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Dyes and Pigments 57 (2003) 77–86
DYES and PIGMENTS
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Synthesis and properties of bis(hetaryl)azo dyes

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Received 18 October 2002; received in revised form 29 November 2002; accepted 6 January 2003

Abstract

Unsymmetrical and symmetrical bis(hetaryl)azo dyes were prepared by diazotisation-coupling and oxidation reactions in low to good yields. Their absorption maxima were observed in the range of 427–631 nm, being more bathochromic than the corresponding non-hetarylazo derivatives. No remarkable difference of decomposition temperature in the bis(hetaryl)azo dyes was observed except for the pyridone derivative. The photofading of benzothiazolylazo derivatives in ethanol in air occurred by way of reductive processes.

Keywords: Hetaryl azo compounds; UV–vis absorption spectrum; Solvatochromism; Thermostability; Photostability

1. Introduction

Azo compounds are very important in the fields of dyes, pigments and advanced materials [1]. Though many kinds of azo dyes have been synthesised, bis(hetaryl) derivatives are relatively rare. Unsymmetrical bis(hetaryl)azo dyes can be synthesised by the diazotisation of hetarylamines followed by a coupling reaction with heteroaromatic compounds. Though most hetarylamines can act as diazotisation components, hetaryl coupling components are limited. Electron-rich heteroaromatic substrates such as pyridones [2], imidazolones [3], thiophenes [4–6], thiazoles [4–6], and bithiazoles [7] can act as coupling components. Symmetrical bis(hetaryl)azo dyes have been prepared by the chemical and electrochemical oxidation of hetarylamines [8–12], hydrazines [13], oximes [14], reduction of nitro derivatives [15] and coupling of nitrenes produced from azides [16]. Bis(hetaryl)azo dyes are also interesting compounds from the viewpoint of their use as advanced materials. We report herein the synthesis, UV–vis absorption spectra, photo- and thermostabilities of bis(hetaryl)azo dyes.

2. Results and discussion

2.1. Synthesis

Unsymmetrical bis(hetaryl)azo dyes **3** were synthesised by the diazotisation-coupling reaction shown in Scheme 1 and Table 1. Hetarylamines **1** were diazotised using sodium nitrite in the presence of sulfuric acid followed by coupling with heteroaromatic substrates **2** to produce unsymmetrical bis(hetaryl)azo dyes **3** in low to good yield.

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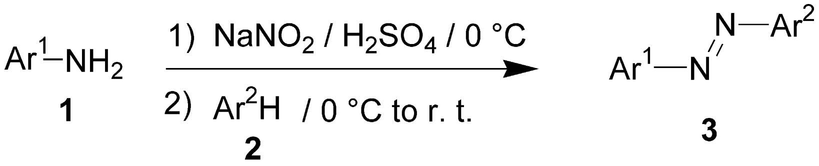
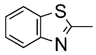
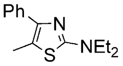
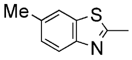
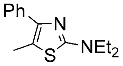
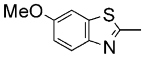
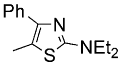
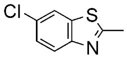
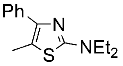
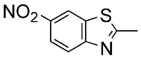
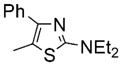
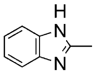
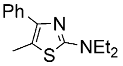
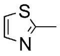
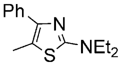
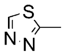
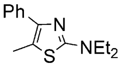
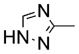
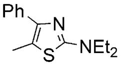
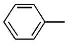
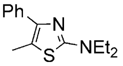
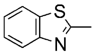
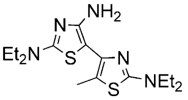
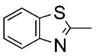
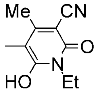
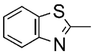
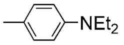
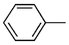
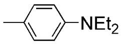
doi:10.1016/S0143-7208(03)00011-1



Scheme 1.

Table 1
Synthesis and properties of unsymmetrical bis(hetaryl)azo dyes 3

Compd	Ar^1	Ar^2	Yield[a] (%)	λ_{max} (nm) (ε)[b]	Mp (°C)	T_d (°C)	E_{red}[c] (V)	E_{ox}[c] (V)
3a			66	532 (43 900)	159	252	−1.188	0.813
3b			74	534 (30 300)	203	265	−1.190	0.798
3c			59	534 (34 800)	186	274	−1.190	0.714
3d			37	570 (21 000)	253	273	−0.964	1.095
3e			41	551 (17 100)	260 (dec)	263	−0.952	0.976
3f			2.6	510 (24 500)	291 (dec)	291	–[d]	–[d]
3g			71	515 (30 900)	108	267	–[d]	–[d]
3h			38	510 (39 000)	211	266	–[d]	–[d]
3i			44	489 (25 500)	261 (dec)	261	–[d]	–[d]
3j			60	471 (28 000)	107	249	–[d]	–[d]
3k			15	453 (24 100), 631 (33 000)	262 (dec)	262	−1.154	0.214
3l			80	440 (41 600)	332 (dec)	332	−0.952	1.048
3m			70	511 (54 100)	166	278	−1.381	0.738
3n			25[e]	420 (26 300)	102	269	–[d]	–[d]

[a] Isolated yields.

