



## Arylazo Dyes Containing a Built-In Hindered-Amine Moiety\*

Harold S. Freeman, Sung-Dong Kim, Richard D. Gilbert  
& Ralph McGregor

Department of Textile Engineering, Chemistry, and Science,  
North Carolina State University, Raleigh, North Carolina  
27695-8301, USA

(Received 8 January 1991; accepted 14 February 1991)

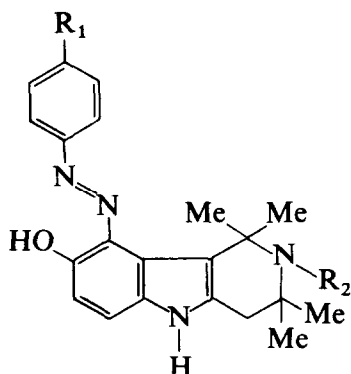
### ABSTRACT

*This paper describes the synthesis, spectral properties, and photolytic behavior of some 5-arylazo-6-hydroxy- $\gamma$ -carbolines. Like 1-arylazo-2-naphthols, these novel dyes exist primarily in the hydrazone form. Interestingly, however, the arylazo- $\gamma$ -carboline dyes are significantly more light-stable in a polymer matrix than their 1-arylazo-2-naphthol counterparts. This suggests that the use of a built-in hindered-amine residue is an effective way to inhibit the light-induced oxidation of arylhydrazone-type dyes. The preparation of novel nitroxide derivatives of the arylazo- $\gamma$ -carbolines for electron spin resonance spin-probe studies is also described.*

### INTRODUCTION

It is well known that the chemical structure of a dye and its chemical environment play key roles in determining the stability of that dye to incident radiation.<sup>1</sup> It has also been suggested that the local molecular mobility of a penetrant molecule in a solid polymer may modify its stability to incident radiation<sup>2</sup> and to atmospheric pollutants.<sup>3</sup> For instance, it has

\* Abstracted in part from the PhD thesis of Sung-Dong Kim, College of Textiles, North Carolina State University, Raleigh, NC, USA.



	R <sub>1</sub>	R <sub>2</sub>
1	NO <sub>2</sub>	O <sup>•</sup>
2	SO <sub>3</sub> Na	O <sup>•</sup>
3	CO <sub>2</sub> Na	O <sup>•</sup>
4	NO <sub>2</sub>	H
5	SO <sub>3</sub> Na	H
6	CO <sub>2</sub> Na	H

been shown<sup>4,5</sup> that the hydrazone tautomer of arylazonaphthols is more susceptible to light-induced degradation than the azo form, and it is believed that singlet oxygen<sup>6</sup> is a major contributor to the low light stability of these dyes. To protect dyes and the host polymer against photodegradation, stabilizers which either preferentially absorb the UV component of sunlight, accept the transfer of energy from an excited dye or polymer, or quench the effects of singlet oxygen are commonly used. Included in the third category are the hindered-amine light stabilizers that are useful antioxidants in the protection of polyolefins, especially poly(propylenes).<sup>7</sup> The photostability of fluorescent brighteners in poly(ethylene terephthalate) fibers has been related to the molecular mobility of these molecules in the polymer matrix.<sup>2</sup> The same observation has been made with regard to the ozone fading of dyed nylon carpet yarns.<sup>3</sup>

While designing colored spin probes to study the local environments and the molecular mobility of penetrant molecules in polymer matrices at different temperatures using electron spin resonance (ESR) spectroscopy,<sup>8,9</sup> it seemed that nitroxide radicals such as 1–3 not only would permit the achievement of our initial objective but, due to the presence of the built-in nitroxide moiety and to their low volatility, might also possess enhanced photostability in solid polymers. In addition to these three colorants, dyes 4–6, which contain a hindered-amine structure, were synthetic targets.

## RESULTS AND DISCUSSION

The synthesis of dyes 1–6 is outlined in Scheme 1. The sequence began with the commercial aniline hydrochloride, 7. Diazotization and stannous chloride reduction gave the arylhydrazine, 8. This compound was condensed with tetramethylpiperidone 9,<sup>10</sup> to give the key intermediate  $\gamma$ -carboline 10. Compound 10 was either subjected to hydrogenolysis<sup>10</sup> (10  $\rightarrow$  11), to remove

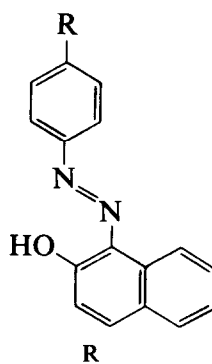
the benzyl group, followed by diazo coupling to give dyes **4–6**, or carried through steps **10** → **12** → **13** → **14** → **1–3** to obtain the desired colored spin probes. At the outset of this synthetic work, it was anticipated that compound **11** would be the common intermediate to all six dyes; however, it was not possible to convert **11** to the nitroxide **14** by known methods.

The structure of each dye and of key intermediates was established by a combination of 250-MHz  $^1\text{H-NMR}$  and fast atom bombardment (FAB) mass spectrometry. In addition, ESR spectra were recorded on dyes **1–3** and compound **14** to confirm the presence of the nitroxide radical. Typical spectra are shown in Figs 2–4. The mass spectra of the ionic dyes contained prominent  $[\text{M-H}]^-$  and  $[\text{M-Na}]^-$  ions, while the spectra of dyes **1** and **4** contained a major  $[\text{M-H}]^-$  ion peak. As expected, NMR spectra could not

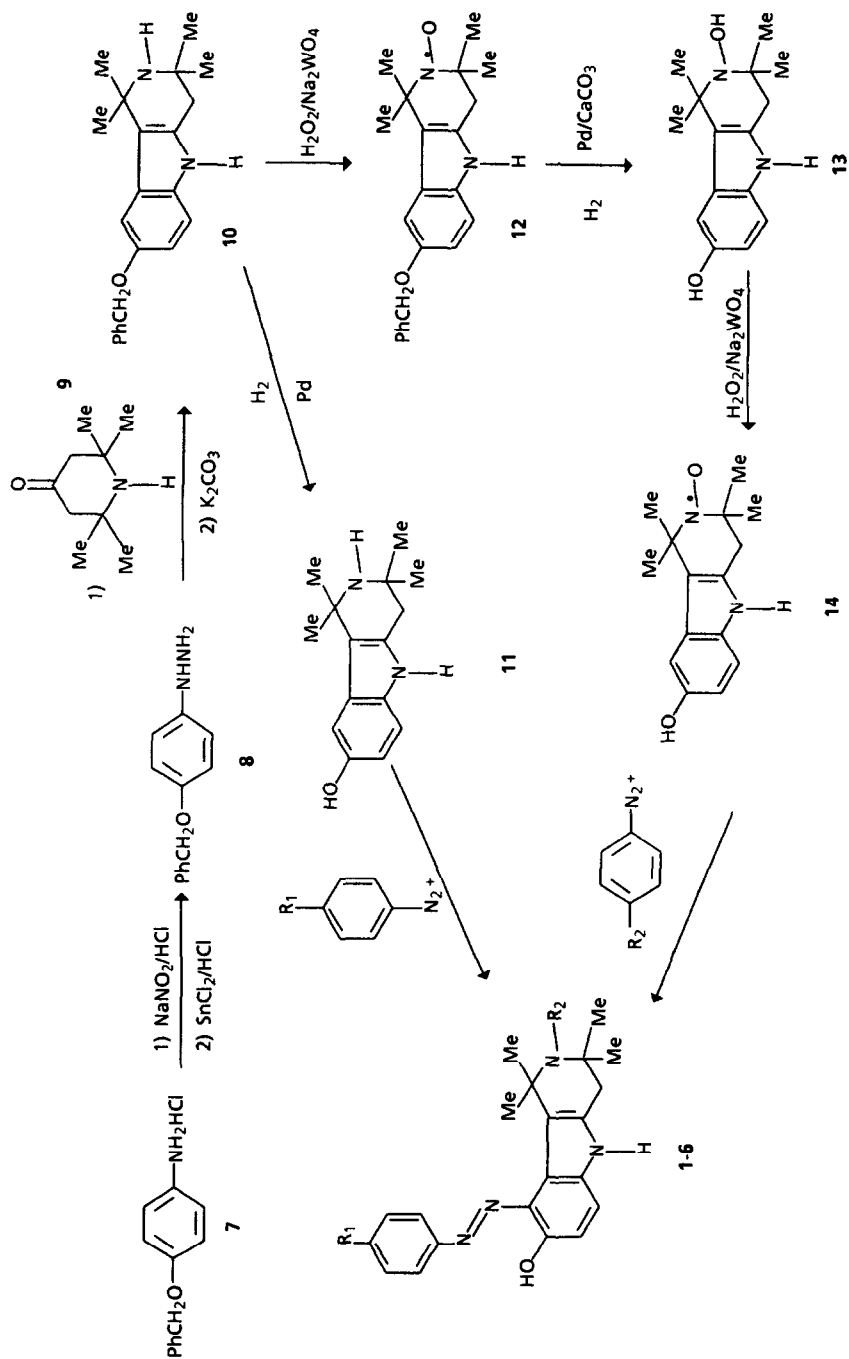
**TABLE 1**  
Visible Absorption Spectral Data<sup>a</sup> for the Dyes Used in  
this Study

