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Synthesis and properties of some disazo disperse dyes derivatives of 2-amino-6-phenylazobenzothiazole and 2-amino-6-(4′-nitro)-phenylazobenzothiazole

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Abstract

This paper is concerned with the synthesis and evaluation of some red, violet and bluish violet disperse disazo dyes. They were synthesised via diazotisation of 2-amino-6-phenylazobenzothiazole or its nitro-substituted analogue followed by the coupling with a variety of coupling components. The spectral properties (^{1}H NMR and visible spectra) of obtained dyes are reported. The basic fastness properties (light fastness, dry-heat treatment fastness) of the dyes on polyester fibre are also discussed in terms of their chemical structure.

Keywords: Benzothiazolyl dyes; Disperse dyes; Light fastness; Fastness to heat; Polyester fibre

1. Introduction

During the last 40 years a significant effort has been made to replace red and blue anthraquinone disperse dyes with more economical substitutes. The success has been achieved with the discovery of heterocyclic amines which produce red and blue azo disperse dyes. Dyes with heterocyclic diazo components have received much attention because of high tinctorial power and excellent brightness. Most hetarylazo disperse dyes of technical interest for polyester are derived from diazo components consisting of five-membered ring containing one sulphur atom in which one or two nitrogen atoms may also be present. Dyes prepared from 2-aminothiazoles [1] and 2-aminobenzothiazoles [2] have a long history and a significant role in disperse dyes technology [3]. Technically important are CI Disperse Red 177 and CI Disperse Violet 52. Azo dyes for polyester are normally of the monoazo type although a number of disazo compounds have reached commercial status. They are usually produced via coupling reaction of the diazotised *p*-aminoazobenzene with phenol or its derivatives giving good yellow-reddish dyes for polyester. They are sometimes duller when compared with the monoazo dyes, but it is not a disadvantage because they are often used in the mixture with other dyes to obtain black dyeings.

The intention of this paper is to describe the synthesis and to characterise red, violet and bluish violet disazo colorants **I–XXIV** in which the benzothiazole has been used as the middle component. The benzothiazolyl colorants bearing the phenylazo residue in the 6 position have been synthesised in connection with the preparation of reactive disperse dyes [4]. Some of them have also been described in patent literature [5].

2. Results and discussion

It is well known that 2-aminobenzothiazole can be readily obtained by treating phenylthiourea with bromine [6], chlorine [7] or halogen compounds such as sulphur monochloride [8], sulphur dichloride [8], and sulphuryl chloride [9]. Since in the case of negatively substituted ring of the phenylthiourea

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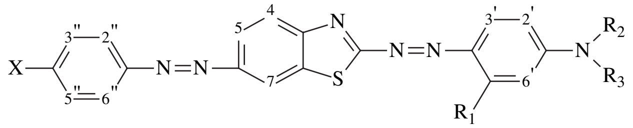
somewhat lower yields are obtained [10]. 2-Amino-6-phenylazobenzothiazole and its nitro analogue were synthesised in an alternative manner [11–13]. In the procedure applied 4-aminoazobenzene **XXV** or 4′-nitro-4-aminoazobenzene **XXVI** was thiocyanated in *ortho* position to the amino group with ammonium thiocyanate in glacial acetic acid followed by bromine action to form the required intermediate compounds **XXVII** and **XXVIII** (Scheme 1).

The target disazo dyes were synthesised in 50–62% yield by diazotisation of 2-amino-6-phenylazobenzothiazole or 2-amino-4′-nitrophenylazobenzothiazole with solid $NaNO_2$ at −15 °C in 85% orthophosphoric acid [5] and subsequent coupling reaction with some commercial or previously described [14–17] components **XXIX** (Scheme 1).



