Synthesis, structure, and UV–VIS absorption spectra of azo dyes derived from (dialkylamino)thiazole dimers †

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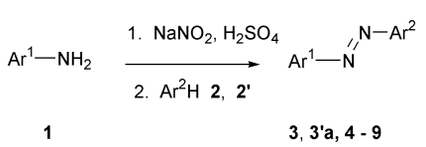
(Dialkylamino)thiazole dimers act as very strong electron-donating coupling components in azo dyes, the first and second UV–VIS absorption bands of which were observed at λ = 568–737 (ε = 24000–88000) and 404–475 (ε = 9200–52000) nm in dichloromethane, respectively. The azo compounds derived from the (dialkylamino)thiazole dimers having very strong electron-withdrawing moieties such as 4-(perfluoroalkylsulfonyl)phenyls, 2,4-dinitrophenyl, and thiazol-2-yls exhibited a negative solvatochromism. This is the first example of a negative solvatochromism in neutral azo dyes.

Azo dyes contain intramolecular charge-transfer chromophores and therefore, their UV–VIS absorption bands depend on the combination of electron-donating and -withdrawing moieties in the molecules.[1] Nitrophenyl and thiazoles are known as electron-withdrawing diazotisation components. 2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (julolidine),[2] 5-acetylamino-2-methoxy-*N*,*N*-dialkylanilines,[3] and 2,3-dihydroperimidines[4] are strong electron-donating coupling components in azo dyes. Azo dyes derived from these compounds have very important applications. They have been used as dyestuffs,[5] inks,[6] dichroic dyes,[7] and near-infrared absorbing dyes.[8] Recently, (dialkylamino)thiazole dimers, assumed to be electron-rich substrates, have been synthesized.[9] These compounds can act as novel coupling components in dye synthesis. Although a few azo dyes derived from (dialkylamino)thiazole dimers have been synthesized, detailed information on them has not yet been reported. We report here the synthesis, structure, and UV–VIS absorption spectra of the azo dyes derived from (dialkylamino)thiazole dimers.

Results and discussion

The azo dyes **3** and **3′a** derived from (dialkylamino)thiazole dimers **2** and **2′** were synthesized by the diazotisation–coupling reaction shown in Scheme 1. The coupling reaction of the diazonium salts of **1** with **2** and **2′** proceeded to give the azo dyes **3** and **3′a**, respectively. A series of other azo dyes **4–9** was also prepared by the same reaction in order to compare their UV–VIS absorption spectra.



Scheme 1 Synthesis of **3**, **3′a**, and **4–9**.

To synthesize an azo dye with a much stronger electron-withdrawing moiety, the formylthiazolyl azo derivative **3q** was reacted with a pyridone to give **3r**, as shown in Scheme 2.

The UV–VIS absorption spectrum of **3a** is depicted in Fig. 1. The first and second absorption bands were observed at λ = 637 and 449 nm in dichloromethane, respectively.

The shape of the absorption bands of **3a** did not change in the range of dye concentration of 1×10^{-5}–1×10^{-3} mol dm^{-3}, suggesting that the dye **3a** did not aggregate at these dye concentrations. The UV–VIS absorption spectra of azo dyes **3**, **3′a**, and **4–9** are summarized in Table 1. The azo dyes **3** and **3′a** showed their first and second absorption bands at λ = 568–737 and 404–475 nm, respectively.

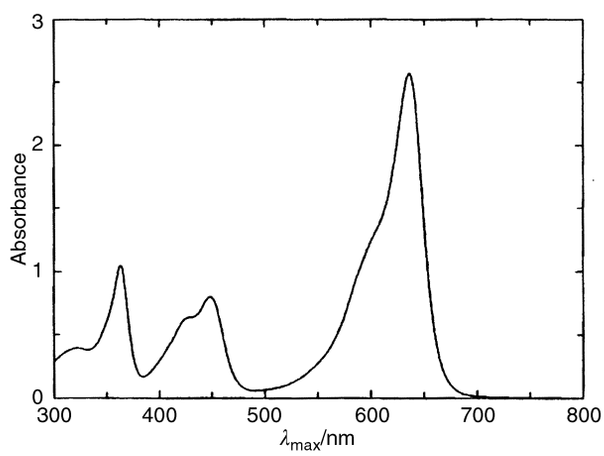


Fig. 1 UV–VIS absorption spectrum of **3a** measured in dichloromethane.

† Physical and spectral data for **4a**, **4p**, **5a**, **6a**, **6p**, **7a**, **8a**, **8c**, **8p**, and **9a** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b006991o/

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The azo dyes **3** and **3′a** derived from the (dialkylamino)-thiazole dimers showed three characteristic points in their UV–VIS absorption spectra compared with usual azo dyes such as **4–9**.

