1H, s, thienyl-H) 7.25-7.76 (9H, m, Ar-H). IR (KBr) $\upsilon_{\max}$ (cm^{-1}) 3100, 2936, 1730 (C=O), 1631, 1598, 1536, 1498, 1450, 1370, 1319, 1260, 1233, 1163, 1083, 1025, 901, 858, 802, 753. ^{13}C-NMR (100 MHz, CDCl$_3$) (δ_{13C} ppm) 15.02, 20.31, 20.49, 21.80, 23.54, 24.66 (Me); 113.45, 120.36, 123.72, 125.47, 127.62, 128.95 (Ar, CH); 120.01, 126.41, 129.25, 133.63, 133.78, 134.13, 136.26, 141.43, 141.69, 143.76, 145.80, 146.74 (C); 156.26 (C=N) and 162.87 (C=O).

Results and discussion

Fulgimides **2(a-d)-E** were prepared by refluxing fulgide **1-E** with aromatic amines in the presence of hexam-ethyldisilazane (HMDS) in dry toluene using a Dean-Stark adaptor (Scheme 1). Under similar conditions fulgide **3-E** when reacted with 4,5-dimethyl-1,2-diaminobenzene in dry toluene gave photochromic benzimidazole[1,2-a]pyrrolidine-2-one derivative **4-E** in 29% yield (Scheme 2).
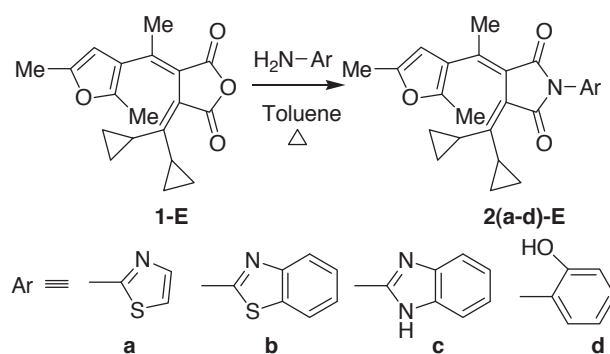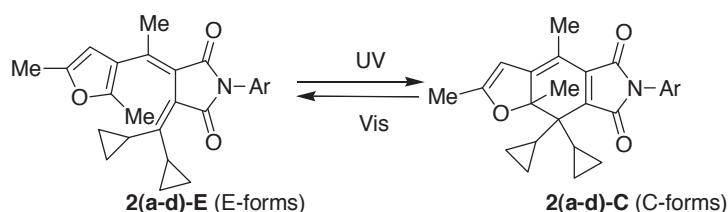
Scheme 1. Synthesis of E-fulgimides **2(a-d)-E**.
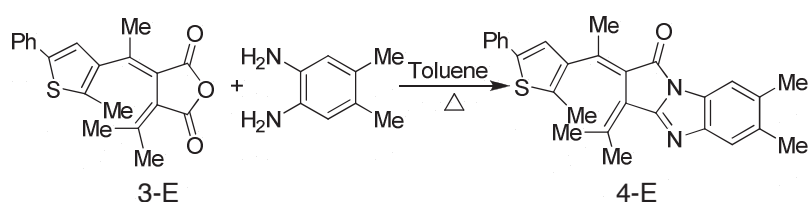
Scheme 2. Synthesis of benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E**.

On irradiation (365 nm), the E-fulgimides **2(a-d)-E** in toluene cyclized to the thermally stable red photochromes **2(a-d)-C**. The red photochromes **2(a-d)-C** underwent reverse reactions on exposure to white light (Scheme 3).

Scheme 3. Photoreactions of E-fulgimide **2(a-d)-E**.

UV-Vis spectra of the compound **2c-E** and its ring-closed form **2c-C** in toluene (1×10^{-4} M) are shown in Figure 1. The ring-closed forms **2a-C**, **2b-C**, **2c-C**, and **2d-C** showed λ_{max} at 533, 541, 540, and 523 nm, respectively, which represented 9 to 27 nm bathochromic shift of the absorption bands compared to the corresponding colored form of the parent fulgide **1-C** ($\lambda_{max} = 514$ nm). The C-forms of N-benzo-annulatedfulgimide **2(a-c)-C** displayed similar λ_{max} but were longer than those of the N-phenolfulgimide **2d-C**. The reason why the benzo-annulated aromatic rings caused bathochromic shifts longer than the phenol ring is not clear.
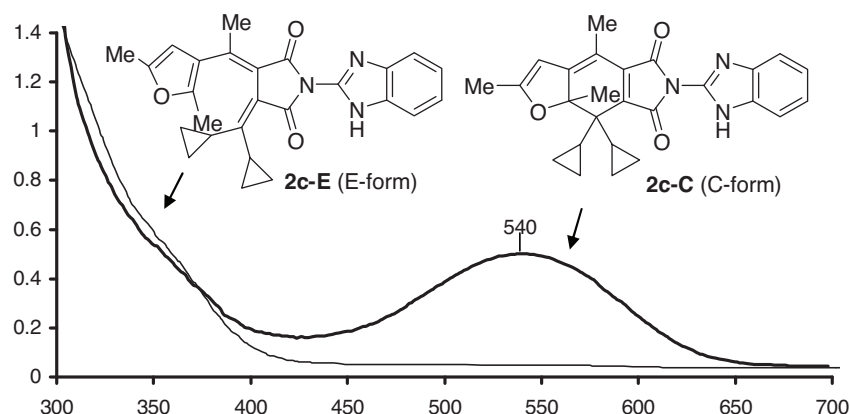
Figure 1. Photoreactions of the fulgimide **2c-E** [in toluene (1×10^{-4} mol dm^{-3}) at $\lambda = 365$ nm].