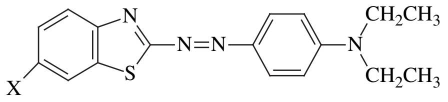
Dyes	X	R$_1$	R$_2$	R$_3$
I	H	H	Et	Et
II	NO_2	H	Et	Et
III	H	Me	Et	CH_2CH_2CN
IV	NO_2	Me	Et	CH_2CH_2CN
V	H	H	CH_2CH_2OH	CH_2CH_2CN
VI	NO_2	H	CH_2CH_2OH	CH_2CH_2CN
VII	H	H	CH_2CH_2OCOMe	CH_2CH_2CN
VIII	NO_2	H	CH_2CH_2OCOMe	CH_2CH_2CN
IX	H	H	CH_2Ph	CH_2CH_2COOEt
X	H	Me	CH_2Ph	CH_2CH_2COOEt
XI	H	H	CH_2Ph	CH_2CH_2CN
XII	NO_2	H	CH_2Ph	CH_2CH_2CN
XIII	H	Me	CH_2Ph	CH_2CH_2COOMe
XIV	NO_2	Me	CH_2Ph	CH_2CH_2COOMe
XV	NO_2	Me	CH_2Ph (*p*-Me)[a]	CH_2CH_2COOMe
XVI	H	OMe	CH_2Ph	CH_2CH_2COOMe
XVII	H	OMe	CH_2Ph	CH_2CH_2COOEt
XVIII	H	OMe	CH_2Ph	CH_2CH_2CN
XIX	H	H	CH_2Ph (*p*-OMe)[a]	CH_2CH_2COOMe
XX	H	H	CH_2Ph (*p*-Me)[a]	CH_2CH_2COOMe
XXI	NO_2	H	CH_2Ph (*p*-Me)[a]	CH_2CH_2COOMe
XXII	H	H	CH_2CH_2Ph	CH_2CH_2CN
XXIII	H	H	CH_2CH_2Ph	CH_2CH_2COOMe
XXIV	H	H	CH_2CH_2Ph	CH_2CH_2COOEt

[a] Benzyl phenyl ring contains *p*-OMe or *p*-Me substituent.

The crude dyes were purified by recrystallization from toluene until a constant molar extinction coefficient and TLC purity were attained.

The chemical structure of the dyes **I**–**XXIV** was verified by ^1H NMR (Table 1). The chemical shifts, multiplicity and integration of the groups of protons provided data in accord with the dyes structure.

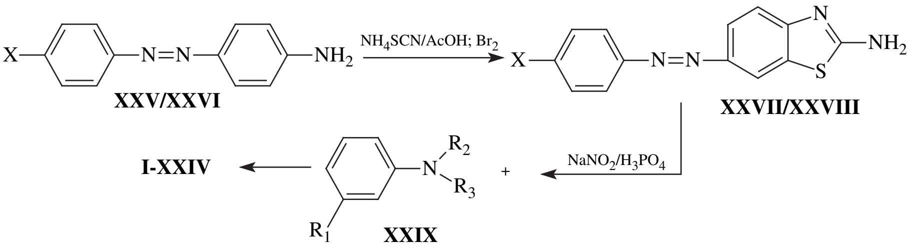
It is well known that benzothiazolyl azo dyes with negative substituent in the 6th position of the benzothiazole ring have improved light fastness and exhibit a strong bathochromic shift of λ_{max} in comparison with the unsubstituted analogue [18,19]. The typical examples are **XXX** and **XXXI** with λ_{max} = 513 nm and 549 nm in ethanol, respectively [20].



XXX (X: H; light fastness: 2) [20]

XXXI (X: NO_2; light fastness: 6) [20]

Absorption spectra (Table 2) of the dyes **I**–**XXIV** recorded in ethanolic solutions show that they are red, violet and bluish violet. The obtained data for the dye **I** and our previous results [20] demonstrate that on replacement of a strong electron-withdrawing nitro group with the phenylazo residue in the dye **XXXI** only very small (3 nm) hypsochromic shift of absorption of the former dye, is observed. In addition, upon further substitution of the phenylazobenzothiazole ring with the 4′-nitro group (X) the absorption of the disazo dyes results in a bathochromic shift in λ_{max} by 6–15 nm (examples are **I** and **II**, **III** and **IV**, **V** and **VI**, **VII** and **VIII**, **XI** and **XII** and finally **XIII** and **XIV**). It is also evident that all dyes **III**–**XXII** with the exception of **XIV** and **XV** show hypsochromic effect in comparison with the dyes **I** and **II**. It is obviously caused by the presence of electron attracting groups such as *N*-β-cyanoethyl or benzyl moiety attached to the amino group of the coupler [21]. As could be anticipated, both methyl and methoxy substitution of the coupler in *ortho* position to the azo link produce a bathochromic shifts of 10–13 nm when compared to unsubstituted analogues. This is exemplified by the dyes **IX**, **X** and **XVII**. The exceptional behaviour of the dyes **XIV** and **XV** mentioned above is apparently caused by two operating factors: they contain 4′-nitro-substituent in the diazo component and *ortho* methyl group in the coupler, as well. In addition, they do not contain *N*-β-cyanoethyl moiety shifting the absorption towards blue region.