First, the absorption bands of azo dyes **3** and **3′a** were bathochromically shifted compared with azo dyes **4–9**. The relationship between the absorption maxima (λ_{max}) of azo dyes **3a**, **3′a**, **4a**, **5a**, **6a**, **7a**, **8a**, and **9a** and the oxidation potentials (E_{ox}) of their coupling components is indicated in Fig. 2. It is clear that the lower the oxidation potential of the coupling components, the more bathochromic the absorption band of their azo derivatives. It is of importance that the E_{ox} of the (dialkylamino)thiazole dimers **2** and **2′** are very low (−0.16 and −0.07 V *vs.* $Ag/AgNO_3$ in CH_3CN, respectively) compared with those of the other coupling components (0.19–0.93 V). The λ_{max} of the azo dye derived from the (dialkylamino)thiazole monomer, 2,4-bis(dimethylamino)-5-(4-nitrophenylazo)thiazole has been reported to be 545 nm ($\varepsilon = 45000$) in chloroform,[10] being more hypsochromic than **3c** ($\lambda_{max} = 669$ nm ($\varepsilon = 64000$) in dichloromethane). Thus, the azo dyes **3** and **3′a** are compounds with a bathochromically shifted absorption band arising from the strong electron-donating nature of the (dialkylamino)thiazole dimers.

Secondly, the azo dyes **3** and **3′a** showed both positive and negative solvatochromism depending on the type of electronic effect in the diazotisation moiety. It is known that azo dyes normally show a positive solvatochromism.[11] Recently, 5-(4-nitrophenylazo)-2-alkylaminothiazoles, in which the thiazole moiety acts as a coupling component, have also been reported to exhibit positive solvatochromism.[12] Only two types of ionic azo compounds, 4-[2-(triphenylphosphonio)phenylazo]phenolates and (1-methylpyridinium-2-ylazo)- and (1-methylquinolinium-2-ylazo)tetracyanocyclopentadienides, have been reported to reveal negative solvatochromic behavior.[13] However, no negative solvatochromism in neutral azo dyes has been reported so far. The typical solvatochromic effects in **3** are shown in Fig. 3. The azo dyes **3a**, **3p** and **3r** showed a negative solvatochromism, while **3c** exhibited positive solvatochromic behavior. In particular, dye **3r**, having very strong electron-withdrawing pyridone-substituted thiazolylazo and electron-donating bithiazolyl moieties, showed a large negative solvatochromism. The solvatochromism of the other azo dyes was also examined in toluene (molar electron transition energy $E_T = 33.9$ kcal mol^{-1}),[14] dichloromethane (40.7 kcal mol^{-1}), and dimethyl sulfoxide (DMSO, 45.1 kcal mol^{-1}). These results are summarized in Table 2. Azo dyes **3a**, **3b**, **3m**, **3p**, **3q**, **3r**, and **3′a** having very strong electron-withdrawing moieties such as 4-(perfluoroalkylsulfonyl)phenyls, 2,4-dinitrophenyl, and thiazol-2-yls showed negative solvatochromism. This result is in contrast to the positive solvatochromism of the near-infrared absorbing push–pull 5-acetylamino-4-(4-chloro-5-substituted thiazol-2-ylazo)-2-methoxy-*N*-(hexan-2-yl)aniline derivative.[8] The other azo dyes **3c–l**, **3o**, and **4a–9a** exhibited positive solvatochromism. The dipole moments (μ) of the azo dyes in the excited and ground states of their optimized structures were calculated with the MOPAC AM-1 program. The μ values of **3c** in the ground and excited states were calculated to be 14.58 and 18.98 D, respectively. These calculations are consistent with the

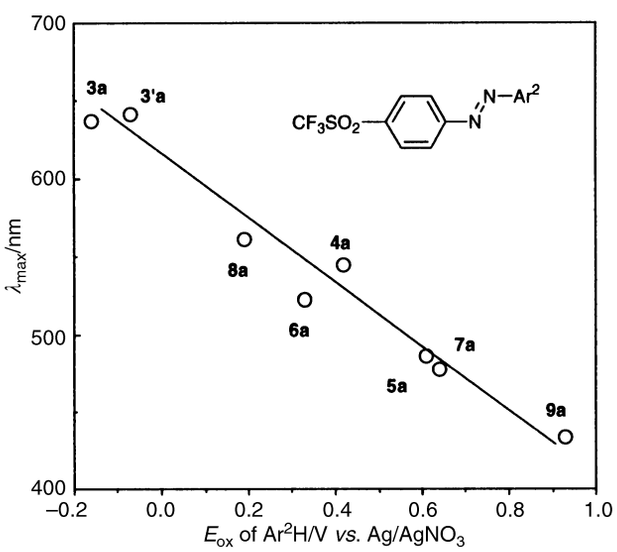


Fig. 2 Relationship between the first absorption band and the ionization potential of couplers. Measured at Au electrodes *vs.* Ag/Ag^+ in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (scan rate: 200 mV s^{-1}).

