Negative solvatochromism of azo dyes derived from (dialkylamino)thiazole dimers

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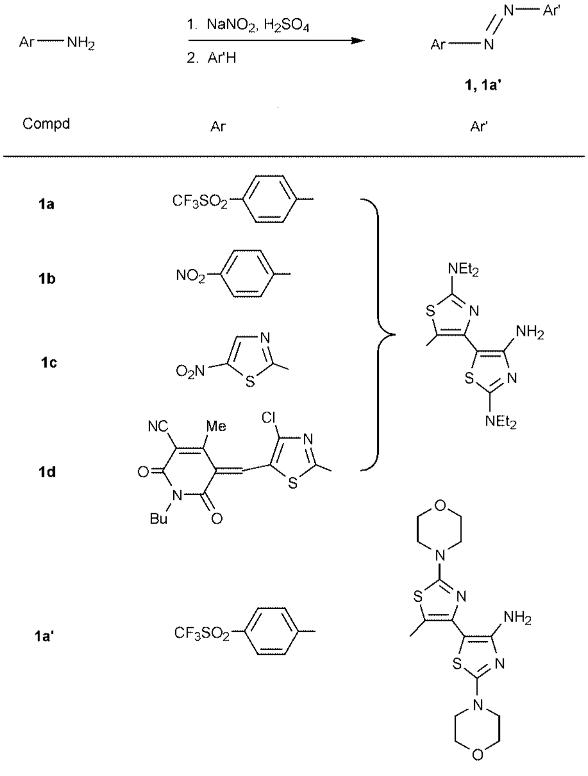
The first examples of negative solvatochromism in neutral azo dyes containing both strongly electron-donating bis-(dialkylamino)thiazolyl and electron-withdrawing 4-(trifluoromethylsulfonyl)phenyl or 2-thiazolyl moieties are reported.

The absorption bands of azo dyes depend on the combination of electron-donating and -withdrawing moieties in the molecules.[1] Recently, (dialkylamino)thiazole dimers, assumed to be very electron-rich substrates, have been synthesized.[2] It was of interest to examine the solvatochromic behavior of azo dyes having both strong electron-donating and -withdrawing moieties in a molecule. We report here, the solvatochromism of azo dyes derived from (dialkylamino)thiazole dimers.

The azo dyes **1a–d** and **1a′** derived from (dialkylamino)thiazole dimers were synthesized in low to good yields by the diazotisation-coupling reaction shown in Scheme 1.[3,4] The absorption spectrum of **1a** is shown in Fig. 1. The azo dye **1a** showed absorption bands at 637 nm (ε = 82 000 dm^3 mol^{-1} cm^{-1}) and 449 (25 000) in dichloromethane, while the absorption spectra of the other azo dyes are summarized in Table 1. The lower energy absorption band of **1d**, containing a very strong electron-withdrawing moiety, was most bathochromic among the azo dyes **1**.



Scheme 1

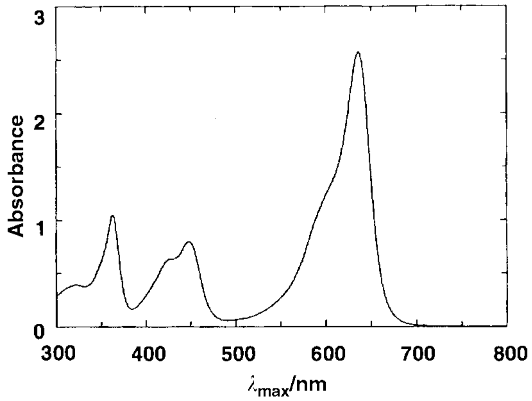


Fig. 1 Absorption spectrum of **1a** in dichloromethane.

Neutral azo dyes have been reported to show a positive solvatochromism[5–12] while two types of ionic azo dyes, 4-[2-(triphenylphosphonio)phenylazo]phenolates and 2-(1-methylpyridiniumazo)- and 2-(1-methylqunoliniumazo)-tetracyanocyclopentadienides, have been reported to reveal negative solvatochromic behavior.[13,14]

Interestingly, the azo dyes **1** showed either positive and negative solvatochromism depending on the diazo components. Typical solvatochromism is shown in Fig. 2 where the $\lambda_{\max}$ values of the first (lower energy) absorption band are plotted against the molar electronic transition energy (E_{T}) of the solvent.[15] Azo dyes **1a**, **1c** and **1d** showed negative solvatochromism, especially, so for **1d**. While azo dye **1b** showed a positive solvatochromic behavior, azo dye **1a′** also showed negative solvatochromic behavior.[16] Thus the azo dyes containing very strong electron-withdrawing moieties such as 4-(trifluoromethylsulfonyl)phenyl and 2-thiazolyls showed negative solvatochromism. This result is in contrast to a positive

Table 1 Absorption spectra of **1a–d** and **1a′** in dichloromethane

Compound	$\lambda_{\max}$/nm	ε/dm^3 mol^{-1} cm^{-1}
1a	449	25 000
	637	82 000
1b	431	29 000
	669	64 000
1c	441	35 000
	665	48 000
1d	457	51 000
	737	24 000
1a′	445	22 000
	641	69 000