Scheme 1. The route of the synthesis of the dyes **I**–**XXIV**; X, R$_1$, R$_2$, R$_3$ as indicated earlier.

Table 1
^{1}H NMR spectral assignments of dyes **I–XXIV**

Dyes	^{1}H NMR [$CDCl_3$, TMS int. δ (ppm), J (Hz)]
I	1.28t (6H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.0$), 3.50q (4H, $\mathit{CH_2}\mathrm{CH_3}$, $J = 7.0$), 6.70–6.75m (2H, 2′, 6′), 7.45–7.56m (3H, 3″, 4″, 5″), 7.91–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.60$).
II	1.25t (6H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.0$), 3.45q (4H, $\mathit{CH_2}\mathrm{CH_3}$, $J = 7.0$), 6.70–6.75m (2H, 2′, 6′), 7.95–8.20m (5H, 4, 3′, 5′, 2″, 6″), 8.35–8.48m (4H, 5, 7, 3″, 5″).
III	1.31t (3H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.0$), 2.68s (3H, Ph-$\mathit{CH_3}$), 2.72t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.61q (2H, $\mathit{CH_2}\mathrm{CH_3}$, $J = 7.0$), 3.81t (2H, $\mathit{CH_2}\mathrm{CH_2CN}$, $J = 7.0$), 6.58–6.64m (2H, 2′, 6′), 7.46–7.58m (3H, 3″, 4″, 5″), 7.91–8.20m (5H, 4, 5, 3′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.60$).
IV	1.31t (3H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.0$), 2.68s (3H, Ph-$\mathit{CH_3}$), 2.72t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.61q (2H, $\mathit{CH_2}\mathrm{CH_3}$, $J = 7.0$), 3.81t (2H, $\mathit{CH_2}\mathrm{CH_2CN}$, $J = 7.0$), 6.58–6.65m (2H, 2′, 6′), 7.85–8.25m (5H, 4, 5, 3′, 2″, 6″), 8.40–8.45m (3H, 7, 3″, 5″).
V	2.65t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.75–4.00m (6H, $\mathit{CH_2}\mathrm{CH_2CN}$, $\mathrm{CH_2}\mathit{CH_2}\mathrm{OH}$, $\mathit{CH_2}\mathrm{CH_2OH}$), 4.85m (1H, $\mathrm{CH_2CH_2}\mathit{OH}$), 6.60–6.70m (2H, 2′, 6′), 7.46–7.58m (3H, 3″, 4″, 5″), 7.91–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.60$).
VI	2.65t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.75–4.00m (6H, $\mathit{CH_2}\mathrm{CH_2CN}$, $\mathrm{CH_2}\mathit{CH_2}\mathrm{OH}$, $\mathit{CH_2}\mathrm{CH_2OH}$), 4.85m (1H, $\mathrm{CH_2CH_2}\mathit{OH}$), 6.60–6.70m (2H, 2′,6′), 8.00–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.35m (3H, 7, 3″, 5″).
VII	2.03s (3H, $\mathrm{CH_2CH_2OCO}\mathit{CH_3}$), 2.80t ($\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.70–4.10m (4H, $\mathit{CH_2}\mathrm{CH_2OCOMe}$, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2CN}$), 4.36t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{OCOMe}$, $J = 7.2$), 6.60–6.70m (2H, 2′, 6′), 7.46–7.58m (3H, 3″, 4″, 5″), 7.90–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.60$).
VIII	2.03s (3H, $\mathrm{CH_2CH_2OCO}\mathit{CH_3}$), 2.80t ($\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.70–4.10m (4H, $\mathit{CH_2}\mathrm{CH_2OCOMe}$, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2CN}$), 4.36t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{OCOMe}$, $J = 7.2$), 6.70–7.00m (2H, 2′, 6′), 7.95–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40–8.45m (3H, 7, 3″, 5″).