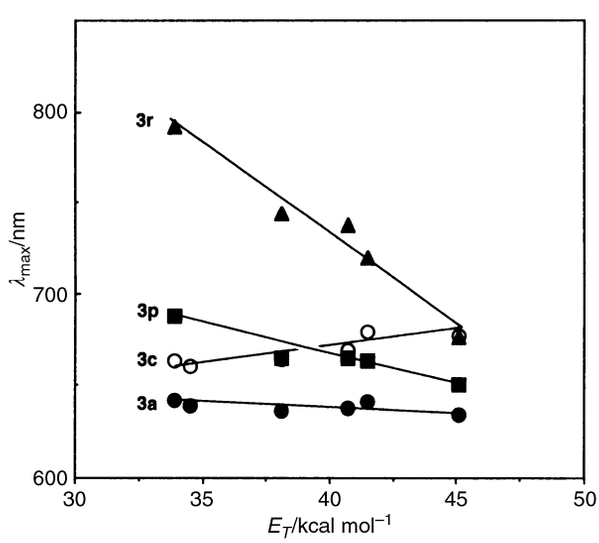
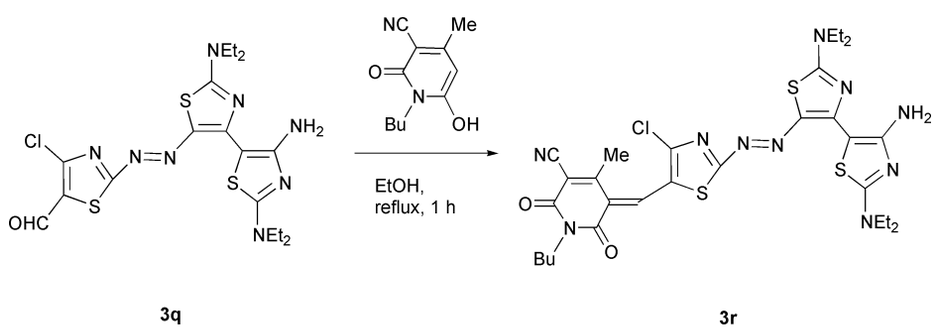


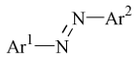
Fig. 3 Solvatochromism of **3a**, **3c**, **3p**, and **3r**. The spectra were measured in toluene (E_T: 33.9 kcal mol^{-1}), diethyl ether (34.5), ethyl acetate (38.1), dichloromethane (40.7), benzonitrile (41.5), DMSO (45.1). The compounds **3p** and **3r** were insoluble in diethyl ether.



3q **3r**

Scheme 2 Synthesis of **3r**.

Table 1 UV–VIS absorption bands of azo dyes measured in dichloromethane



3, **3′a**, **4–9**

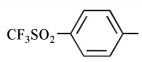
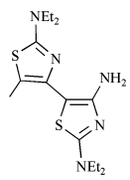
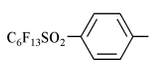
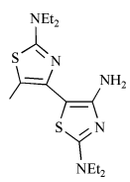
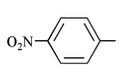
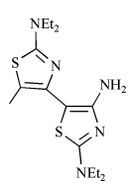
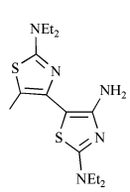
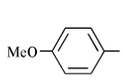
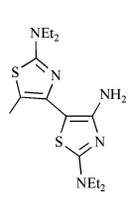
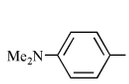
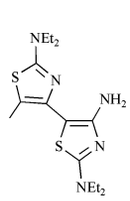
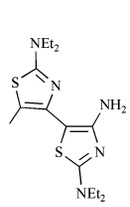
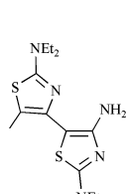
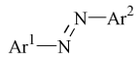
Compound	Ar^1	Ar^2	λ_{max}/nm (ε/l mol^{-1} cm^{-1})
3a			449 (25000) 637 (82000)
3b			450 (23000) 640 (76000)
3c			431 (29000) 669 (64000)
3d			405 (13000) 572 (30000)
3e			423 (15000) 568 (40000)
3f			413 (9200) 582 (27000)
3g			432 (17000) 611 (37000)
3h			436 (18000) 614 (39000)

Table 1 (*Contd.*)



3, **3′a**, **4–9**

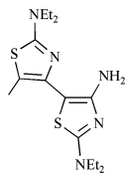
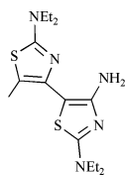
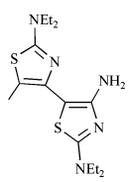
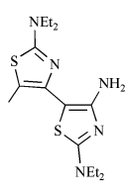
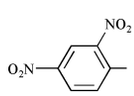
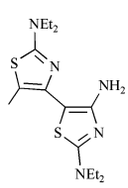
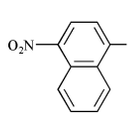
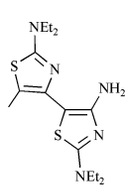
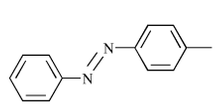
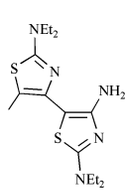
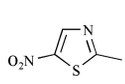
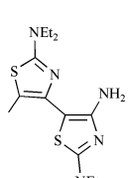
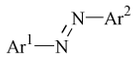
Compound	Ar^1	Ar^2	λ_{max}/nm (ε/l mol^{-1} cm^{-1})
3i			409 (14000) 583(36000)
3j			438 (21000) 619 (56000)
3k			413 (16000) 587 (38000)
3l			404 (19000) 572 (43000)
3m			435 (32000) 668 (88000)
3n			447 (36000) 721 (69000)
3o			435 (52000) 663 (81000)
3p			441 (35000) 665 (48000)

Table 1 (*Contd.*)