Dye	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$
<b>1</b>	490	18 700
<b>2</b>	474	17 800
<b>3</b>	480	18 000
<b>4</b>	488	18 400
<b>5</b>	478	17 400
<b>6</b>	490	16 800
<b>15</b>	484	16 200
<b>16</b>	480	16 700
<b>17</b>	486	16 300

<sup>a</sup> DMF used as the solvent.



<b>15</b>	$\text{NO}_2$
<b>16</b>	$\text{SO}_3\text{Na}$
<b>17</b>	$\text{CO}_2\text{Na}$



**Fig. 1.** Synthesis of some arylazo- $\gamma$ -carbolines.

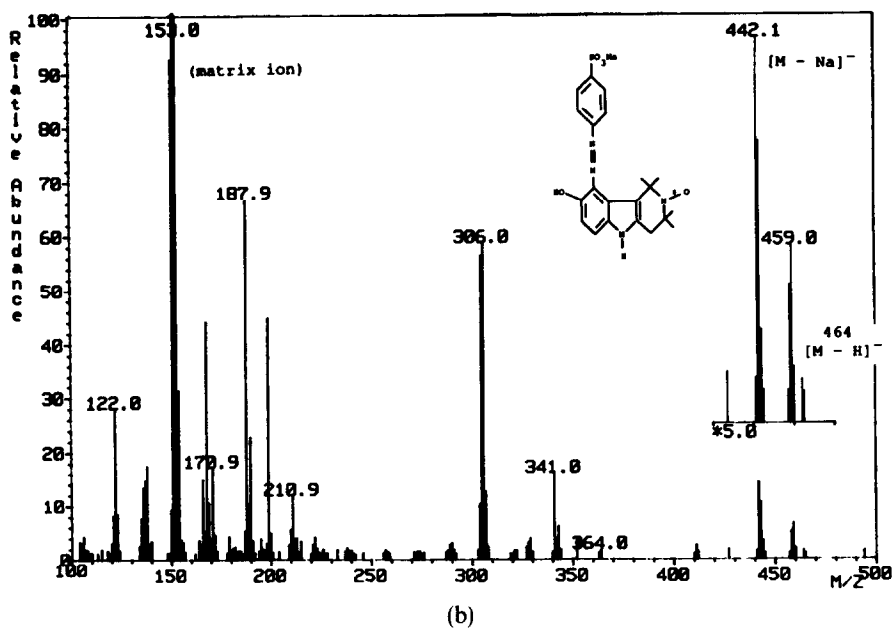
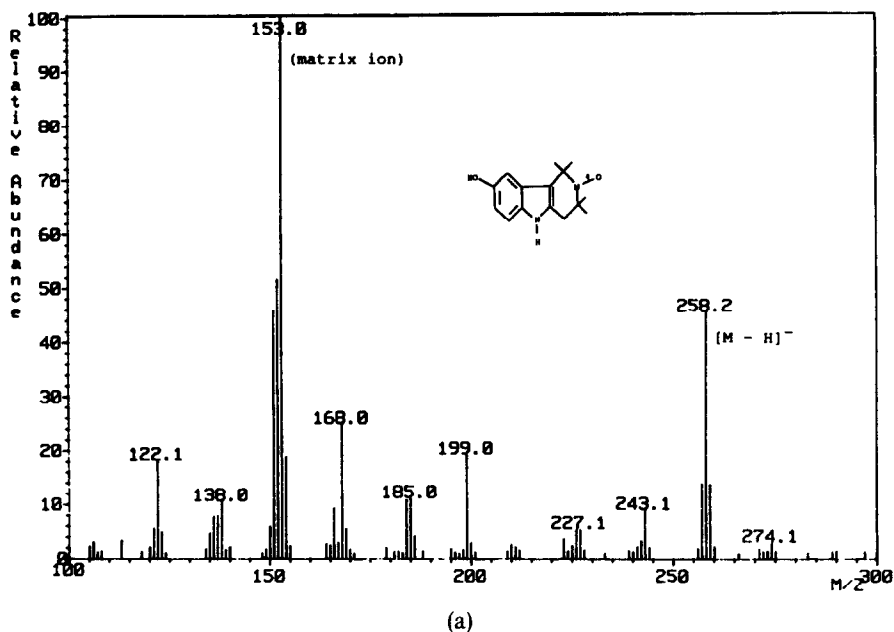
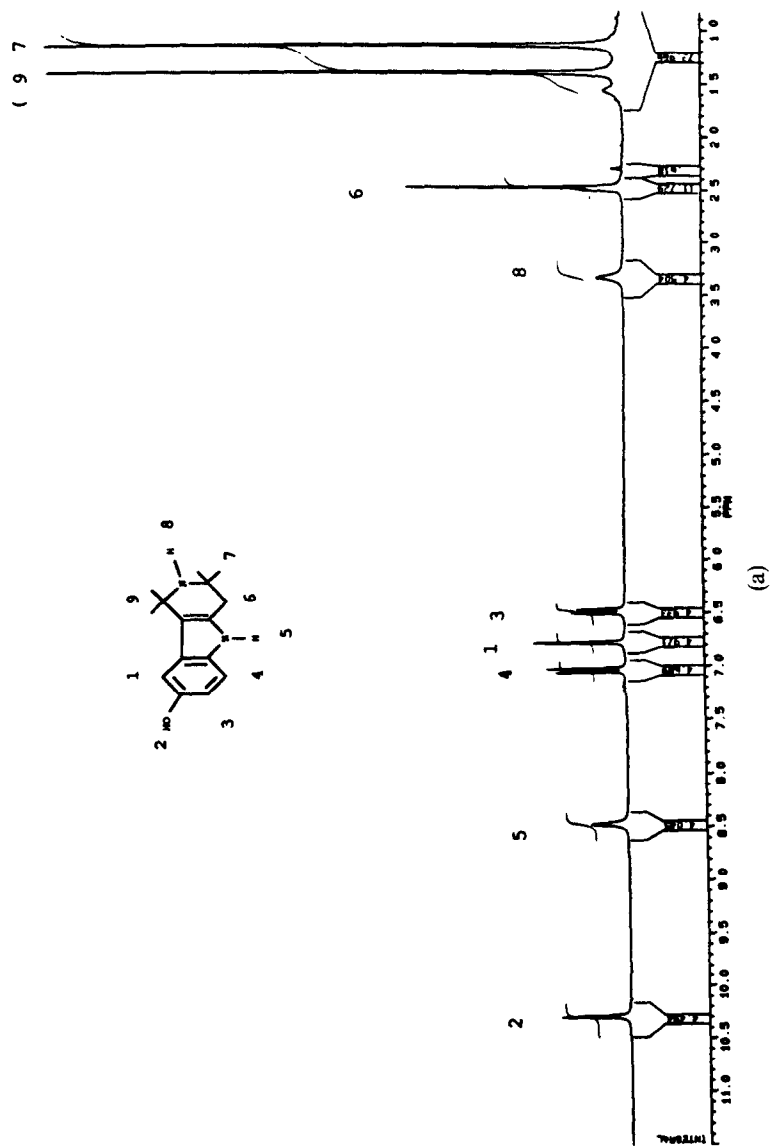


Fig. 2. Negative-ion FAB mass spectra of (a) compound 14 and (b) dye 2.