IX	1.25t (3H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.0$), 2.73t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOEt}$, $J = 7.0$), 3.91t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.0$), 4.13q (2H, $\mathrm{COO}\mathit{CH_2}\mathrm{CH_3}$, $J = 7.0$), 4.76bs (2H, Ph-$\mathit{CH_2}$), 6.80–6.84m (2H, 2′, 6′), 7.15–7.48m (5H, *Ph*-$\mathrm{CH_2}$), 7.50–7.58m (3H, 3″, 4″, 5″), 7.90–8.13m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.30$).
X	1.28t (3H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.33$), 2.66s (3H, Ph-$\mathit{CH_3}$), 2.70t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOEt}$, $J = 7.33$), 3.97t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.33$), 4.19q (2H, $\mathrm{COO}\mathit{CH_2}\mathrm{CH_3}$, $J = 7.33$), 4.75bs (2H, Ph-$\mathit{CH_2}$), 6.64–6.67m (2H, 2′, 6′), 7.17–7.35m (5H, *Ph*-$\mathrm{CH_2}$), 7.50–7.51m (3H, 3″, 4″, 5″), 7.94–8.16m (5H, 4, 5, 3′, 2″, 6″), 8.38d (1H, 7, $J_{\mathrm{m}} = 1.47$).
XI	2.75t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 6.60$), 3.93t (2H, $\mathit{CH_2}\mathrm{CH_2CN}$, $J = 6.60$), 4.75bs (2H, Ph-$\mathit{CH_2}$), 6.80–6.85m (2H, 2′, 6′), 7.18–7.40m (5H, *Ph*-$\mathrm{CH_2}$), 7.50–7.55m (3H, 3″, 4″, 5″) 7.90–8.13 m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 2.0$).
XII	2.75t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.0$), 3.95t (2H, $\mathit{CH_2}\mathrm{CH_2CN}$, $J = 7.0$), 4.80bs (2H, $\mathrm{Ph}\mathit{CH_2}$), 6.70–6.80m (2H, 2′, 6′), 7.15–7.40m (5H, *Ph*-$\mathrm{CH_2}$), 8.00–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.35–8.40m (7, 3″, 5″).
XIII	2.68s (3H, Ph-$\mathit{CH_3}$), 2,74t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.33$), 3.75s (3H, $\mathrm{COO}\mathit{CH_3}$), 3.88t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.33$), 4.75bs (2H, Ph-$\mathit{CH_2}$), 6.63–6.68m (2H, 2′, 6′), 7.23–7.37m (5H, *Ph*-$\mathrm{CH_2}$), 7.50–8.16m (8H, 4, 5, 3′, 2″, 3″, 4″, 5″, 6″), 8.38d (1H, 7, $J_{\mathrm{m}} = 1.47$).
XIV	2.65s (3H, Ph-$\mathit{CH_3}$), 2.75t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.0$), 3.70s (3H, $\mathrm{COO}\mathit{CH_3}$), 3.90t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.0$), 4.80bs (2H, Ph-$\mathit{CH_2}$), 6.50–6.70m (2H, 2′, 6′), 7.12–7.38m (5H, *Ph*-$\mathrm{CH_2}$), 7.95–8.15m (5H, 4, 5, 3′, 2″, 6″), 8.35–8.45m (3H, 7, 3″, 5″).
XV	2.35s (3H, Ph-$\mathit{CH_3}$), 2.65s (3H, Ph-$\mathit{CH_3}$), 3.65s (3H, $\mathrm{COO}\mathit{CH_3}$), 3.85t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.0$), 4.75bs (2H, Ph-$\mathit{CH_2}$), 6.50–6.70m (2H, 2′, 6′), 7.05–7.20m (5H, $\mathit{Ph}\mathrm{CH_2}$), 7.94–8.16m (5H, 4, 5, 3′, 2″, 6″), 8.35–8.48m (3H, 7, 3″, 5″).
XVI	2.75t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.34$), 3.75t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.34$), 3.94s (3H, Ph-$\mathit{OCH_3}$), 4.75bs (2H, Ph-$\mathit{CH_2}$), 6.44–6.46m (2H, 2′, 6′), 7.18–7.38m (5H, *Ph*-$\mathrm{CH_2}$), 7.51–7.53m (3H, 3′, 4″, 5″), 7.94–8.16m (5H, 4, 5, 3′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.47$).
XVII	1.25t (3H, $\mathrm{CH_2}\mathit{CH_3}$, $J = 7.33$), 2.74t (2H, $\mathit{CH_2}\mathrm{CH_2COOEt}$, $J = 7.33$), 3.94s (3H, Ph-$\mathit{OCH_3}$), 4.16q (2H, $\mathit{CH_2}\mathrm{CH_3}$, $J = 7.33$), 4.76bs (2H, Ph-$\mathit{CH_2}$), 6.44–6.46m (2H, 2′, 6′), 7.18–7.38m (5H, *Ph*-$\mathrm{CH_2}$), 7.50–7.56m (3H, 3″, 4″, 5″), 7.94–8.12m (5H, 4, 5, 3′, 2″, 6″), 8.38d (1H, 7, $J_{\mathrm{m}} = 2.0$).