[b] Measured in dichloromethane.

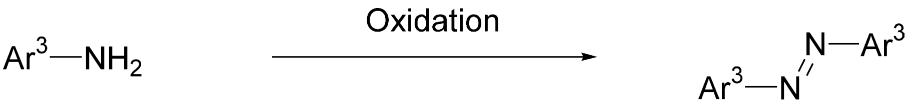
[c] Measured at Au electrode vs Ag/Ag$^+$ in acetonitrile containing 0.1 mol dm^{-3} of tetrabutylammonium perchlorate at the scan rate of 200 mV s^{-1}.

[d] Not measured.

[e] Prepared by the reaction of nitrosobenzene with *N,N*-diethyl-*p*-phenylenediamine in a 25% yield.

The reference compounds **3j** and **3m** were also obtained by the same reaction.

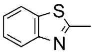
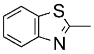
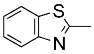
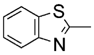
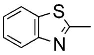
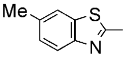
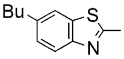
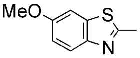
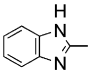
The symmetrical bis(hetaryl)azo dyes **4** were prepared by the oxidation of hetarylamines **1** as shown in Scheme 2. As the type of oxidising reagent has been shown to affect product yield [17], screening of the oxidising reagents for the formation of 2,2′-azobenzothiazole (**4a**) was undertaken. The results are displayed in Table 2. Although the yield of **4a** was low, manganese (IV) oxide was the best reagent among silver (II) oxide, sodium hypochlorite, lead tetraacetate, potassium permanganate, and manganese (IV) oxide (runs 1–5). The other symmetrical azo dyes **4b–e** were also



1 **4**

Scheme 2.

Table 2
Synthesis and properties of symmetrical bis(hetaryl)azo dyes **4**

Run	Compd	Ar^3	Reaction conditions[a]				Yield[b] (%)	λ_{max} (nm) (ε)[c]	Mp (°C)	T_d (°C)	E_{red}[d] (V)	E_{ox}[d] (V)
			Oxidizing reagent (mol amt)	Solvent (ml)	Temp (°C)	Time (h)						
1	**4a**		AgO/3	C_6H_6/30	25–reflux	48	0					
2	**4a**		NaOCl/12	MeCN/5	25	8	12	427 (28 700)	268	302	−0.632	>1.500
3	**4a**		$Pb(OAc)_4$/2	C_6H_6/30	25	24	14					
4	**4a**		$KMnO_4$/9	CH_2Cl_2/30	Reflux	12	17					
5	**4a**		MnO_2/30	C_6H_6/30	Reflux	12	18					
6	**4b**		MnO_2/30	C_6H_6/30	Reflux	12	14	460 (33 000)	302 (dec)	302	–[e]	–[e]
7	**4c**		MnO_2/30	C_6H_6/30	Reflux	12	12	463 (34 000)	170	243	–[e]	–[e]
8	**4d**		MnO_2/30	C_6H_6/30	Reflux	12	5.6	510 (43 100)	289	289	–[e]	–[e]
9	**4e**		MnO_2/30	C_6H_6/30	Reflux	12	4.5	457 (14 500)[f]	260 (dec)	260	–[e]	–[e]

[a] The amount of starting material is 3.0 mmol.

[b] Isolated yields.

[c] Measured in dichloromethane.

[d] Measured at Au electrode vs Ag/Ag^+ in acetonitrile containing 0.1 mol dm^{-3} of tetrabutylammonium perchlorate at the scan rate of 200 mV s^{-1}.

[e] Not measured.

[f] Measured in acetone.

prepared using manganese (IV) oxide in low yield (runs 6–9). 2,2′-Azobenozothiazole (**4a**) has been prepared by the electrochemical oxidation of 2-aminobenzothiazole [12] and the oxidation of 2-hydrazinobenzothiazole with nickel (IV) oxide (11% yield) [13]. Thus, the yield of **4a** obtained in this paper is slightly higher than that reported. 2,2′-Azobenzimidazole (**4e**) has been also prepared by the electrochemical oxidation [11] and reaction of 1-substituted 2-aminobenzimidazoles with sodium metal in liquid ammonia (55% yield), respectively [18]. Thus, the yield obtained for **4e** by the oxidation of 2-aminobenzimidazole with manganese (IV) oxide was lower than the reported one.

2.2. *UV–vis absorption spectra*

Typical UV–vis absorption spectra of bis(hetaryl)azo compounds **3a**, **3k**, **3l**, **3m**, **3n**, and **4a** are shown in Fig. 1. The absorption maxima (λ_{max}) were observed in the range of 427–631 nm. The UV–vis absorption spectra of **3** and **4** are also indicated in Tables 1 and 2.