On irradiation at 365 nm, the isomer **4-E** in toluene cyclized to give the thermally stable purple photochrome **4-C**, which underwent the reversible reaction on exposure to white light. Photoreactions and UV-Vis spectrums of the benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E** are shown in Figure 2. The longest absorption maximum wavelength ($\lambda_{max} = 596$ nm) recorded for **4-C** is 50 nm longer than that for the colored form of the parent fulgide **3-C** ($\lambda_{max} = 545$ nm). The phenyl ring on position 2 of the thienyl group as well as the benzimidazole[1,2-a]pyrrolidin moiety of **4-C** formed the longest conjugation system to realize the longest absorption.
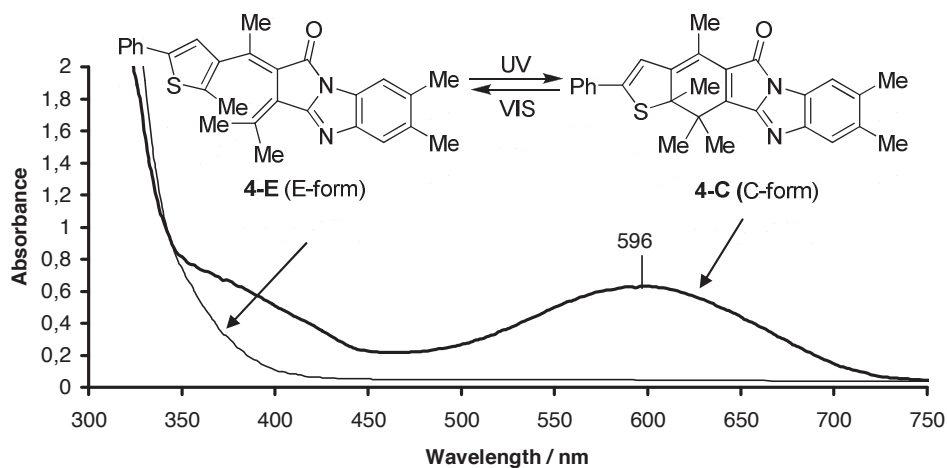

Figure 2. Photoreaction and UV-Vis spectrum of the benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E** (1×10^{-4} M in toluene).

Quantum yields of ring closure ($\Phi_{E \to C}$) for the **2(a-d)-E** and **4-E**, and the ring opening quantum yield ($\Phi_{C \to E}$) for the colored forms **2(a-d)-C** and **4-C** were measured using a chemical actinometer, Aberchrome 540, as described by Heller et al.[12] Spectral data and quantum yields are given in Table 1.

Table 1. Quantum yields and molar absorption coefficients at λ_{max} for fulgimides **2(a-d)-E** and benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E** in toluene (1×10^{-4} M).

Compd.	λ_{max}/nm (ε_{max} /mol^{-1}L cm^{-1}) (E-form)	λ_{max}/ nm (A) C-form (at pss)	$\phi_{E \to C}$ (365 nm)	$\phi_{C \to E}$ (546 nm)
1-E	367 (13,200)	514 (0.689)	-	-
2a-E	356 (9680)	533 (0.819)	0.42	0.079
2b-E	365 (9420)	541 (0.604)	0.32	0.073
2c-E	277 (46,000)	540 (0.736)	0.31	0.08
2d-E	343 (16,110)	523 (1.069)	0.56	0.033
3-E	310 (18,100)	545 (1.187)	-	-
4-E	278 (21,000)	596 (0.628)	0.272	0.015

Although the coloring quantum yields ($\Phi_{E \to C}$) of the **2(a-d)-E** and **4-E** are higher than those of the Aberchrome 540 ($\Phi_{E \to C} = 0.20$), the bleaching quantum yields ($\Phi_{C \to E}$) take various values. The lowest bleaching quantum yield ($\Phi_{C \to E}$) was recorded for **4-C**. It is usual that such low quantum yields for the higher conjugated systems were observed for some fulgides[13,14] and diarylethenes.[15,16]

Solvent effects on the absorption spectral data for the compound **2c-E** and its ring-closed form **2c-C** were investigated in 4 different solvents, and the data are listed in Table 2. The higher polarity of the solvent caused a bathochromic shift of both open and colored forms.