XVIII	2.74t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 6.60$), 3.74t (2H, $\mathit{CH_2}\mathrm{CH_2CN}$, $J = 6.60$), 3.95s (3H, Ph-$\mathit{OCH_3}$), 4.81bs (2H, Ph-$\mathit{CH_2}$), 6.42–6.48m (2H, 2′, 6′), 7.20–7.40m (6H, *Ph*-$\mathrm{CH_2}$, 3′), 7.45–7.60m (3H, 3″, 4″, 5″), 7.94–8.00m (6H, 4, 5, 3′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.47$).
XIX	2.80t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.0$), 3.69s (3H, $\mathrm{COO}\mathit{CH_3}$), 3.90s (3H, Ph-$\mathit{OCH_3}$), 3.95t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.33$), 4.70bs (2H, Ph-$\mathit{CH_2}$), 6.80–7.10m (6H, 2′, 6′, *Ph*-$\mathrm{CH_2}$), 7.50–7.55m (3H, 3″, 4″, 5″), 7.94–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.42d (1H, 7, $J_{\mathrm{m}} = 1.5$).
XX	2.34s (3H, Ph-$\mathit{CH_3}$), 2.74t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.33$), 3.69s (3H, $\mathrm{COO}\mathit{CH_3}$), 3.90t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.33$), 4.71bs (2H, Ph-$\mathit{CH_2}$), 6.83m (2H, 2′, 6′), 7.00–7.18m (4H, *Ph*-$\mathrm{CH_2}$), 7.51–7.54m (3H, 3″, 4″, 5″), 7.90–8.20m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.5$).
XXI	2.35s (3H, Ph-$\mathit{CH_3}$), 2.75t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.33$), 3.65s (3H, $\mathrm{COO}\mathit{CH_3}$), 3.85t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2}$, $J = 7.0$), 4.75bs (2H, Ph-$\mathit{CH_2}$), 6.50–6.70m (2H, 2′, 6′), 7.12–7.35m (4H, *Ph*-$\mathrm{CH_2}$), 7.95–8.15m (6H, 4, 5, 3′, 5′, 2″,6″), 8.35–8.45m (3H, 7, 3″, 5″).
XXII	2.52t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CN}$, $J = 7.40$), 2.99t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{Ph}$, $J = 7.40$), 3.57t (2H, $\mathit{CH_2}\mathrm{CH_2Ph}$, $J = 7.40$), 6.80m (2H, 2′, 6′), 7.20–7.34m (5H, $\mathrm{CH_2CH_2}\mathit{Ph}$), 7.49–7.56m (3H, 3″, 4″, 5″), 7.96–8.21m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.43d (1H, 7, $J_{\mathrm{m}} = 1.3$).
XXIII	2.62t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOMe}$, $J = 7.40$), 2.96t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{Ph}$, $J = 7.40$), 3.62–3.69m (7H, $\mathrm{CH_2CH_2COO}\mathit{CH_3}$, $\mathit{CH_2}\mathrm{CH_2Ph}$, $\mathit{CH_2}\mathrm{CH_2COOMe}$), 6.80m (2H, 2′, 6′), 7.22–7.35m (5H, $\mathrm{CH_2CH_2}\mathit{Ph}$), 7.49–7,55m (3H, 3″, 4″, 5″), 7.96–8.19m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.5$).
XXIV	1.26t (3H, $\mathrm{COOCH_2}\mathit{CH_3}$, $J = 7.50$), 2.60t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{COOEt}$, $J = 7.50$), 2.96t (2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{Ph}$, $J = 7.50$), 3.62t (2H, $\mathit{CH_2}\mathrm{CH_2Ph}$, $J = 7.50$), 3.68t (2H, $\mathrm{N}\mathit{CH_2}\mathrm{CH_2COOEt}$, $J = 7.50$), 4.09q (2H, $\mathrm{COO}\mathit{CH_2}\mathrm{CH_3}$, $J = 7.50$), 6.60m (2H, 2′, 6′), 7.25–7.35m (5H, $\mathrm{CH_2CH_2}\mathit{Ph}$), 7.49–7.55m (3H, 3″, 4″, 5″), 7.96–8.19m (6H, 4, 5, 3′, 5′, 2″, 6″), 8.40d (1H, 7, $J_{\mathrm{m}} = 1.5$).

Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad.

When the benzyl residue is separated from the nitrogen atom of the amino group of the coupler by a methylene group like in dyes **XXIII–XXIV**, containing *N*-β-phenylethyl moiety, their $\lambda_{\max}$ values show a bathochromic effect in comparison with all other dyes (with the exception of **XV** again).

The dyes **I–XXIV** were applied to polyester and their basic fastness properties were evaluated. Dyeings on polyester fibre have good brightness, high intensity and showed complete dyebath exhaustion. The overall fastness properties are generally satisfactory (Table 2).

The mechanism of photodegradation of colorants on polyester fibre is still controversial. Our recent results proved the formation of singlet oxygen during irradiation of some benzothiazolyl azo dyes [22] and its participation in their photodegradation. The obtained data demonstrate that the introduction of the second azo group into the molecule of the

Table 2
Visible spectra and fastness of dyeings for dyes **I–XXIV**

Dyes	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$	Fastness[a] to dry-heat treatment 180 °C						Rubbing Wet/dry	Light fastness[b]
			1	2	3	4	5	6		
I	546	3.38	5	5	5	5	5	5	5/5	4
II	552	3.53	5	5	5	5	5	5	5/5	5
III	535	3.10	5	4–5	5	5	5	5	5/5	4
IV	545	3.20	5	5	5	5	5	5	5/5	4–5
V	520	3.50	5	5	5	5	5	5	5/5	4
VI	535	3.52	5	5	5	5	5	5	5/5	4–5
VII	522	3.65	5	5	5	4–5	5	5	4/5	5
VIII	532	4.16	5	5	5	4–5	5	5	4/5	6
IX	530	3.36	5	4–5	5	5	5	5	5/5	4
X	540	4.34	5	4–5	4–5	5	5	5	5/5	4–5
XI	526	3.95	5	5	5	5	5	5	5/5	5
XII	536	4.00	5	5	5	5	5	5	5/5	5
XIII	542	3.78	5	5	5	5	5	5	4/5	4–5
XIV	555	4.20	5	5	5	4–5	5	5	4/5	6
XV	560	3.76	5	5	5	5	5	5	4/5	5–6
XVI	543	3.36	4–5	5	5	5	5	5	5/5	3–4
XVII	543	3.20	4–5	5	5	5	5	5	4/5	3–4
XVIII	536	3.88	4–5	5	4–5	5	5	5	5/5	3–4
XIX	535	4.02	5	5	5	5	5	5	5/5	5
XX	534	4.13	5	5	5	5	5	5	5/5	5
XXI	540	4.15	5	5	5	5	5	5	5/5	5–6
XXII	529	3.33	5	5	5	5	5	5	5/5	5
XXIII	555	4.00	5	5	5	5	5	5	5/5	4–5
XXIV	555	3.76	5	5	5	5	5	5	5/5	4–5

[a] 1: Change of shade of dyed fabric; 2: staining wool; 3: staining polyacrylonitrile; 4: staining polyester; 5: staining nylon; 6: staining cotton.