The unsymmetrical dyes were more bathochromic in the following order: **3a** (532 nm) > **3g** (515), **3f** (510), **3h** (510) > **3i** (489), **3j** (471). The λ_{max} of benzothiazolylazo dyes having an electron-withdrawing group **3d** (570) and **3e** (551) were more bathochromic than the unsubstituted one **3a** (532). The λ_{max} was also affected by the coupling components used. The λ_{max} was more bathochromic in the order: **3k** (631) > **3a** (532), **3m** (511) > **3l** (440). The oxidation potentials (E_{ox}) of 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole, 2-diethylamino-4-phenylthiazole, *N,N*-diethylaniline, and 3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone have been reported to be −0.15, 0.32, 0.64, and 0.95 V vs Ag/Ag$^+$, respectively [19]. Thus, the larger the electron-withdrawing nature of the diazotisation moiety and the electron-donating nature of the coupling moiety, the more bathochromic were the unsymmetrical bis(hetaryl)azo dyes **3**.

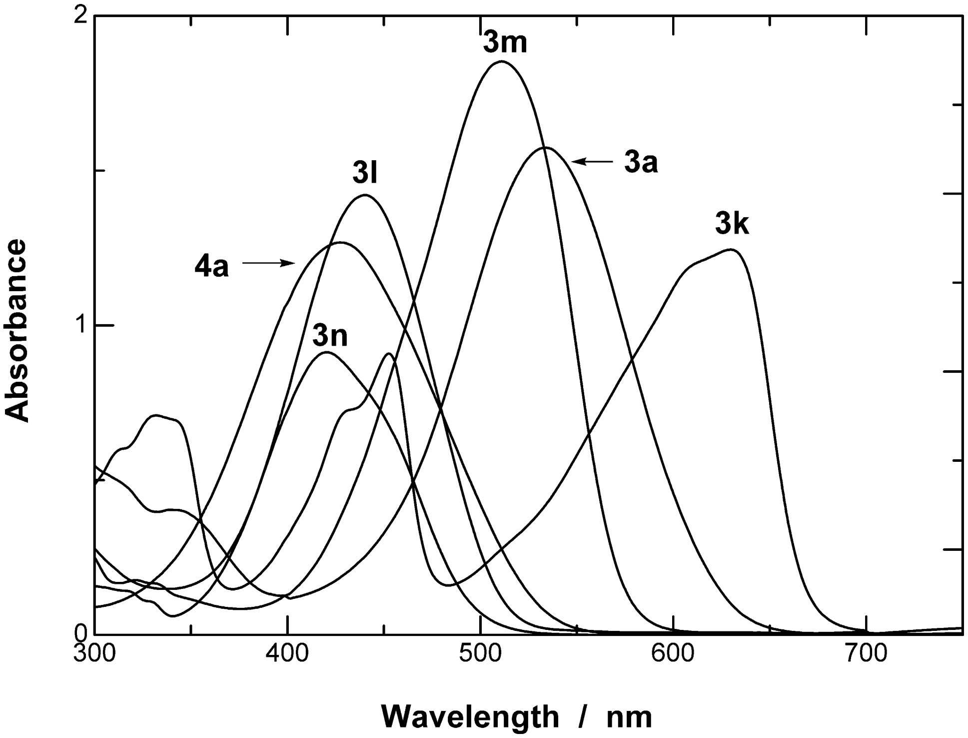


Fig. 1. UV–vis absorption spectra of **3a**, **3k**, **3l**, **3m**, **3n**, and **4a** in dichloromethane.