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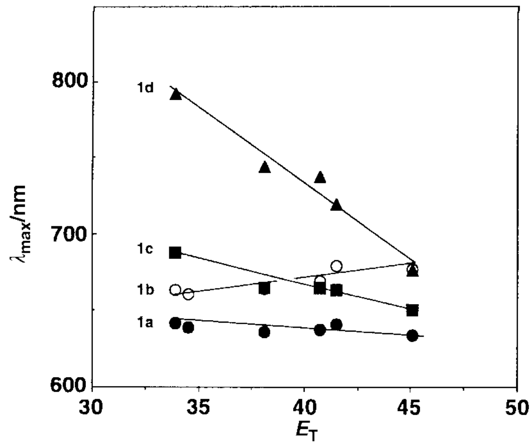

Fig. 2 Solvatochromism of azo dyes **1**. The absorption spectra were measured in toluene (E_T: 33.9 kcal mol^{-1}), diethyl ether (34.5), ethyl acetate (38.1), dichloromethane (40.7), benzonitrile (41.5), dimethyl sulfoxide (45.1). Azo dyes **1c** and **1d** were insoluble in diethyl ether.

solvatochromism of the near-IR absorbing push–pull 5-acetylamino-4-[2-(4-chloro-5-substituted thiazolylazo)]-2-methoxy-*N*-(2-hexyl)aniline derivative.[17] The structures of the azo dyes were optimized by a MOPAC AM-1 program and the dipole moment (μ) of the azo dyes in the excited and ground states were calculated by a CNDO/S program. The μ values of **1b** in the ground and excited states were calculated to be 14.58 and 18.98 D, respectively. This calculation is consistent with the positive solvatochromic behavior of **1b**. Interestingly, the electron-withdrawing nature of the nitro group [$\sigma_p(NO_2)$ = 0.78] was not strong enough to cause a negative solvatochromism in the azo dyes **1**. The ground state of the 4-(trifluoromethylsulfonyl) derivative **1a** [$\sigma_p(CF_3SO_2)$ = 0.93][18] was calculated to be slightly more polar (μ = 15.96 D) than the excited state (15.85 D). The ground state of **1d** was also calculated to be more polar (24.67 D) than the excited state (23.26 D). These results support the negative solvatochromism of **1a** and **1d**.[19]

The possible structures of **1a** in the ground and excited states are depicted in Fig. 3.

More polar charge-separated diazamerocyanine structures **A**, **A′** and **A″** could be predominant in the ground state and with a less polar neutral azo form **B** in the excited state. The other azo dyes **1c**, **1d** and **1a′** which showed negative solvatochromism can also have charge-separated diazamerocyanine structures. This is different from the reported negatively solvatochromic azo compounds, which can have charge-separated azo and neutral diazamerocyanine structures in the ground and excited states, respectively.[13,14]

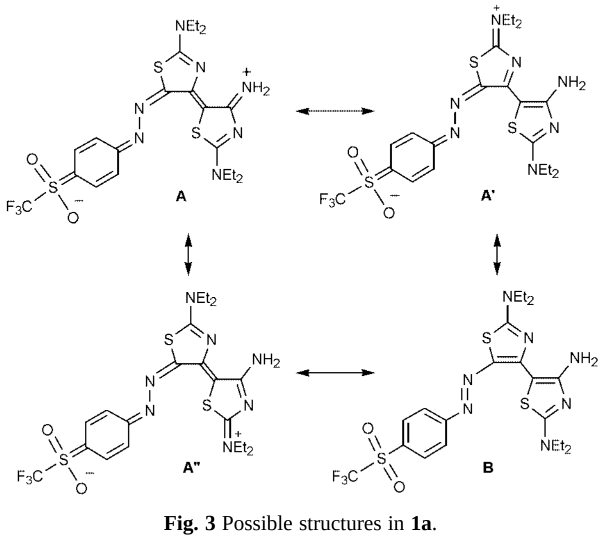

Fig. 3 Possible structures in **1a**.

In conclusion, we have synthesized azo dyes derived from strong electron-donating coupling components, (dialkylamino)thiazole dimers. The azo dyes derived from diazo components with strong electron-withdrawing substituents such as 4-(trifluoromethylsulfonyl)aniline and 2-aminothiazoles showed a negative solvatochromism, owing to the ground state having a predominantly charge-separated polar diazamerocyanine structure.

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Notes and references

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3 *Typical procedure* for the synthesis of **1**: to a DMF solution (5 mL) of arylamines (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 coupling components (1.5 mmol), and the mixture was stirred at room temperature overnight. After the reaction was completed, 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 recrystallized from chloroform–hexane. All the products showed satisfactorily spectral and elemental analysis data. **1a**: 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(400 MHz, $CDCl_3$) 1.36 (12H, t, *J* 7.1 Hz), 3.50–3.78 (8H, m), 7.61 (2H, d, *J* 9.0 Hz), 7.83 (2H, d, *J* 9.0 Hz); *m/z* (EI, 70 eV) 561 (M$^+$; 100), 444 (14), 428 (19), 398 (32), 263 (30), 226 (17), 135 (53), 99 (29), 77 (34), 72 (56).

4 Compound **1d** was prepared by diazotisation-coupling reaction followed by condensation with a pyridone derivative: yield 30%; 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(400 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.3 Hz), 1.29–1.47 (16 H, m), 2.46 (3H, s), 3.74–3.86 (8H, m), 3.94 (2H, t, *J* 7.3 Hz), 7.83 (1H, s).

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19 **1c**: ground state: 14.99 D, excited state: 14.86 D. **1a**: ground state: 14.50 D, excited state: 12.89 D.