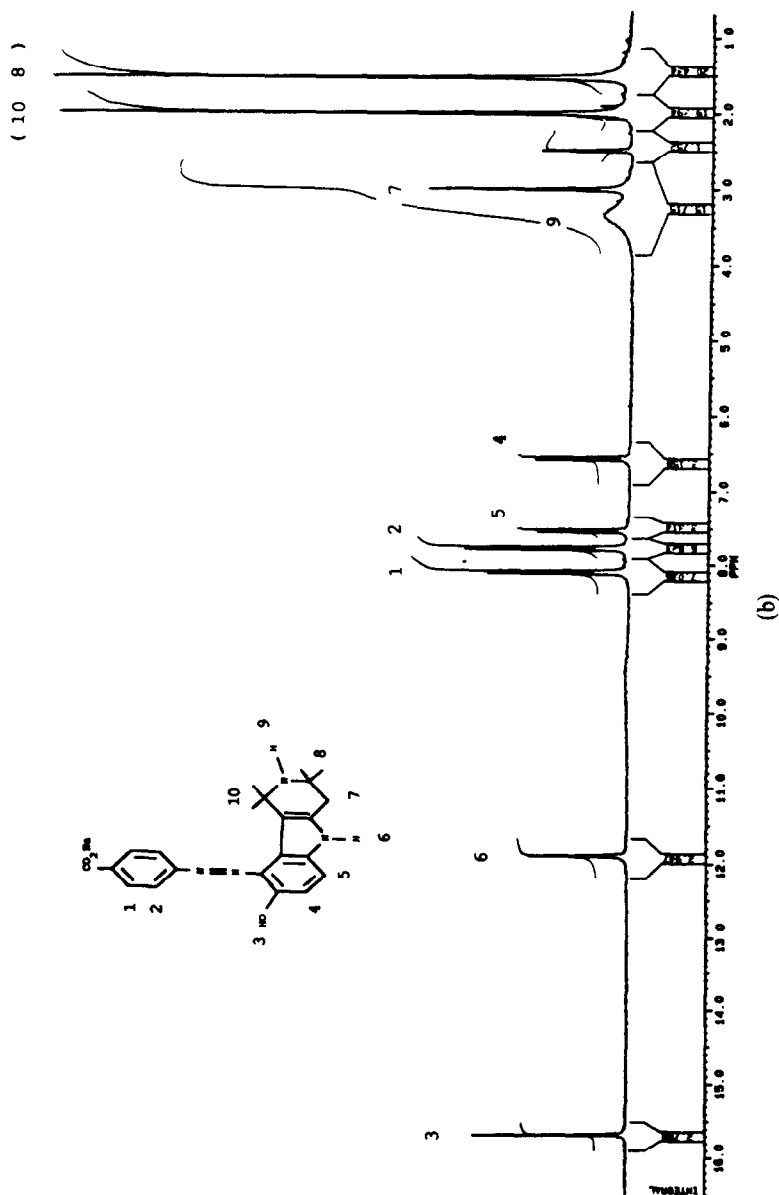


Fig. 3. <sup>1</sup>H-NMR spectra (250 MHz) of (a) compound 11 and (b) dye 6.

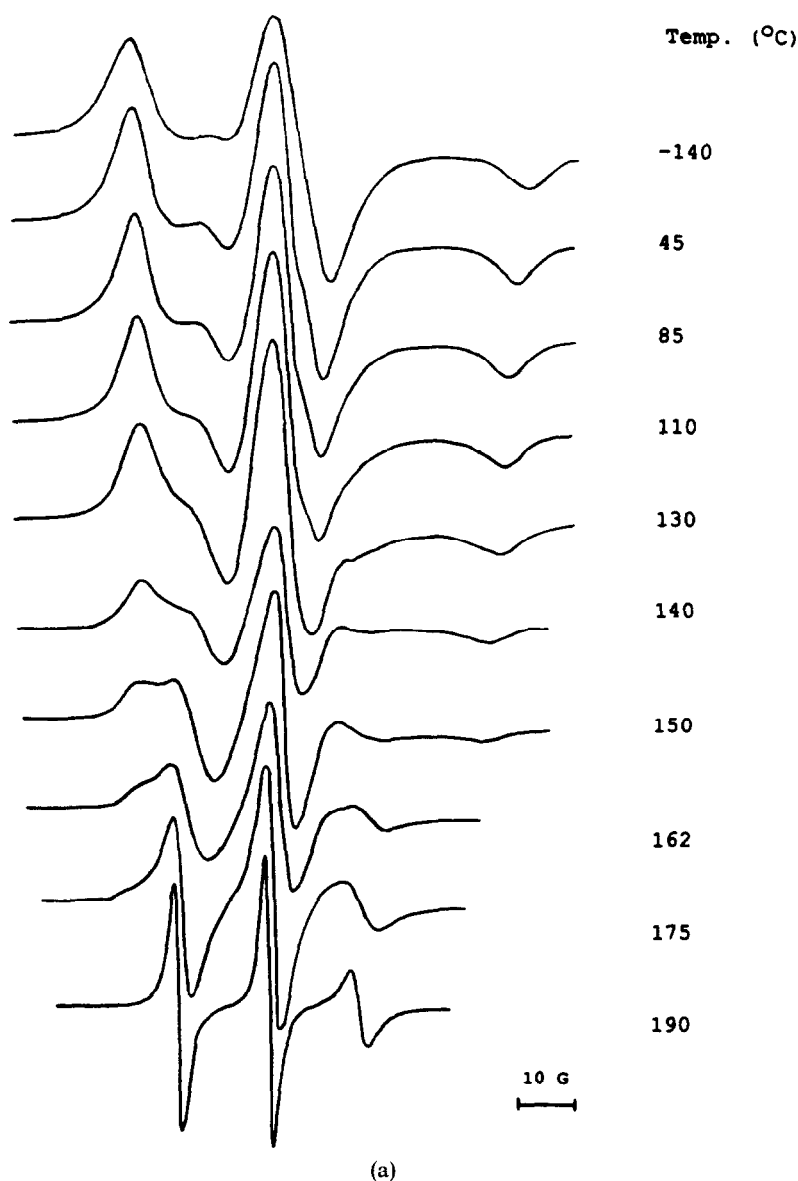
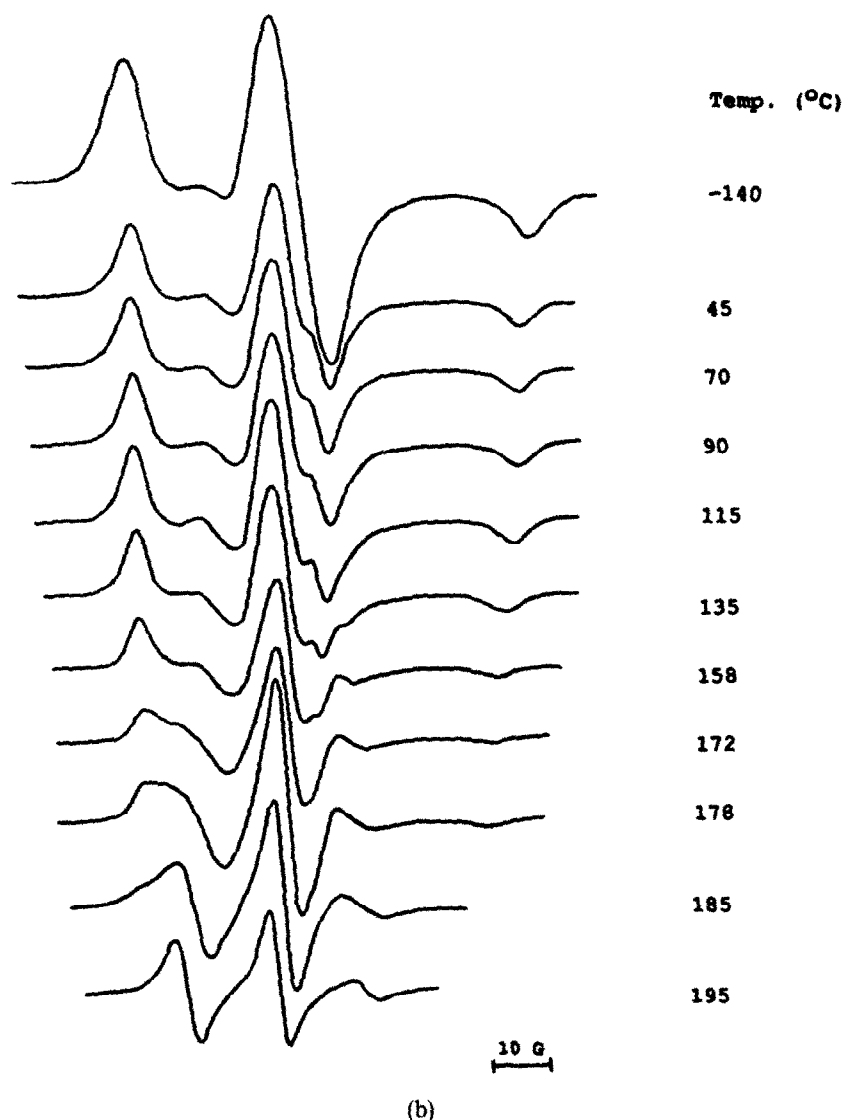