3, **3′a**, **4–9**

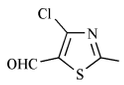
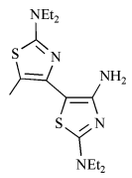
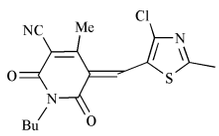
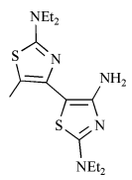
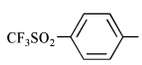
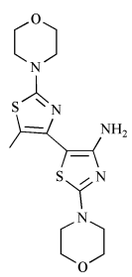
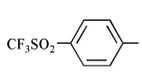
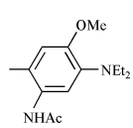
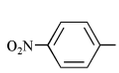
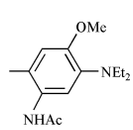
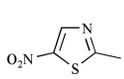
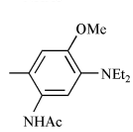
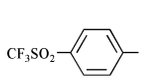
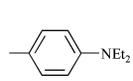
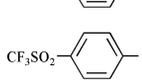
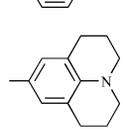
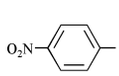
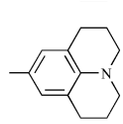
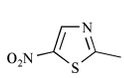
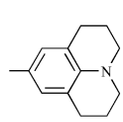
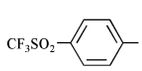
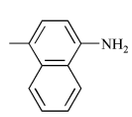
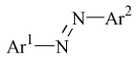
Compound	Ar^1	Ar^2	λ_{max}/nm (ε/l mol^{-1} cm^{-1})
3q			475 (22000) 640 (35000)
3r			457 (51000) 737 (24000)
3′a			445 (22000) 641 (69000)
4a			545 (41000)
4c			550 (30000)
4p			362 (19000) 648 (11000)
5a			486 (38000)
6a			522 (45000)
6c			529 (32000)
6p			629 (47000)
7a			478 (26000)

Table 1 (*Contd.*)



3, **3′a**, **4–9**

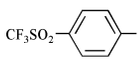
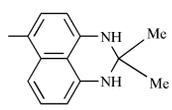
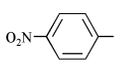
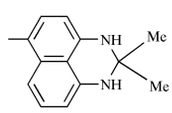
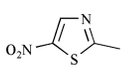
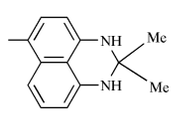
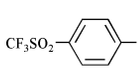
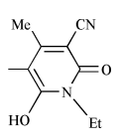
Compound	Ar^1	Ar^2	λ_{max}/nm (ε/l mol^{-1} cm^{-1})
8a			552 (22000)
8c			557 (22000)
8p			665 (29000)
9a			423 (52000)

Table 2 Solvatochromism of azo dyes

Compound	Solvato-chromism[a]	λ_{max}[b]/nm		
		Toluene	Dichloro-methane	DMSO
3a	N	642	637	634
3b	N	646	640	638
3c	P	663	669	677
3d	P	568	572	581
3e	P	565	568	582
3f	P	574	582	593
3g	P	611	611	614
3h	P	609	614	615
3i	P	576	583	590
3j	P	616	619	620
3k	P	584	587	612
3l	P	570	572	583
3m	N	669	668	657
3n	—[c]	709	721	715
3o	P	656	663	696
3p	N	688	665	650
3q	N	667	640	619
3r	N	792	737	676
3′a	N	642	641	639
4a	P	541	545	546
5a	P	472	486	503
6a	P	505	522	538
7a	P	476	478	546
8a	P	553	561	589
9a	P	421	423	434

[a] P and N represent positive and negative solvatochromism, respectively. [b] First absorption band. [c] Not defined.

positive solvatochromic behavior of **3c**. Thus, the electron-withdrawing nature of the nitro group (σ_p (NO_2) = 0.78) is not strong enough to cause a negative solvatochromism in the azo dyes **3**. The ground state of the 4-(trifluoromethylsulfonyl) derivative **3a** (σ_p (CF_3SO_2) = 0.93)[15] was calculated to be slightly more polar (μ = 15.96 D) than the excited state (15.85 D). The ground state of compound **3r**, showing a large negative solvatochromism, was also calculated to be more polar (24.67 D) than the excited state (23.26 D). The other azo derivatives showing a negative solvatochromism **3b**, **3m**, **3p**, **3q**, and **3′a** were also calculated to be more polar in their ground states than in their excited states. The possible mesomeric structures of **3a** in the ground and excited states are depicted in Fig. 4. The more polar, charge-separated diazamerocyanine structures **A**, **A′**, and **A″** could be predominant in the ground state and with the less polar neutral azo form **B** in the excited state. This is different from the reported negative solvatochromic azo compounds, which could have charge-separated azo and neutral diazamerocyanine structures in the ground and excited states, respectively.[13]