[b] The dye application level was 0.5% o.w.f. (weight of fibre).

benzothiazolyl azo dye lowers light stability by 1 or 2 points in the 1–8 scale in comparison with the dye **XXXI** for which the light fastness 6 is reported [20]. It indicates that phenylazo residue does not affect the light fastness on polyester in a way similar to the nitro group and only few dyes with 6′-nitrophenylazobenzothiazole skeleton as the middle component exhibit the comparable light fastness with **XXXI**. As the final conclusion it is noticed that the presence of *N*-β-cyanoethyl group does not improve significantly the fastness to light, as expected [23].

The excellent fastness to dry-heat treatment of dyes **I–XXIV** results from their relatively low diffusion coefficient connected with the increase in their relative molecular mass. For a group of examined dyes the difference between their fastness to dry-heat treatment is small. It is evident from the data concerning the dyes **V–VIII** that the presence of free hydroxyl group leads to inferior light stability of the dye. On the other hand, the acylation of a hydroxyl group improves the fastness to light of the dyes, however, lowering their fastness to heat. Our results are in good agreement with the literature [23].

3. Experimental

3.1. General

The chemicals were purchased from Aldrich. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker spectrometer in $CDCl_3$ solutions, using TMS as an internal standard. Chemical shifts (δ) are measured in ppm and the coupling constants (J) in Hz. Visible spectra of the dyes were recorded on a Perkin Elmer Lambda 40 spectrometer in ethanolic solution at a concentration of 2.5×10^{-5} mol dm^{-3}. Dyeings and fastness properties were determined according to Polish Standards, which are similar to the respective British Standards [24]. Light fastness and dry-heat treatment fastness were measured with a Xenotest apparatus (Hanau) and Fixotest apparatus (Hanau), respectively.

3.2. Synthesis

*3.2.1. Preparation of 2-amino-6-phenylazobenzothiazole (**XXVII**)*

Ammonium thiocyanate (3.8 g, 0.05 mol) was slowly added to the solution of *p*-aminoazobenzene (3.94 g, 0.02 mol) in 60 cm^3 of acetic acid at 30–35 °C. After cooling the reaction mixture to the room temperature, bromine (4.0 g, 0.05 mol) in 10 cm^3 of acetic acid was slowly added within 1/2 h. The reaction was carried out for 4 h at room temperature and then the reaction mixture was neutralised with 10% sodium carbonate solution. The precipitate was filtered off, washed with water and dried. Product of 4.46 g was obtained (87.7% yield). M.p. = 195–198 °C.

^{1}H NMR: $CDCl_3$: 5.45bs (2H), 7.48–7.55m (4H), 7.88–8.00m (3H), 8.20d (1H, $J = 2.0$ Hz).

*3.2.2. Preparation of 2-amino-6-(4′-nitro)-phenylazobenzothiazole (**XXVIII**)*

The synthesis was similar to that described for the compound **XXVII**. The yield was 89%. The chemical structure of the compound **XXVIII** was confirmed by ^{1}H NMR.

^{1}H NMR: $CDCl_3$: 5.50bs (2H), 7.60–7.65d (1H, $J = 8.62$), 7.95–8.05m (3H), 8.25–8.40m (3H).

*3.2.3. Preparation of dye **I***

2-Amino-6-phenylazobenzothiazole (2.54 g, 0.01 mol) was dissolved at 50 °C in 30 g 85% orthophosphoric acid. After cooling this solution to −15 °C, sodium nitrite (0.69 g, 0.01 mol) was added. The diazotisation was carried out for 3 h at −10 °C. The resulting diazonium salt was added slowly to the solution of *N*,*N*-diethylaniline (1.73, 0.01 mol) in 50 cm^3 of ethanol. The reaction mixture was stirred for 1 h at 0 °C. Next 200 g of ice was added and the stirring was continued for 1 h. The precipitated dye was filtered, washed with water and dried. Dye of 2.27 g was obtained (52%). It was additionally recrystallised from toluene.

The other dyes were synthesised in the similar way.

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