Fig. 4. ESR spectra of (a) compound **14** and (b) dye **2** in nylon-6 film.

be recorded on those compounds that are paramagnetic. As Fig. 3 demonstrates, the signals in the spectra were well resolved and readily assignable. The signal at 15.7 ppm in the spectrum of **6** indicates that the dye exists in the hydrazone form.<sup>5</sup> The ESR spectra of the radical-containing compounds showed the expected three-line spectrum of an immobilized nitroxide, were temperature sensitive, and are consistent with Brownian



Fig. 4.—*contd.*

rotation of the probes at higher temperatures. The  $T_{50G}$  (K) values of the ESR active dyes range from 416 to 454 and are significantly higher than that reported for a simple azobenzene derivative (404 K).<sup>11</sup> This indicates significantly lower molecular mobility of these probes in nylon-6 film at a given temperature.

Figure 5 shows the visible absorption spectra of dyes **2**, **5**, and the known commercial dye Acid Orange 7 (**16**) in dimethylformamide (DMF). The

spectra of the former two dyes are consistent with the indication by  $^1\text{H-NMR}$  that each exists predominantly in the hydrazone form. Table 1 gives  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  data for the nine dyes used in this study.

To determine whether the presence of the stable nitroxide radical of dyes 1–3 and the hindered-amine structure of dyes 4–6 would afford light-stable azo dyes, dyes 1–6 and 16–17 were irradiated in DMF and in nylon-6 film using 254-nm light. When the nylon model DMF was used, there was no significant difference in the rate of fading when dyes 1–6 were compared with 15–17, and the level of degradation was extensive (cf. Figs 6(a), 7(a), 8(a)). However, when the photolysis was conducted using dyed films, the arylazo- $\gamma$ -carbolines were significantly more light-stable than the arylazo-2-naphthols (cf. Figs 6(b), 7(b) and 8(b)). Figures 6–8 also provide a further illustration of the protective effects of a polymer matrix, as all nine dyes were appreciably more light-stable in nylon-6 than in DMF. In addition, at least 50% of the original dye was still present after 2.5–3.0 h when dyes 1–6 were irradiated in nylon film. The results of these experiments suggest that a built-in hindered-amine moiety enhances the photostability of the hydrazone

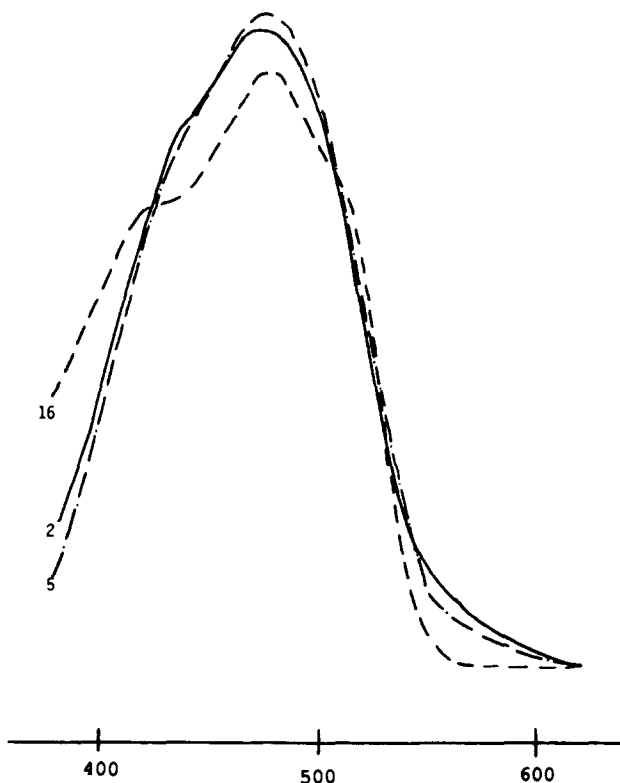


Fig. 5. Visible absorption spectra (nm) of dyes 2, 5, and 16 in DMF.