Finally, the absorption band of 2-(5-nitrothiazolylazo) derivative **3p** was more hypsochromic than that of the 4-nitrophenylazo derivative **3c**. In the case of the usual intramolecular charge-transfer azo dyes, the 2-(5-nitrothiazolylazo) derivatives are more bathochromic than the 4-nitrophenylazo derivatives. The 2-(5-nitrothiazolylazo) derivatives **4p** [λ_{max} = 648 nm (ε = 11000)], **6p** [λ_{max} = 629 nm (ε = 47000)], and **8p** [λ_{max} = 665 nm (ε = 29000)] were much more bathochromic than the 4-nitrophenylazo derivatives **4c** [λ_{max} = 550 nm (ε = 30000)], **6c** [λ_{max} = 529 nm (ε = 32000)], and **8c** [λ_{max} = 557 nm (ε = 22000)] respectively, the $\Delta\lambda_{max}$ being 98–108 nm. In contrast, the first absorption bands of **3p** and **3c** were observed at λ = 665 and 669 nm respectively, *i.e.*, 4 nm hypsochromic for the 2-(5-nitrothiazolylazo) derivative **3p**. The positive solvatochromic 4-nitrophenylazo derivative **3c** and negative solvatochromic 2-(5-nitrothiazolylazo) derivative **3p** could have intramolecular charge-transfer azo (neutral azo) and charge-separated diazamerocyanine structures in their ground states, respectively. Therefore, the λ_{max} of **3p** is not comparable to that of **3c** because of their different chromophores.

In conclusion, we have synthesized a series of azo dyes derived from unique coupling components: (dialkylamino)-thiazole dimers. The bithiazolyl moiety showed a very strong electron-donating nature. These dyes exhibited their first and second absorption bands at λ = 568–737 and 404–475 nm in dichloromethane, respectively. The dyes having very strong electron-withdrawing moieties showed negative solvatochromism owing to their charge-separated, polar diazamerocyanine structures in the ground state.

Experimental

Instruments

Melting points were measured with a Yanagimoto micro-melting-point apparatus. NMR spectra were recorded in $CDCl_3$ on a JEOL α 400 spectrometer using tetramethylsilane as an

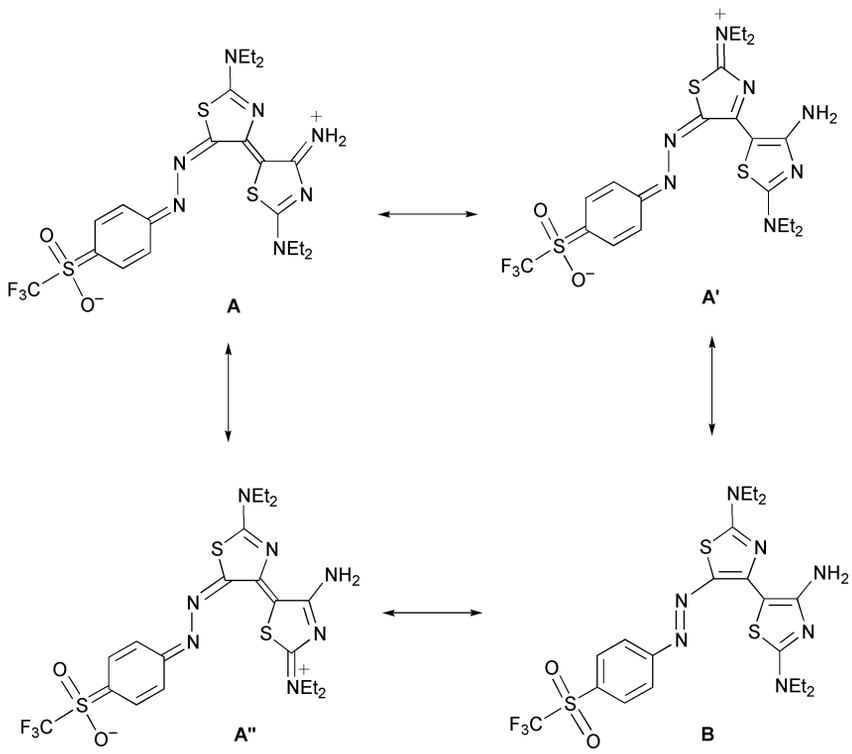


Fig. 4 Possible mesomeric structures of **3a**.

internal standard. Mass spectra (70 eV, EI) were taken on a Shimadzu QP 1000 spectrometer. UV–VIS spectra were measured with a Shimadzu UV 160A spectrometer.

Materials

4-(Trifluoromethylsulfonyl)aniline (**1a**) was purchased from JRD Fluorochemicals Ltd. 4-Nitroaniline (**1c**), aniline (**1d**), 4-anisidine (**1e**), *N*,*N*-dimethylamino-*p*-phenylenediamine (**1f**), 3-nitroaniline (**1g**), 2-nitroaniline (**1h**), 2-anisidine (**1i**), 2-cyanoaniline (**1j**), 2-(trifluoromethyl)aniline (**1k**), 2-*sec*-butylaniline (**1l**), 2,4-dinitroaniline (**1m**), 1-amino-4-nitronaphthalene (**1n**), 4-aminoazobenzene (**1o**), 2-amino-5-nitrothiazole (**1p**), *N*,*N*-diethylaniline and 1-naphthylamine were purchased from Tokyo Kasei Co., Ltd. Julolidine was purchased from Sigma-Aldrich Co., Ltd. 5-Acetylamino-2-methoxy-*N*,*N*-diethylaniline was supplied by Mitsubishi Chemical Co., Ltd. 4-(Perfluorohexylsulfonyl)aniline (**1b**),[16] 2-amino-4-chloro-5-formylthiazole (**1q**),[17] 2,3-dihydro-2,2-dimethylperimidine,[18] 3-cyano-1-ethyl-5-hydroxy-4-methyl-2-pyridone,[19] 4-amino-2-diethylamino-5-(2-diethylaminothiazol-4-yl)thiazole (**2**),[9] 4-amino-2-morpholino-5-(2-morpholinothiazol-4-yl)thiazole (**2′**),[9] 5-acetylamino-2-methoxy-4-nitrophenylazo-*N*,*N*-diethylaniline (**4c**),[20] 9-(4-nitrophenylazo)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (**6c**)[21] and 1-butyl-3-cyano-5-hydroxy-4-methyl-2-pyridone[19] were prepared as described in the literature.