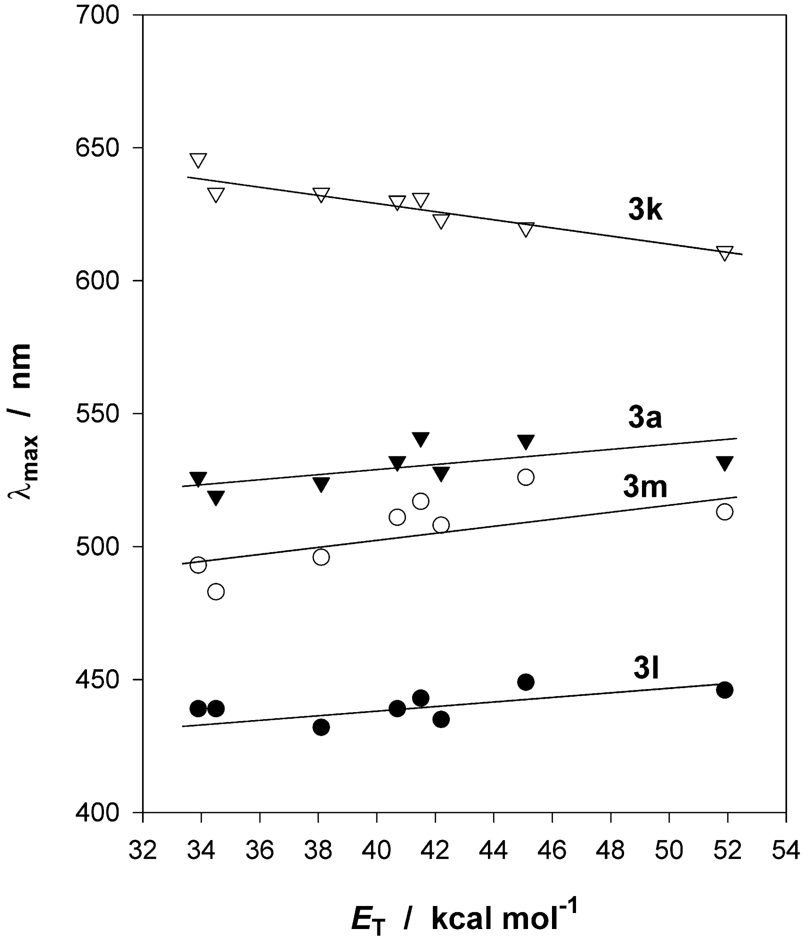


Fig. 2. Solvatochromism of **3a**, **3k**, **3l**, and **3m**. UV–vis absorption spectra were measured in toluene (E_T: 33.9 kcal mol^{-1}), diethyl ether (34.5), ethyl acetate (38.1), dichloromethane (40.7), benzonitrile (41.5), acetone (42.2), dimethylsulfoxide (45.1), and ethanol (51.9).

Most of the symmetrical dyes **4** were more hypsochromic (427–510 nm) than the unsymmetrical derivatives **3** (440–631 nm). No remarkable difference in λ_{max} between the symmetrical bis(hetaryl)azo derivatives **4a** and **4e** and azobenzene (444 nm in dichloromethane) was observed.

The solvatochromism of azo derivatives **3a**, **3k**, **3l**, and **3m** are shown in Fig. 2; most neutral azo dyes show postitive solvatochromism; interestingly, the bis(hetaryl)azo dye **3k** showed negative solvatochromism. A plausible schemetic explanation is shown in Fig. 3. Since dye **3k** comprises a very strong push–pull chromophoric system, this compound can exist as the more polar diazacyanine tautomer in the ground state and the less polar neutral azo tautomer in the excited state. The dipole moment of **3k** in the ground and excited states were calculated to be 9.419 and 5.623 debye, respectively, using the PI SYSTEM 98 program, supporting its negative solvatochromism.

2.3. Thermostability

Thermogravimetric differential thermal analysis (TG-DTA) of **3a** is shown in Fig. 4. This compound showed an endothermic peak corresponding to melting at 161 °C and then decomposed with exothermic peaks at 253 and 520 °C; the decomposition temperature (T_d) was 252 °C. The

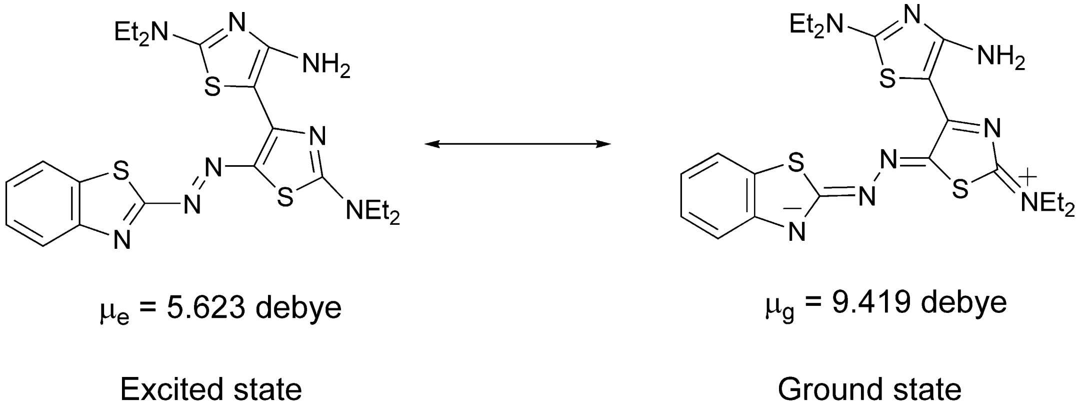


Fig. 3. Plausible schemetic explanation for negative solvatochromism of **3k**.