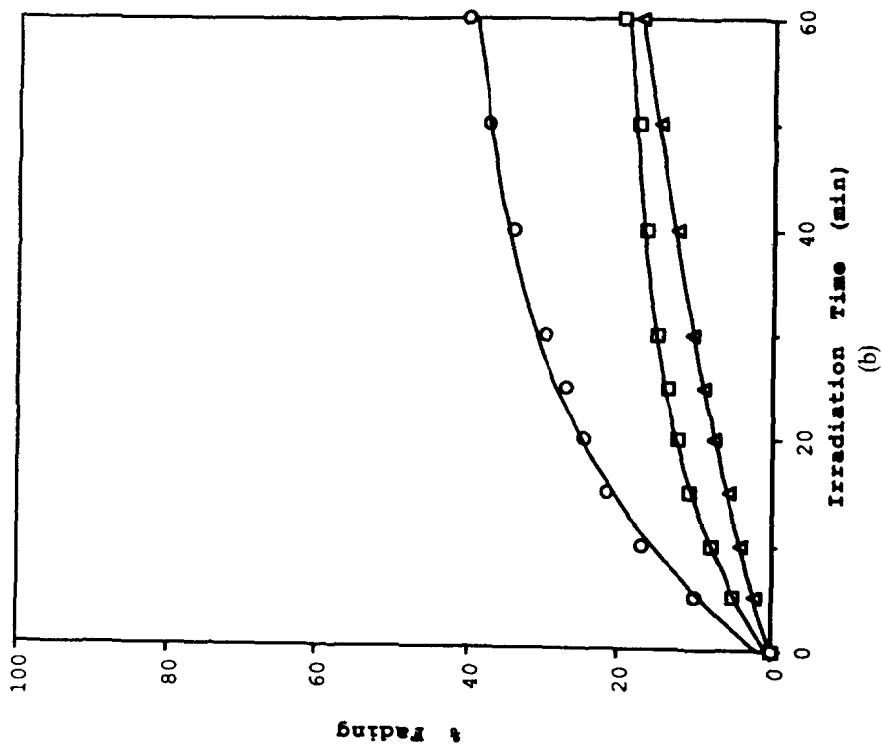
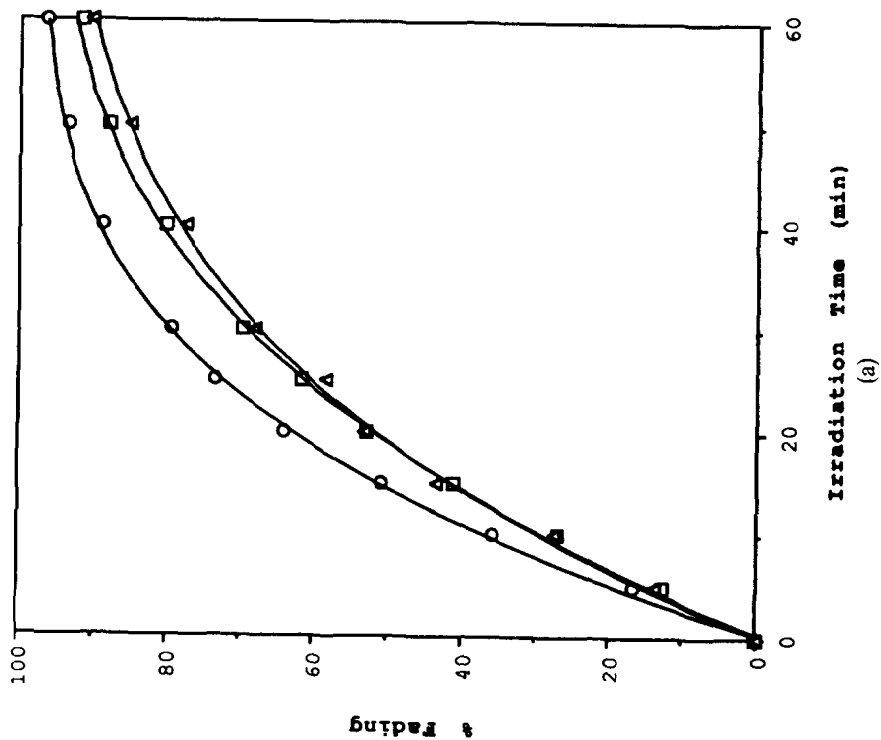


Fig. 6. Data from the irradiation of dyes **1** ( $\Delta$ ), **4** ( $\square$ ), and **15** ( $\circ$ ) in (a) DMF and (b) nylon-6 film using 254-nm light.