Synthesis of azo dyes 3, 3′ and 4–9

To a DMF solution (5 ml) of arylamine **1** (1.5 mmol) were added sodium nitrite (1.5 mmol) and concentrated sulfuric acid (0.5 ml), and the mixture was stirred at 0 °C for 3 h. To the mixture was added a DMF solution (15 ml) of the coupling components (1.5 mmol), and the mixture was stirred at room temperature overnight. After the reaction was complete, the mixture was poured into water, neutralized, and extracted with dichloromethane (200 ml × 2). After evaporation of the solvent *in vacuo*, the product was isolated by column chromatography (SiO_2, AcOEt) and recrystallised from a chloroform–hexane mixture. The physical and spectral data of the products are given below.

4-Amino-2-(diethylamino)-5-{2-(diethylamino)-5-[4-(trifluoromethylsulfonyl)phenylazo]thiazol-4-yl}thiazole 3a. Yield 30%; mp 218–220 °C (Found: C, 45.16; H, 4.69; N, 17.03. $C_{21}H_{26}F_3N_7O_2S_3$ requires C, 44.91; H, 4.67; N 17.46%); δ_H 1.36 (12H, t, *J* 7.1), 3.50–3.78 (8H, m), 7.61 (2H, d, *J* 9.0), 7.83 (2H, d, *J* 9.0); *m*/*z* 561 (M^+; 100%), 444 (14), 428 (19), 398 (32), 263 (30), 226 (17), 135 (53), 99 (29), 77 (34), 72 (56).

4-Amino-2-(diethylamino)-5-{2-(diethylamino)-5-[4-(perfluorohexylsulfonyl)phenylazo]thiazol-4-yl}thiazole 3b. Yield 18%; mp 235–237 °C (Found: C, 38.27; H, 3.22; N, 12.02. $C_{26}H_{26}F_{13}N_7O_2S_3$ requires C, 38.47; H, 3.23; N, 12.08%); δ_H 1.35 (12H, t, *J* 7.2), 3.55–3.71 (8H, m), 7.60 (1H, d, *J* 8.7), 7.82 (2H, d, *J* 8.7); *m*/*z* 811 (M^+; 18%), 445 (37), 444 (59), 428 (100), 226 (16), 99 (18), 76 (30), 72 (34).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(4-nitrophenylazo)thiazol-4-yl]thiazole 3c. Yield 29%; mp 252–253 °C (Found: C, 50.76; H, 5.54; N, 23.24. $C_{20}H_{26}N_6O_2S_2$ requires C, 50.61; H, 5.52; N, 23.61%); δ_H 1.35 (12H, t, *J* 7.2), 3.59–3.67 (8H, m), 7.52 (2H, d, *J* 8.2), 8.16 (2H, d, *J* 8.2); *m*/*z* 474 (M^+; 100%), 387 (17), 226 (26), 101 (20), 99 (40), 72 (53).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(phenylazo)-thiazol-4-yl]thiazole 3d. Yield 46%; mp 226–228 °C (Found: C, 56.19; H, 6.43; N, 22.46. $C_{20}H_{27}N_7S_2$ requires C, 55.91; H, 6.33; N, 22.82%); δ_H 1.30 (6H, t, *J* 6.6), 1.32 (6H, t, *J* 6.8), 3.48–3.68 (8H, m), 7.10 (1H, t, *J* 7.3), 7.35 (2H, t, *J* 7.3), 7.65 (2H, d, *J* 7.3); *m*/*z* 429 (M^+; 100%), 342 (10), 226 (14), 99 (18).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(4-methoxyphenylazo)thiazol-4-yl]thiazole 3e. Yield 12%; mp 193–194 °C (Found: C, 54.49; H, 6.30; N, 20.87. $C_{21}H_{29}N_7OS_2$ requires C, 54.88; H, 6.36; N, 21.33%); δ_H 1.26–1.33 (12H, m), 3.56 (8H, q, *J* 7.2), 3.84 (3H, s), 6.90 (2H, d, *J* 9.2), 7.62 (2H, d, *J* 9.2); *m*/*z* 459 (M^+; 100%), 444 (51), 99 (16), 72 (24).