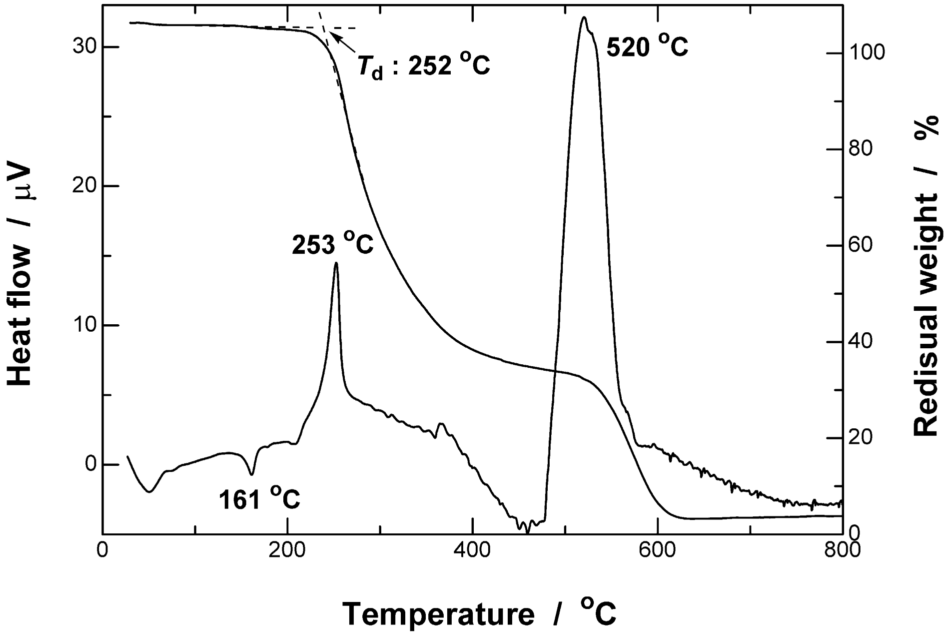


Fig. 4. TG-DTA curve of **3a**.

thermostability of other dyes were also measured in the same way; the results are shown in Tables 1 and 2. No remarkable differences in T_d between the bis(hetaryl)azo dyes **3** and **4** were observed except for the pyridone derivative **3l** whose T_d was rather high (332 °C). As it is well known that azopyridones exist as hydrazone tautomers, the azopyridone dye **3l** can have two carbonyl groups and a cyano group. Compounds having high melting point can show high T_d, and so, the rather high T_d of **3l** could be attributed to strong intermolecular interactions in the polar pyridone moiety.

2.4. Photostability

The photostability of the azo dyes measured in ethanol in air is shown in Fig. 5. The stability of dyes increased in the order: **3m** > **3a** > **3l** > **4a** > **3k**. The order of photostability is consistent with

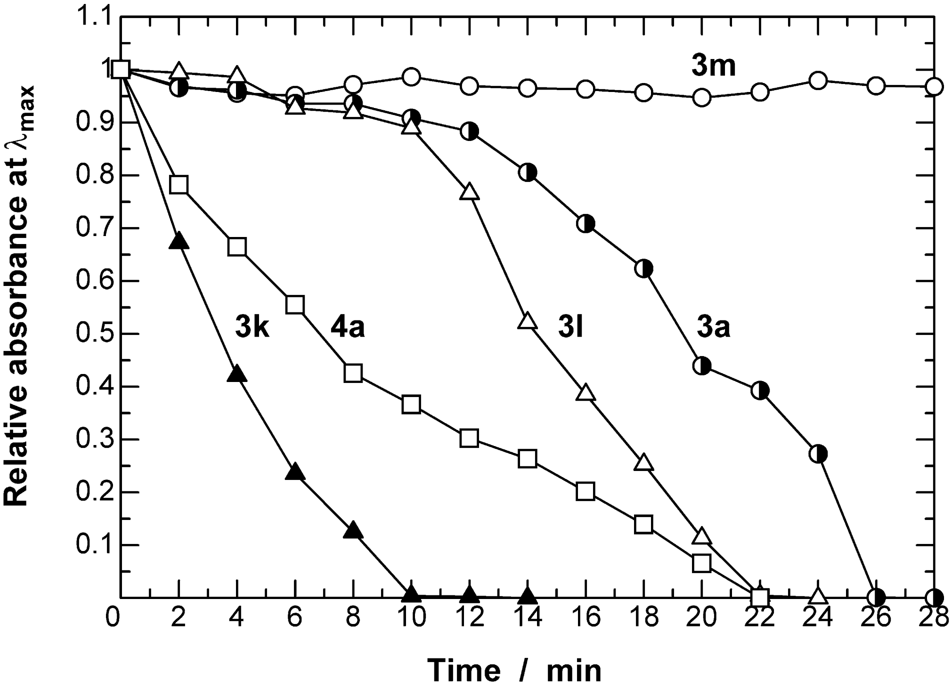


Fig. 5. Photostability of **3a**, **3k**, **3l**, **3m**, and **4a**.

that of E_{red} except for **3k**. Dye **3m** has the highest E_{red} (−1.381 V vs Ag/Ag^+) followed by **3a** (−1.188), **3l** (−0.952), and **4a** (−0.632). The substituent effect on the phtostability of benzothiazolylazo dyes **3a–e** is shown in Fig. 6. It is clear that the larger the electron-withdrawing nature of the substituent or the lower was the E_{red} of substrate, the less stable were the dyes under UV irradiation. Since dye **3k** has an extremely low E_{ox} (0.214), this compound may be easily oxidised by UV-irradiation under an air atmosphere. These results indicate that the photofading of the dyes, with the exception of **3k**, could proceed by way of reductive processes in ethanol even in air.