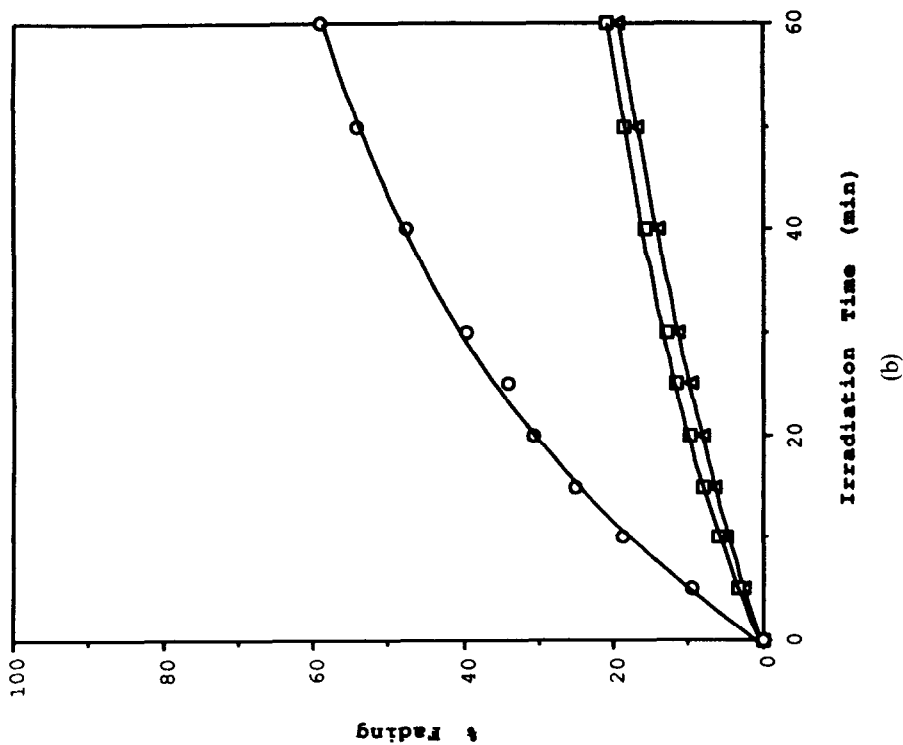
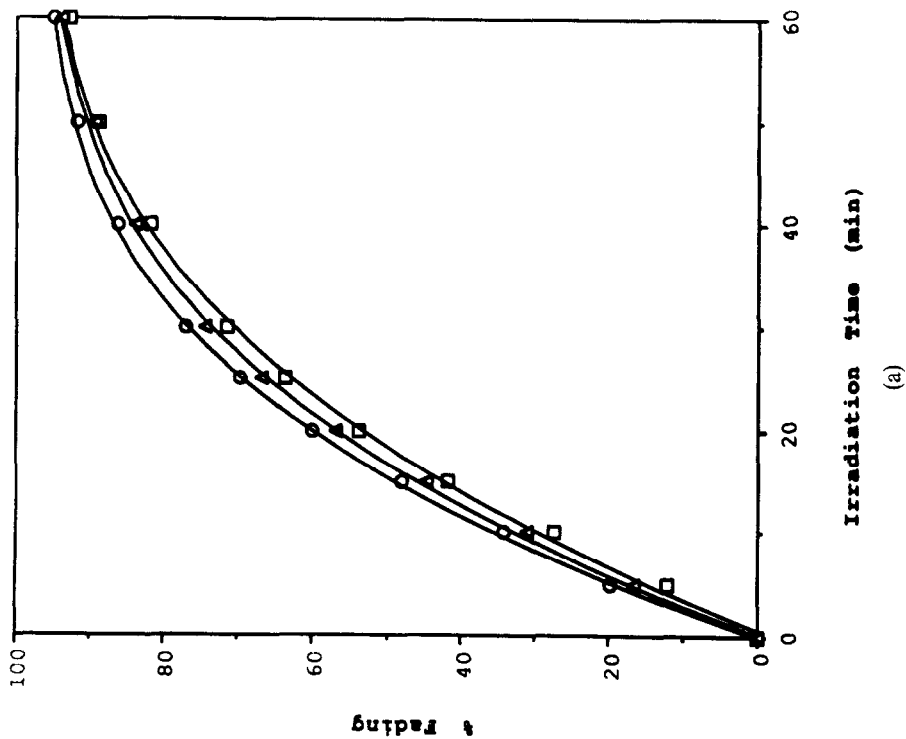
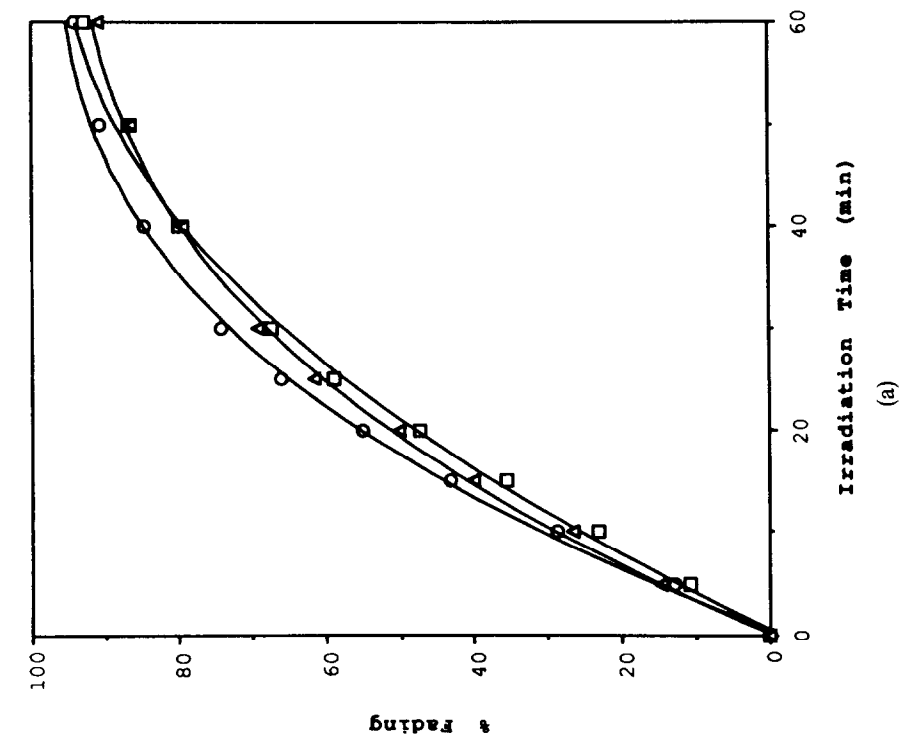
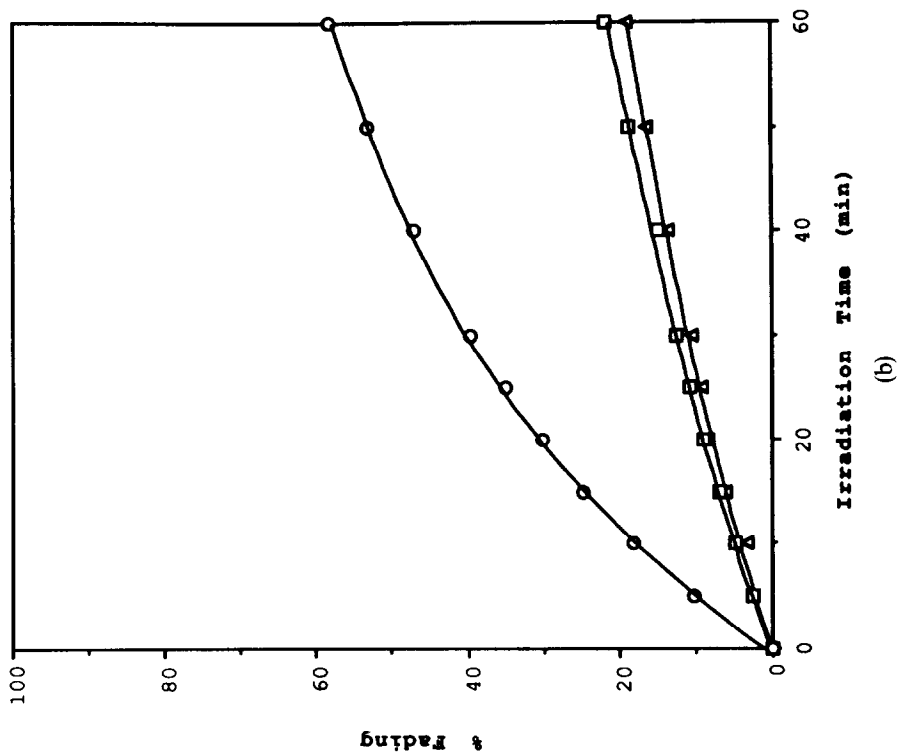


Fig. 7. Data from the irradiation of dyes 2 ( $\Delta$ ), 5 ( $\square$ ), and 16 ( $\circ$ ) in (a) DMF and (b) nylon-6 film using 254-nm light.



(a)



(b)

Fig. 8. Data from the irradiation of dyes 3 ( $\Delta$ ), 6 ( $\square$ ), and 17 ( $\circ$ ) in (a) DMF and (b) nylon-6 film using 254-nm light.

tautomer of arylazo dyes in polymer matrices, and that the molecular environment and the molecular mobility of a dye dispersed in a polymer may significantly modify its photostability.

## EXPERIMENTAL

### General

All of the chemicals used as starting materials and solvents were purchased from Aldrich Chemical Company (Milwaukee, WI, USA).

$^1\text{H}$ -NMR spectra were recorded on a Bruker 250-MHz spectrometer. All samples were dissolved in  $\text{DMSO-d}_6$  and chemical shifts are reported in parts per million relative to tetramethylsilane. Negative- and positive-ion fast atom bombardment (FAB) mass spectra were recorded using a JEOL HX 110HF double focusing mass spectrometer equipped with a DA-5000 data system. Visible spectra were recorded on a Perkin Elmer 559A UV-visible spectrophotometer. Electron spin resonance (ESR) spectra were recorded on a Varian E3 spectrometer. Thin-layer chromatography (TLC) was performed using Whatman 250- $\mu\text{m}$  silica gel 60 AMK6F plates. Flash column chromatography was conducted using Fisher chromatographic silica gel 230–245 mesh type 150 Å. The photolysis experiments were conducted in a Rayonnet Model 100 photochemical reactor (Southern New England Ultraviolet Company, Branford, CT, USA). Melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected.

### Syntheses

#### *4-Benzyloxyphenylhydrazine hydrochloride (8)*

To a suspension of 4-benzyloxyaniline hydrochloride (100 g, 0.42 mol) in 200 ml of warm water was added 100 ml conc. HCl. The mixture was stirred at  $-5^\circ\text{C}$  as a solution of 29.3 g  $\text{NaNO}_2$  in 120 ml  $\text{H}_2\text{O}$  was slowly added. The resulting dark solution was stirred at  $0^\circ\text{C}$  for 1 h and then filtered. A cooled solution of 287.2 g stannous chloride in 350 ml conc. HCl was added dropwise to the filtrate at  $0^\circ\text{C}$ , and the mixture stirred until the initial bright red color became pale pink; it was then refrigerated overnight and filtered. White crystals were obtained after recrystallization from 95% ethanol. The yield was 82.1 g (90%), mp  $261\text{--}263^\circ\text{C}$ , and  $R_f$  0.73 (methanol).  $^1\text{H}$ -NMR:  $\delta$  5.05 (s, 2H),  $\delta$  6.93–7.05 (m, 4H),  $\delta$  7.27–7.44 (m, 5H),  $\delta$  10.11 (s, 2H). Mass spectrum (EI):  $m/z$  (relative intensity) 91 (100,  $\text{PhCH}_2^+$ ), 123 (98,  $\text{M} - 91$ ), 214 (94,  $\text{M}^+$ ), 108 (75,  $\text{M} - 106$ ), 199 (56,  $\text{M} - 15$ ).