4-Amino-2-(diethylamino)-5-{2-(diethylamino)-5-[4-(dimethylamino)phenylazo]thiazol-4-yl}thiazole 3f. Yield 21%; mp 231–232 °C (Found: C, 56.20; H, 6.43; N, 22.46. $C_{22}H_{32}N_8S_2$ requires C, 55.90; H, 6.82; N, 23.71%); δ_H 1.30 (12H, t, *J* 6.3), 1.53 (6H, s), 3.45–3.69 (8H, m), 6.99 (2H, s), 7.52 (2H, s); *m*/*z* 472 (M^+; 100%), 135 (14), 120 (17).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(3-nitrophenylazo)thiazol-4-yl]thiazole 3g. Yield 44%; mp 224–226 °C (Found: C, 50.45; H, 5.61; N, 23.25. $C_{20}H_{26}N_8O_2S_2$ requires C, 50.61; H, 5.52; N 23.61%); δ_H 1.35 (12H, t, *J* 7.3), 3.67 (8H, q, *J* 7.3), 7.42 (1H, t, *J* 7.8), 7.78–7.83 (2H, m), 8.60 (1H, s); *m*/*z* 474 (M^+; 100%), 99 (17), 72 (24).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(2-nitrophenylazo)thiazol-4-yl]thiazole 3h. Yield 14%; mp 212–214 °C (Found: C, 50.94; H, 5.62; N, 23.13. $C_{20}H_{26}N_6O_2S_2$ requires C, 50.61; H, 5.52; N, 23.61%); δ_H 1.32 (6H, t, *J* 5.9), 1.33 (6H, t, *J* 5.9), 3.40–3.78 (8H, m), 6.96 (1H, t, *J* 7.3), 7.40 (1H, t, *J* 7.3), 7.69 (1H, d, *J* 7.3), 7.79 (1H, d, *J* 7.3); *m*/*z* 474 (M^+; 100%), 340 (25), 226 (19), 116 (43), 99 (36).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(2-methoxyphenylazo)thiazol-4-yl]thiazole 3i. Yield 58%; mp 194–195 °C (Found: C, 56.50; H, 6.52; N, 21.68. $C_{21}H_{29}N_7OS_2$ requires C, 54.88; H, 6.36; N, 21.33%); δ_H 1.27–1.33 (12H, m), 3.53–3.58 (8H, m), 3.95 (3H, s), 6.93 (1H, d, *J* 7.8), 6.95 (1H, t, *J* 7.8), 7.08 (1H, t, *J* 7.8), 7.72 (1H, d, *J* 7.8); *m*/*z* 459 (M^+; 100%), 352 (23), 267 (11), 116 (38), 99 (39).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(2-cyanophenylazo)thiazol-4-yl]thiazole 3j. Yield 36%; mp 220–222 °C (Found: C, 55.70; H, 5.89; N, 24.66. $C_{21}H_{26}N_8S_2$ requires C, 55.48; H, 5.76; N, 24.65%); δ_H 1.32 (12H, t, *J* 7.1), 3.43–3.77 (8H, m), 6.96 (1H, t, *J* 7.6), 7.43 (1H, t, *J* 7.6), 7.55 (1H, d, *J* 7.6), 7.67–7.76 (1H, m); *m*/*z* 454 (M^+; 100%), 383 (16), 325 (17), 226 (20), 102 (37), 72 (32).

4-Amino-2-(diethylamino)-5-{2-(diethylamino)-5-[2-(trifluoromethyl)phenylazo]thiazol-4-yl}thiazole 3k. Yield 13%; mp 230–231 °C (Found: C, 50.71; H, 5.12; N, 19.79. $C_{21}H_{26}F_3N_7S_2$ requires C, 50.69; H, 5.27; N, 19.70%); δ_H 1.31 (12H, t, *J* 5.8), 3.46–3.78 (8H, m), 7.05 (1H, t, *J* 7.4), 7.44 (1H, t, *J* 7.4), 7.60 (1H, d, *J* 7.4), 7.75–7.85 (1H, m); *m*/*z* 497 (M^+; 100%), 226 (26), 145 (47), 99 (27).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(2-*sec*-butylphenylazo)thiazol-4-yl]thiazole 3l. Yield 34%; mp 220–222 °C (Found: C, 59.12; H, 7.12; N, 19.76. $C_{24}H_{35}N_7S_2$ requires C, 59.35; H, 7.26; N, 20.19%); δ_H 0.87 (3H, t, *J* 7.3), 1.27–1.30 (12H, m), 1.33 (3H, d, *J* 7.3), 1.57–1.77 (2H, m), 3.52–3.60 (8H, m), 3.72 (1H, sextet, *J* 7.3), 6.30–6.54 (1H, m), 7.10 (1H, t, *J* 7.1), 7.16 (1H, t, *J* 7.1), 7.66 (1H, d, *J* 7.1); *m*/*z* 485 (M^+; 91%), 339 (41), 267 (67), 72 (100).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(2,4-dinitrophenylazo)thiazol-4-yl]thiazole 3m. Yield 35%; mp 287–288 °C (Found: C, 45.89; H, 4.75; N, 24.04. $C_{20}H_{25}N_9O_4S_2$ requires C, 46.23; H, 4.85; N, 24.26%); δ_H 1.37 (12H, t, *J* 7.1), 3.48–3.82 (8H, m), 7.68 (1H, d, *J* 9.3), 8.10 (1H, d, *J* 9.3), 8.65 (1H, s); *m*/*z* 519 (M^+; 100%), 340 (24), 116 (43), 99 (43), 72 (65).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(4-nitronaphthylazo)thiazol-4-yl]thiazole 3n. Yield 61%; mp 269–270 °C (Found: C, 54.76; H, 5.40; N, 21.16. $C_{24}H_{26}N_6O_2S_2$ requires C, 54.94; H, 5.38; N, 21.36%); δ_H 1.39 (12H, t, *J* 7.3), 3.55–3.82 (8H, m), 7.51 (1H, t, *J* 7.9), 7.58 (1H, d, *J* 9.2), 7.67 (1H, t, *J* 7.9), 8.52 (1H, d, *J* 9.2), 9.00 (1H, d, *J* 7.9), 9.01 (1H, d, *J* 7.9); *m*/*z* 524 (M^+; 100%), 494 (15), 226 (18), 116 (21), 99 (30), 72 (45).