3. Conclusions

Bis(hetaryl)azo dyes were synthesized by diazotisation-coupling and oxidation reactions in low to good yield. Their λ_{max} were observed in the range of 427–631 nm and molecular absorption coefficient 14 500–54 100 $dm^3\ mol^{-1}\ cm^{-1}$. Their decomposition temperatures were found to be in the range 243–332 °C. Their photofading probably proceeds by reduction in ethanol in air.

4. Experimental

4.1. Equipments

NMR spectra were recorded on a Varian Inova 400 spectrometer and EIMS spectra were recorded on a Shimadzu QP-1000 spectrometer. UV–vis absorption spectra were taken on a Hitachi U-3500 spectrometer. Thermoanalysis was performed on Shimadzu TGA-50 and DTA-50 instruments. Cyclic voltamometry was performed using a Hokuto Denko HSV-100 Automatic Polarisation System.

4.2. Materials

Arylamines 1, *N,N*-diethylaniline (**2m**), azobenzene, and lead tetraacetate were purchased

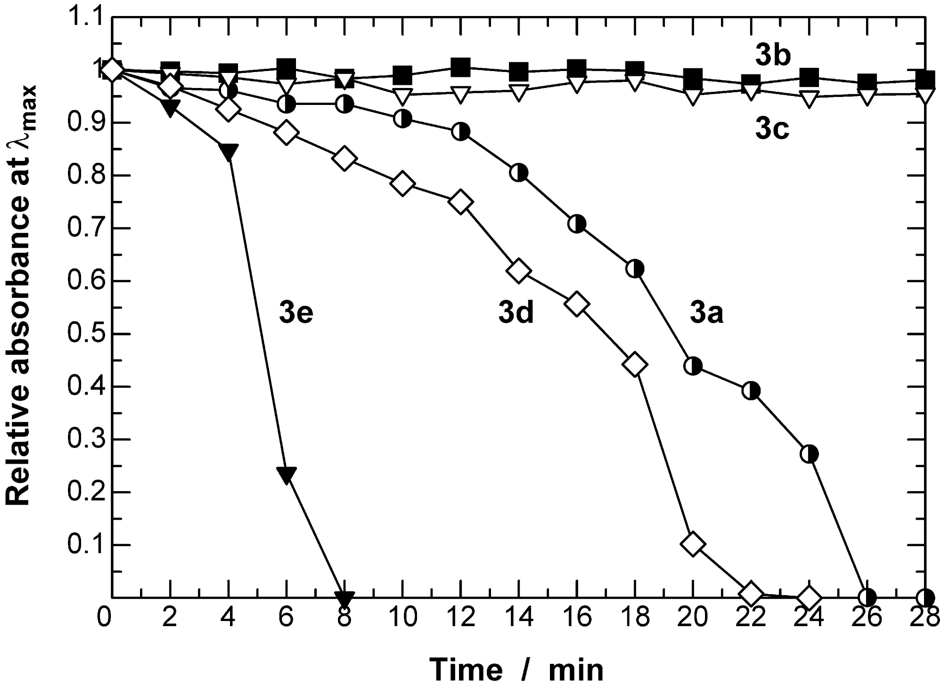


Fig. 6. Substituent effect on photostability of 5-(2-benzothiazolylazo)-2-diethylamino-4-phenylazothiazoles **3a**–**e**.

from Tokyo Kasei Co., Ltd. Manganese (IV) oxide, sodium hypochlorite, and potassium permanganate were purchased from Nakarai Tesque. Silver (II) oxide was purchased from Kanto Chemical Co., Ltd. 2-Diethylamino-4-phenylthiazole (**2a**) [20], 4′-amino-2,2′-bis(diethylamino)-4,5′-bithiazole (**2k**) [21], 3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone (**2l**) [22] were prepared as described in the literature.

4.3. Synthesis of unsymmetrical bis(hetaryl)azo dyes 3

To an acetic acid solution (6 ml) of hetaryl amine **1** (1 mmol) were added concentrated sulfuric acid (2 ml) and an aqueous solution (3 ml) of sodium nitrite (76 mg, 1.1 mmol). The mixture was stirred at 0 °C for 2 h, to which was added a methanol solution (10 ml) of coupling component **2** (1 mmol) and the mixture was stirred at 0 °C to room temperature overnight. After reaction was complete, the resulting precipitate was filtered and the product purified by column chromatography (SiO_2, AcOEt) and recrystallised from chloroform. The physical and spectral data are shown below.

*4.3.1. 5-(2-Benzothiazolylazo)-2-diethylamino-4-phenylthiazole (**3a**)*

^{1}H NMR ($CDCl_3$) δ 1.39 (t, $J=7.2$ Hz, 6H), 3.58 (br, 2H), 3.91 (br, 2H), 7.32 (t, $J=7.9$ Hz, 1H), 7.43 (t, $J=7.9$ Hz, 1H), 7.51–7.54 (m, 3H), 7.77 (d, $J=7.9$ Hz, 1H), 7.98 (d, $J=7.9$ Hz, 1H), 8.39–8.41 (m, 2H); EIMS (70 eV) m/z (rel intensity) 393 (M^+; 73), 364 (100), 322 (54), 133 (60), 89 (45).