Table 2. UV-VIS maximum absorption and extinction coefficients of **2c-E** and its ring-closed form **2c-C** in various solvents.

Solvent	2c-E		2c-C	
	λ_{max} (nm)	ε_{max} / (mol^{-1}L cm^{-1})	λ_{max} (nm)	Abs. (at Pss)
Hexane	253	34,500	521	0.611
Toluene	277	46,000	540	0.736
Ethanol	291	26,000	543	0.971
Acetonitrile	297	22,300	545	0.797

Thermal stabilities of the fulgide **1-E**, fulgimide **2c-E**, and benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E** in 1:2 toluene-ethanol solutions at room temperature were examined. As shown in Figure 3a, **4-E** did not show any sign of degradation, whereas other isomers **1-E** and **2c-E** showed weaker thermal stability.

In the solid PMMA film, thermal stabilities of the isomers showed very similar patterns to the original compounds (Figure 3b). Upon heating for several days at 80 °C, fulgide **1-E** degraded largely, while **4-E** was thermally more stable.

The reason why **4E** and **2c-E** are more stable than the corresponding fulgide is simple. The fulgide, which is weak both in protic solvent and in polymer film, has an anhydride group responsible for the degradation. When the reactive anhydride group of fulgide is replaced by an imide group to yield a fulgimide, resistance toward hydrolysis is much enhanced so that **2c-E** became thermally more stable than **1-E**.

Replacement of the anhydride group in fulgide **3E** by benzimidazole[1,2-a]pyrrolidin-2-one moiety gave photochromic benzimidazole[1,2-a]pyrrolidin-2-one derivatives **4E**, which displayed the highest thermal stability. It is obvious that benzimidazole[1,2-a]pyrrolidin-2-one moiety is much more stable than that of imides or anhydride groups.
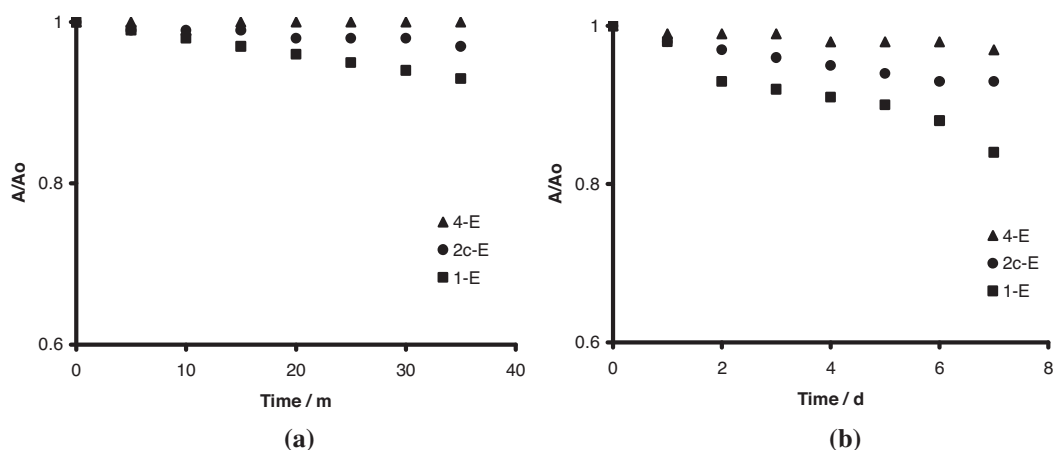

Figure 3a and 3b. Thermal stabilities of fulgide **1-E**, fulgimide **2c-E**, and benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E** (a) in 1:2 toluene-ethanol solutions at room temperature and (b) in PMMA film (20 wt,%) at 80 °C. A/A_0 refers to the absorbance relative to the initial value, at the maximum wavelength of E-forms.