**6-Benzoyloxy-1,2,3,4-tetrahydro-2,2,4,4-tetramethyl- $\gamma$ -carboline (10)**

A mixture of **8** (92.1 g, 0.37 mol) and 2,2,6,6-tetramethyl-4-piperidone hydrochloride (**9**, 70.4 g) in 800 ml of 4% HCl in ethanol was refluxed for 2 h, and the resulting mixture was refrigerated overnight. Yellow crystals, the hydrochloride of **10**, were collected by filtration and dried to give 6.2 g. The free amine was obtained by suspending the hydrochloride in 30 ml H<sub>2</sub>O containing 3 g K<sub>2</sub>CO<sub>3</sub>. The precipitate was extracted into EtOAc to give, upon evaporation, 5.65 g **10**, mp 145–148°C, R<sub>f</sub> 0.35 (methanol). <sup>1</sup>H-NMR:  $\delta$  1.24 (s, 6H),  $\delta$  1.52 (s, 6H),  $\delta$  2.50 (s, 1H),  $\delta$  2.61 (s, 2H),  $\delta$  5.10 (s, 2H),  $\delta$  6.72–6.76 (d, 2H),  $\delta$  7.03 (s, 1H),  $\delta$  7.16–7.19 (d, 2H),  $\delta$  7.28–7.49 (m, 5H),  $\delta$  10.63 (s, 1H). Mass spectrum (positive-ion FAB):  $m/z$  335 (M + H)<sup>+</sup>.

**6-Benzoyloxy-1,2,3,4-tetrahydro-2,2,4,4-tetramethyl- $\gamma$ -carboline-3-oxy (12)**

To a solution of **10** (5 g, 0.015 mol) in methanol (110 ml) were added 90 mg of sodium tungstate, 3.2 ml of 30% H<sub>2</sub>O<sub>2</sub>, and 9 mg EDTA. The reaction mixture was stirred for 4 h and then allowed to stand at room temperature for 5 days to give 3.1 g of orange crystals, mp 208–210°C, R<sub>f</sub> 0.59 (PhMe:EtOAc/2:1). Mass spectrum (negative-ion FAB):  $m/z$  348 (M – H)<sup>–</sup>.

**1,2,3,4-Tetrahydro-3,6-dihydroxy-2,2,4,4-tetramethyl- $\gamma$ -carboline (13)**

A solution of **12** (2.5 g, 7.2 mmol) in 200 ml of methanol was hydrogenated over 0.3 g Pd on calcium-carbonate catalyst until hydrogen uptake ceased. After the catalyst and solvent were removed, 1.8 g **13** was obtained, mp 190–192°C (from PhMe), R<sub>f</sub> 0.41 (PhMe:EtOAc/2:1). <sup>1</sup>H-NMR:  $\delta$  1.14 (s, 6H),  $\delta$  1.43 (s, 6H),  $\delta$  2.64 (s, 2H),  $\delta$  3.37 (s, 1H),  $\delta$  4.12 (s, 1H),  $\delta$  6.50 (s, 1H),  $\delta$  6.80 (s, 1H),  $\delta$  7.03 (s, 1H),  $\delta$  8.28 (s, 1H),  $\delta$  10.14 (s, 1H). Mass spectrum (negative-ion FAB):  $m/z$  259 (M – H)<sup>–</sup>.

**6-Hydroxy-1,2,3,4-tetrahydro-2,2,4,4-tetramethyl- $\gamma$ -carboline-3-oxy (14)**

Compound **13** (1.4 g, 5.4 mmol) was oxidized by using the procedure described above for the conversion of **10** to **12**. After 5 days, pure **49** (0.5 g) was obtained by flash column chromatography using a mixture of PhMe:EtOAc/2:1 (v/v), mp 196–198°C, R<sub>f</sub> 0.43. Mass spectrum (negative-ion FAB):  $m/z$  258 (M – H)<sup>–</sup>.

**1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-5-(4'-nitrophenylazo)-6-hydroxy- $\gamma$ -carboline-3-oxy (1)**

A mixture of 4-nitroaniline (0.12 g, 0.9 mmol), 0.3 ml conc. HCl and 2 ml H<sub>2</sub>O was warmed with stirring until a clear solution was obtained. The solution was cooled to 0°C and stirred as 0.06 g NaNO<sub>2</sub> in 0.5 ml H<sub>2</sub>O was added slowly. The reaction mixture was stirred for 30 min and filtered. The

filtrate was added slowly to a solution of 0.3 g **14** and 0.06 g NaOH in 2 ml H<sub>2</sub>O. After stirring for 1 h, the crude dye was filtered and purified by flash column chromatography using PhMe:EtOAc/1:2 (v/v) to give 0.35 g **1**, mp 199–201°C, R<sub>f</sub> 0.30 (PhMe:EtOAc/2:1). Mass spectrum (negative-ion FAB):  $m/z$  407 (M – H)<sup>–</sup>.

*1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-5-(4'-sulfophenylazo)-6-hydroxy-γ-carboline-3-oxy (2)*

To a solution of sulfanilic acid (0.27 g, 1.6 mmol) in 2 ml H<sub>2</sub>O and 0.2 g Na<sub>2</sub>CO<sub>3</sub>, 0.5 ml conc. HCl was added. After cooling this solution to below 10°C, a solution of 0.1 g NaNO<sub>2</sub> in 1 ml H<sub>2</sub>O was added, and the reaction mixture was stirred for 30 min. The suspension of the diazonium salt was slowly added to a solution of 0.4 g **14** and 0.08 g NaOH in 2 ml H<sub>2</sub>O. The crude dye was filtered and purified by flash column chromatography using 95% ethanol to give 0.41 g **2**, mp 194–197°C, R<sub>f</sub> 0.60 (1-butanol:ethanol:pyridine: ammonium hydroxide/4:1:2:3). Mass spectrum (negative-ion FAB):  $m/z$  442 (M – Na)<sup>–</sup>, 464 (M – H)<sup>–</sup>.

*1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-5-(4'-carboxyphenylazo)-6-hydroxy-γ-carboline-3-oxy (3)*

Dye **3** was prepared by the procedure described above for the synthesis of **2**. The coupling of **14** (0.4 g, 1.2 mmol) with 4-aminobenzoic acid (0.16 g) and purification by flash column chromatography using 95% ethanol gave 0.4 g **3**, mp 199–203°C, R<sub>f</sub> 0.56 (1-butanol:ethanol:pyridine: ammonium hydroxide/4:1:2:3). Mass spectrum (negative-ion FAB):  $m/z$  407 (M – Na)<sup>–</sup>, 429 (M – H)<sup>–</sup>.

*1,2,3,4-Tetrahydro-6-hydroxy-2,2,4,4-tetramethyl-γ-carboline (11)*

A solution of **10** (2.50 g, 7.5 mmol) in 200 ml of methanol was hydrogenated over 5% Pd/C (0.3 g) until hydrogen uptake ceased. The catalyst and solvent were removed, and the product was recrystallized from PhMe to give 1.35 g of pure **11**, mp 209–210°C, R<sub>f</sub> 0.40 (methanol). <sup>1</sup>H-NMR: δ 1.14 (s, 6H), δ 1.40 (s, 6H), δ 2.47 (s, 2H), δ 3.37 (s, 1H), δ 6.47–6.51 (dd, 1H), δ 6.70 (s, 1H), δ 7.02–7.05 (d, 1H), δ 8.47 (s, 1H), δ 10.27 (s, 1H). Mass spectrum (negative-ion FAB):  $m/z$  243 (M – H)<sup>–</sup>.