*4.3.2. 2-Diethylamino-5-(6-methyl-2-benzothiazolylazo)-4-phenylthiazole (**3b**)*

^{1}H NMR ($CDCl_3$) δ 1.37 (t, $J=7.2$ Hz, 6H), 2.48 (s, 3H), 3.54 (br, 2H), 3.91 (br, 2H), 7.23 (d, $J=8.2$ Hz, 1H), 7.50–7.54 (m, 3H), 7.58 (s, 1H), 7.85 (d, $J=8.2$ Hz, 1H), 8.38–8.40 (m, 2H); EIMS (70 eV) m/z (rel intensity) 407 (M^+; 64), 378 (100), 336 (39), 133 (46), 72 (29).

4.3.3. 2-Diethylamino-5-(6-methoxy-2-benzothiazolylazo)-4-phenylthiazole (**3c**)

^{1}H NMR (CDCl$_3$) δ 1.37 (t, J = 7.2 Hz, 6H), 3.57 (br, 2H), 3.88 (br, 2H), 3.89 (s, 3H), 7.03 (d, J = 8.9 Hz, 1H), 7.27 (s, 1H), 7.49–7.54 (m, 3H), 7.85 (d, J = 8.9 Hz, 1H), 8.38–8.39 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 423 (M$^+$; 100), 394 (89), 352 (36), 133 (32), 72 (24).

4.3.4. 5-(6-Chloro-2-benzothiazolylazo)-2-diethylamino-4-phenylthiazole (**3d**)

^{1}H NMR (DMSO-d_6) δ 1.33 (t, J = 7.4 Hz, 6H), 3.65 (d, J = 7.4 Hz, 2H), 3.95 (d, J = 7.4 Hz, 2H), 7.47 (dd, J = 8.7 and 2.2 Hz, 1H), 7.58–7.63 (m, 3H), 7.86 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 2.2 Hz, 1H), 8.29–8.31 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 429 (M$^+$ + 2; 41), 427 (M$^+$; 86), 398 (100), 356 (66), 133 (84), 72 (78).

4.3.5. 2-Diethylamino-5-(6-nitro-2-benzothiazolylazo)-4-phenylthiazole (**3e**)

^{1}H NMR (CDCl$_3$) δ 1.41 (t, J = 7.2 Hz, 6H), 3.60 (br, 2H), 3.99 (br, 2H), 7.55–7.57 (m, 3H), 7.96 (d, J = 8.9 Hz, 1H), 8.28 (d, J = 8.9 Hz, 1H), 8.40–8.41 (m, 2H), 8.68 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 438 (M$^+$; 74), 409 (50), 367 (89), 147 (17), 133 (78), 72 (100).

4.3.6. 2-(Benzimidazolylazo)-2-diethylamino-4-phenylthiazole (**3f**)

^{1}H NMR (DMSO-d_6) δ 1.37 (t, J = 7.2 Hz, 6H), 3.68 (br, 4H), 5.30 (s, 1H), 7.20–7.35 (m, 3H), 7.51–7.57 (m, 3H), 7.80 (br, 1H), 8.20–8.22 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 376 (M$^+$; 59), 347 (100), 305 (23), 133 (18), 72 (18).

4.3.7. 2-Diethylamino-4-phenyl-5-(2-thiazolylazo)-thiazole (**3g**)

^{1}H NMR (CDCl$_3$) δ 1.36 (t, J = 7.2 Hz, 6H), 3.68 (br, 4H), 7.15 (d, J = 3.4 Hz, 1H), 7.45–7.48 (m, 3H), 7.80 (d, J = 3.4 Hz, 1H), 8.34–8.35 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 343 (M$^+$; 99), 314 (58), 272 (87), 133 (50), 72 (100).

4.3.8. 2-Diethylamino-5-[2-(1,3,4-thiaziazolyl)azo]-4-phenylthiazole (**3h**)

^{1}H NMR (CDCl$_3$) δ 1.38 (t, J = 7.3 Hz, 6H), 3.57 (br, 2H), 3.94 (br, 2H), 7.47–7.52 (m, 3H), 8.29–8.31 (m, 2H), 8.87 (s, 1H); EIMS (70 eV) *m/z* (rel intensity) 344 (M$^+$; 44), 273 (68), 246 (37), 133 (57), 104 (25), 89 (35), 71 (100).

4.3.9. 2-Diethylamino-5-[3-(1,2,4-triazolyl)azo]-4-phenylthiazole (**3i**)

^{1}H NMR (CDCl$_3$) δ 1.35 (t, J = 7.3 Hz, 6H), 3.55 (br, 2H), 3.89 (br, 2H), 4.13 (s, 1H), 7.47–7.50 (m, 3H), 8.02 (s, 1H), 8.20–8.24 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 327 (M$^+$; 78), 256 (100), 133 (51), 104 (23), 89 (48), 72 (89).