Thermal analysis of fulgimide **2c-E** and benzimidazole[1,2-a]pyrrolidin-2-one derivative **4-E** was performed by TGA. Figure 4 gives the weight loss as a function of temperature during the pyrolysis of the samples in an inert atmosphere. Thermal degradation of **2c-E** and **4-E** started at 117 °C and 200 °C and completed at about 690 °C and 900 °C, respectively. From the rate of weight loss curve it can be seen that the isomer **4-E** is more stable than **2c-E** and both isomers are stable below 100 °C.
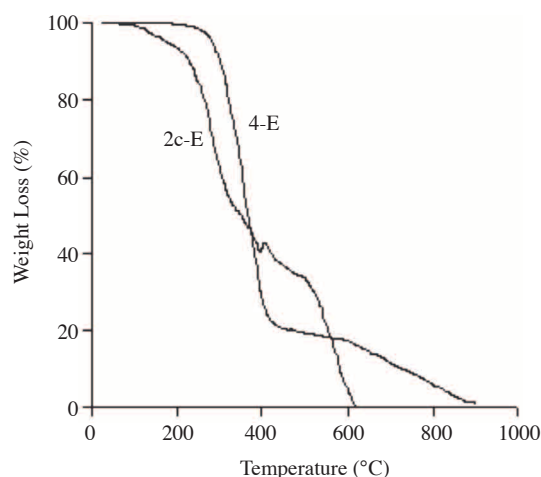

Figure 4. TGA curves for **2c-E** and **4-E**.

Conclusions

New thermally stable photochromic fulgimides and benzimidazole[1,2-a]pyrrolidin-2-one derivatives of fulgide were prepared and their photochromic properties were investigated. Thermal stabilities for some of the new compounds in an alcoholic solution and in the PMMA film, and their pyrolytic behaviors in inert atmosphere were also examined.

The colored form of fulgimides **2(a-d)-C** and benzimidazol[1,2-a]pyrrolidin-2-one derivatives **4-C** show large bathochromic shifts of their long wavelength absorption bands compared to the colored form of the corresponding fulgide. The large bathochromic shifts for **4-C** were attributed to the electron donating ability of the phenyl group on the thiophene ring and the benzimidazole ring system, which extends the conjugation of the photochrome.

Solvent effects on the absorption spectral properties of the compound **2c-E** and its ring-closed form **2c-C** were investigated. The high polarity of the solvent caused a bathochromic shift of both open and colored forms.

All the isomers displayed higher quantum yields for coloring compared to Aberchrome 540, but the bleaching quantum yields ($\Phi_{C \rightarrow E}$) take various values. The low bleaching quantum yield ($\Phi_{C \rightarrow E}$) for **4-C** can be explained on the bases of electronic effects.

Enhancements of thermal stability of fulgide were managed by modifying the anhydride group. The order of the thermal stability of the open-form isomers is as follows: **4E > 2c-E >> 1-E**. Thermally stable photochromic compounds such as **4-E** are potentially applicable to the data storage media for optical recording systems.

Acknowledgements

References

1. Yokoyama, Y. *Chem. Rev.* **2000,** *100*, 1717-1739.

2. Yokoyama, Y.; Kose, M. *J. Photoch. Photobio. A: Chem.* **2004,** *166*, 9-18.

3. Irie, M. *Chem. Rev.* **2000**, *100*, 1685-1716.

4. Kose, M.; Shinoura, M.; Yokoyama, Y.; Yokoyama, Y. *J. Org. Chem.* **2004**, *69*, 8403-8406.

5. Matsushima, R.; Sakaguchi, H. *J. Photoch. Photobio. A: Chem.* **1997**, *108*, 239-245.

6. Liang, Y.; Dvornikov A. S.; Rentzepis, P. M. *Tetrahedron Lett.* **1999,** *40*, 8067-8069.

7. Liang, Y.; Dvornikov, A. S.; Rentzepis, P. M. *J. Chem. Soc. Chem. Commun.* **2000**, 1641-1642.

8. Ramsteiner, I. B.; Hartschuh, A.; Port, H. *Chem. Phys. Lett.* **2001**, *343*, 83-90.

9. Kose, M.; Orhan, E. *J. Photoch. Photobio. A: Chem.* **2006**, *177*, 170-176.

10. Darcy, P. J.; Heller, H. G.; Strydom, P. J.; Whittall, J. *J. Chem. Soc., Perkin Trans 1.* **1981,** 202-205.

11. Glaze, A. P.; Ph. D. Thesis, U. C. W.; Aberystwyth, 1983.

12. Heller, H. G.; Langan, R. J. *Chem. Soc., Perkin Trans. II* **1981,** 341-343.

13. Tomoda, A.; Kaneko, A.; Tsuboi, H.; Matsushima, R. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1262-1267.

14. Wolak, M. A.; Gillespie, N. B.; Thomas, C. J.; Birge, R. R.; Lees, W. J. *J. Photochem. Photobiol. A: Chem.* **2002**, *147*, 39-44.

15. Irie, M.; Eriguchi, T.; Takada, T.; Uchida, K. *Tetrahedron* **1997,** *53*, 214.

16. Kose, M. *J. Photochem. Photobiol. A: Chem.* **2004,** *165*, 97-102.