4-Amino-2-(diethylamino)-5-{2-(diethylamino)-5-[4-(phenylazo)phenylazo]thiazol-4-yl}thiazole 3o. Yield 31%; mp 219–221 °C (Found: C, 58.22; H, 5.89; N, 23.26. $C_{26}H_{31}N_9S_2$ requires C, 58.51; H, 5.85; N, 23.62%); δ_H 1.34 (12H, t, *J* 7.3), 3.61 (8H, q, *J* 7.1), 7.40–7.52 (3H, m), 7.72 (2H, d, *J* 7.3), 7.89 (2H, d, *J* 7.3), 7.94 (2H, d, *J* 8.8); *m*/*z* 533 (M^+; 77%), 226 (15), 116 (10), 77 (100).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(5-nitrothiazol-2-ylazo)thiazol-4-yl]thiazole 3p. Yield 10%; mp 217 °C (decomp.) (Found: C, 42.01; H, 4.77; N, 26.09. $C_{17}H_{23}N_9O_2S_3$ requires C, 42.39; H, 4.81; N, 26.17%); δ_H 1.30–1.39 (12H, m), 3.52–3.84 (8H, m), 8.45 (1H, s); *m*/*z* 481 (M^+; 30%), 436 (28), 338 (68), 307 (71), 293 (93), 72 (93), 55 (100).

4-Amino-2-(diethylamino)-5-[2-(diethylamino)-5-(4-chloro-5-formylthiazol-2-ylazo)thiazol-4-yl]thiazole 3q. Yield 20%; mp 282–284 °C (decomp.) (Found: C, 43.77; H, 4.62; N, 2.09. $C_{18}H_{23}ClN_8OS_3$ requires C, 43.32; H, 4.65; N, 22.45%); δ_H 1.25–1.40 (12H, m), 3.55–3.76 (8H, m), 9.76 (1H, s); *m*/*z* 501 (M^++2; 11%), 499 (M^+; 26), 498 (97), 336 (65), 307 (67), 293 (90) 72 (100).

4-Amino-2-(morpholino)-5-{2-morpholino-5-[4-(trifluoromethylsulfonyl)phenylazo]thiazol-4-yl}thiazole 3′a. Yield 34%; mp > 300 °C (Found: C, 42.77; H, 3.87; N, 16.21. $C_{21}H_{22}F_3N_7O_4S_3$ requires C, 42.78; H, 3.76; N, 16.63%); δ_H 3.71–3.75 (8H, m), 3.86 (8H, t, *J* 4.3), 7.64 (2H, d, *J* 8.3), 7.88 (2H, d, *J* 8.3); *m*/*z* 589 (M^+; 100%), 472 (15), 456 (19), 240 (20).

Synthesis of 4-amino-2-(diethylamino)-5-{2-(diethylamino)-5-[4-chloro-5-(1-butyl-5-cyano-4-methyl-2,6-dioxo-1,6-dihydropyridin-3(2*H*)-ylidenemethyl)thiazol-2-ylazo]thiazol-4-yl}thiazole (3r)

To an ethanol solution (10 ml) of 4-amino-2-(diethylamino)-5-[2-(diethylamino)-5-(4-chloro-5-formylthiazol-2-ylazo)thiazol-4-yl]thiazole **3q** (25 mg, 0.05 mmol) was added 1-butyl-3-cyano-5-hydroxy-4-methyl-2-pyridone (10 mg, 0.05 mmol). The mixture was refluxed for 1 h. After the reaction was complete, the mixture was concentrated. Column chromatography (SiO_2, AcOEt–Me_2CO = 1 : 1) followed by recrystallisation from a chloroform–hexane mixture gave 10 mg (30%) of the desired product. Mp 269 °C (decomp.) (Found: C, 50.25; H, 5.27; N, 20.20. $C_{29}H_{35}ClN_{10}O_2S_3$ requires C, 50.68; H, 5.13; N, 20.38%); δ_H 0.90 (3H, t, *J* 7.3), 1.29–1.47 (16H, m), 2.46 (3H, s), 3.74–3.86 (8H, m), 3.94 (2H, t, *J* 7.3), 7.83 (1H, s).

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