4.3.10. 2-Diethylamino-5-phenylazo-4-phenylthiazole (**3j**)

^{1}H NMR (CDCl$_3$) δ 1.34 (t, J = 7.3 Hz, 6H), 3.67 (br, 4H), 7.30 (t, J = 7.3 Hz, 1H), 7.41–7.48 (m, 5H), 7.74 (d, J = 7.3 Hz, 2H), 8.34–8.36 (m, 2H); EIMS (70 eV) *m/z* (rel intensity) 336 (M$^+$; 81), 335 (100), 133 (61), 132 (47), 89 (44).

4.3.11. 2-Diethylamino-5-(2-benzothiazolylazo)-4-(4-amino-2-diethylamino-5-thiazolyl)thiazole (**3k**)

^{1}H NMR (CDCl$_3$) δ 1.31–1.37 (m, 12H), 3.51–3.75 (m, 8H), 7.11 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 486 (M$^+$; 64), 357 (26), 150 (40), 99 (38), 72 (100).

4.3.12. 5-(2-Benzothiazolylazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridone (**3l**)

^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 7.1 Hz, 3H), 2.62 (s, 3H), 4.05 (q, J = 7.1 Hz, 2H), 7.37 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 339 (M$^+$; 84), 240 (100), 225 (45), 150 (36), 135 (86), 108 (49), 78 (36).

4.3.13. 4-(2-Benzothiazolylazo)-N,N-diethyl-aniline (**3m**)

^{1}H NMR (CDCl$_3$) δ 1.28 (t, J = 7.1 Hz, 6H), 3.51 (q, J = 7.1 Hz, 4H), 6.74 (d, J = 9.4 Hz, 2H), 7.37 (t, J = 7.9 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 9.4 Hz, 2H), 8.06 (d, J = 7.9 Hz, 1H); EIMS (70 eV) *m/z* (rel intensity) 310 (M$^+$; 60), 267 (100), 148 (85), 133 (59), 119 (30), 105 (31), 91 (39), 77 (27).

4.4. Synthesis of symmetrical bis(hetaryl)azo dyes **4** by manganese (IV) oxide

To a benzene solution of hetarylamines **1** (3 mmol) was added manganese (IV) oxide (7.8 g, 90 mmol) and the mixture was refluxed for 12 h. After reaction was complete, the mixture was filtered and the filtrate was concentrated. The product was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallised from methanol. The physical and spectral data are shown below.

4.4.1. 2,2′-Azobenzothiazole (**4a**)

^{1}H NMR ($CDCl_3$) δ 7.57 (t, J=6.9 Hz, 2H), 7.61 (t, J=6.9 Hz, 2H), 7.97 (d, J=6.9 Hz, 2H), 8.28 (d, J=6.9 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 296 (M^+; 2), 268 (100), 134 (74), 108 (33), 90 (47).

4.4.2. 6,6′-Dimethyl-2,2′-azobenzothiazole (**4b**)

^{1}H NMR ($CDCl_3$) δ 2.55 (s, 6H), 7.41 (d, J=8.4 Hz, 2H), 7.74 (s, 2H), 8.12 (d, J=8.4 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 324 (M^+; 5), 296 (100), 164 (37), 148 (34), 121 (58), 104 (30), 77 (56).

4.4.3. 6,6′-Dibutyl-2,2′-azobenzothiazole (**4c**)

^{1}H NMR ($CDCl_3$) δ 0.96 (t, J=7.3 Hz, 6H), 1.42 (sextet, J=7.3 Hz, 4H), 1.70 (quintet, J=7.3 Hz, 4H), 2.80 (t, J=7.3 Hz, 4H), 7.41 (dd, J=8.4 and 1.6 Hz, 2H), 7.75 (d, J=1.6 Hz, 2H), 8.13 (d, J=8.4 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 408 (M^+; 2), 380 (20), 337 (100), 294 (35), 163 (19).

4.4.4. 6,6′-Dimethoxy-2,2′-azobenzothiazole (**4d**)

^{1}H NMR ($CDCl_3$) δ 3.95 (s, 6H), 7.17 (dd, J=9.2 and 2.6 Hz, 2H), 7.35 (d, J=2.6 Hz, 2H), 8.10 (d, J=9.2 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 356 (M^+; 11), 328 (60), 313 (100), 120 (37).

4.4.5. 2,2′-Azobenzimidazole (**4e**)

^{1}H NMR (DMSO-d_6) δ 7.33 (t, J=7.9 Hz, 2H), 7.43 (t, J=7.9 Hz, 2H), 7.57 (d, J=7.9 Hz, 2H), 7.88 (d, J=7.9 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 262 (M^+; 4), 234 (100), 133 (95), 105 (43), 90 (45), 78 (27).

4.5. Thermostability measurement

Thermoanalysis was performed under an air atmosphere at heating rate 10 °C min^{-1}.

4.6. Photostability measurement

An ethanol solution (15 ml) of dye (5×10^{-2} mmol dm^{-3}) in a borosilicate glass tube was irradiated with a 300-W high-pressure mercury lamp using a merry-go-round at 25 °C in air. The UV–vis absorption spectra were measured and the stability of the dye was calculated on the basis of absorbance at λ_{max}.

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