*1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-5-(4'-nitrophenylazo)-6-hydroxy-γ-carboline (4)*

The synthesis of **4** was carried out using the procedure described for dye **1**. The coupling of **11** (0.30 g, 1.2 mmol) with the diazonium salt derived from 4-nitroaniline (0.17 g) gave 0.38 g of essentially pure **4**. This dye decomposed without melting at 230°C, and had a R<sub>f</sub> value of 0.34 (methanol). <sup>1</sup>H-NMR:



$\delta$  1.18 (s, 6H),  $\delta$  1.63 (s, 6H),  $\delta$  2.54 (s, 2H),  $\delta$  6.26–6.30 (d, 1H),  $\delta$  7.45–7.48 (d, 1H),  $\delta$  7.77–7.82 (d, 2H),  $\delta$  8.30–8.34 (d, 2H),  $\delta$  11.42 (s, 1H),  $\delta$  16.17 (s, 1H). Mass spectrum (positive-ion FAB):  $m/z$  394 ( $M + H$ )<sup>+</sup>.

*1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-5-(4'-sulfophenylazo)-6-hydroxy- $\gamma$ -carboline (5)*

The synthesis of **5** was carried out using the procedure described for dye **2**. The coupling of **11** (0.30 g, 1.2 mmol) with the diazonium salt derived from sulfanilic acid (0.20 g) gave 0.37 g **5**, mp 258–260°C,  $R_f$  0.66 (1-butanol: ethanol:pyridine:ammonium hydroxide/4:1:2:3). <sup>1</sup>H-NMR:  $\delta$  1.53 (s, 6H),  $\delta$  1.98 (s, 6H),  $\delta$  3.02 (s, 2H),  $\delta$  6.69–6.73 (d, 1H),  $\delta$  7.51–7.55 (d, 1H),  $\delta$  7.74–7.78 (d, 2H),  $\delta$  7.82–7.86 (d, 2H),  $\delta$  11.72 (s, 1H),  $\delta$  15.05 (s, 1H). Mass spectrum (negative-ion FAB):  $m/z$  427 ( $M - Na$ )<sup>−</sup>.

*1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-5-(4'-carboxyphenylazo)-6-hydroxy- $\gamma$ -carboline (6)*

The synthesis of **6** was carried out using the procedure described for dye **3**. The coupling of **11** (0.30 g, 1.2 mmol) with the diazonium salt derived from 4-aminobenzoic acid (0.17 g) gave 0.38 g **6**, mp 241–243°C,  $R_f$  0.70 (1-butanol:ethanol:pyridine:ammonium hydroxide/4:1:2:3). <sup>1</sup>H-NMR:  $\delta$  1.52 (s, 6H),  $\delta$  1.95 (s, 6H),  $\delta$  2.90 (s, 2H),  $\delta$  6.60–6.64 (d, 1H),  $\delta$  7.49–7.52 (d, 1H),  $\delta$  7.79–7.82 (d, 2H),  $\delta$  8.09–8.13 (d, 2H),  $\delta$  11.71 (s, 1H),  $\delta$  15.29 (s, 1H). Mass spectrum (negative-ion FAB):  $m/z$  391 ( $M - Na$ )<sup>−</sup>.

*1-(4'-Nitrophenylazo)-2-naphthol (15)*

The synthesis of **15** was carried out using the procedure described for dye **1**. The coupling of 2-naphthol (3.0 g, 0.02 mol) with the diazonium salt derived from 4-nitroaniline (2.9 g) gave 4.9 g **15**, mp 249–251°C,  $R_f$  0.44 (PhMe). <sup>1</sup>H-NMR:  $\delta$  6.90–6.93 (d, 1H),  $\delta$  7.44–7.50 (t, 1H),  $\delta$  7.60–7.66 (t, 1H),  $\delta$  7.7–7.86 (m, 5H),  $\delta$  7.95–7.99 (d, 1H),  $\delta$  8.53–8.57 (d, 1H),  $\delta$  15.84 (s, 1H). Mass spectrum (negative-ion FAB):  $m/z$  327 ( $M - Na$ )<sup>−</sup>.

*1-(4'-Carboxyphenylazo)-2-naphthol (17)*

The synthesis of **17** was carried out using the procedure described for dye **3**. The coupling of 2-naphthol (3.0 g, 0.02 mol) with the diazonium salt derived from 4-aminobenzoic acid (2.9 g) gave 5.1 g **17**, mp 294–296°C,  $R_f$  0.60 (1-butanol:ethanol:pyridine:ammonium hydroxide/4:1:2:3). <sup>1</sup>H-NMR:  $\delta$  6.90–6.94 (d, 1H),  $\delta$  7.41–7.47 (t, 1H),  $\delta$  7.58–7.64 (t, 1H),  $\delta$  7.76–7.79 (d, 3H),  $\delta$  7.92–7.95 (d, 1H),  $\delta$  8.03–8.06 (d, 2H),  $\delta$  8.55–8.59 (d, 1H),  $\delta$  15.89 (s, 1H). Mass spectrum (negative-ion FAB):  $m/z$  291 ( $M - Na$ )<sup>−</sup>.

### Photolysis of dyes in solution

Dilute solutions ( $1.0 \times 10^{-4}$  mol/litre) of dye in *N,N*-dimethylformamide were poured into quartz tubes and exposed to 254-nm UV light in the photochemical reactor. After each 5–10 min of exposure, the absorbance was measured on a Perkin Elmer UV–visible spectrometer model 559A. The relative percentage of fading was calculated at the absorption maximum of each dye using the following equation:

$$\text{Relative \% fading} = 100 \times (A_0 - A_t)/A_0$$

where  $A_0$  is an absorbance at  $\lambda_{\text{max}}$  before exposure, and  $A_t$  is an absorbance at  $\lambda_{\text{max}}$  after time  $t$  exposure.

### Photolysis of dyes in nylon-6 film

Nylon-6 film was cut into pieces of approximately 0.2 g. Each dye (4 mg) was dissolved or dispersed in 20 ml  $\text{H}_2\text{O}$ , and the film was added. The dye bath temperature was raised to 100°C over 30 min, and maintained at that point until the absorbance of the dyed nylon films was in the range of 1.2–1.6. After dyeing, the films were rinsed with distilled water, dried at 55°C overnight in a vacuum oven, cut into small pieces ( $0.8 \times 3.0$  cm), and exposed to 254-nm UV. Color loss was then followed by UV–visible spectroscopy as described above for the irradiation of solutions.

### REFERENCES

1. Allen, N. S. & McKellar, J. F. (eds), *Photochemistry of Dyed and Pigmented Polymers*. Applied Science Publishers, London, UK, 1980.
2. Saganuma, K., *Textile Res. J.*, **47** (1977) 361.
3. Haylock, J. C. & Rush, J. L., *Textiles Res. J.*, **46** (1976) 1.
4. Griffiths, J. & Hawkins, C., *J. Chem. Soc. Chem. Commun.*, 1972, 463.
5. Griffiths, J. & Hawkins, C., *J. Chem. Soc.—Perkin II*, 1977, 747.
6. Kuramoto, N. & Kitao, T., *J. Soc. Dyers Colour.*, **91** (1982) 19.
7. Usilton, J. J. & Patel, A. R., *Amer. Chem. Soc. Polym. Prep.*, **18** (1977) 393.
8. Kim, S.-D. Ph thesis, College of Textiles, North Carolina State University, Raleigh, NC, USA.
9. McGregor, R., Iijima, T., Sakai, T., Gilbert, R. D. & Hamada, K., *J. Membrane Sci.*, **18** (1984) 129.
10. Komzolova, N. N., Kucherova, N. F. & Zagorevskii, V. A., *Zh. Obsch. Khimii*, **34**(7) (1964) 2383.
11. Hamada, K., Iijima, T. & McGregor, R., *Macromolecules*, **19** (1986) 1443.