Available online at www.sciencedirect.com

SCIENCE DIRECT®

Dyes and Pigments 72 (2007) 223–227

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

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

Jolanta Sokołowska*, Radosław Podsiadły, Emilia Sochocka

Institute of Polymer and Dye Technology, Technical University of Lodz, Stefanowskiego 12/14, 90-924 Lodz, Poland

Received 2 February 2005; received in revised form 18 May 2005; accepted 17 August 2005
Available online 17 October 2005

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.
© 2005 Elsevier Ltd. All rights reserved.

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

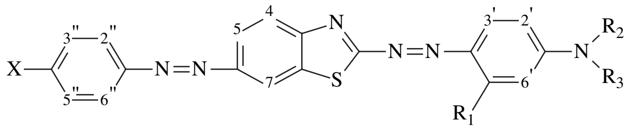
---

* Corresponding author. Fax: +48 42 636 25 96.
E-mail address: jsokolow@p.lodz.pl (J. Sokołowska).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.08.018

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).



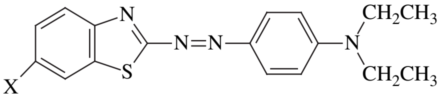
Dyes	X	R_1	R_2	R_3
I	H	H	Et	Et
II	NO_2	H	Et	Et
III	H	Me	Et	CH_2CH_2CN
IV	NO_2	Me	Et	CH_2CH_2CN
V	H	H	CH_2CH_2OH	CH_2CH_2CN
VI	NO_2	H	CH_2CH_2OH	CH_2CH_2CN
VII	H	H	CH_2CH_2OCOMe	CH_2CH_2CN
VIII	NO_2	H	CH_2CH_2OCOMe	CH_2CH_2CN
IX	H	H	CH_2Ph	CH_2CH_2COOEt
X	H	Me	CH_2Ph	CH_2CH_2COOEt
XI	H	H	CH_2Ph	CH_2CH_2CN
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.

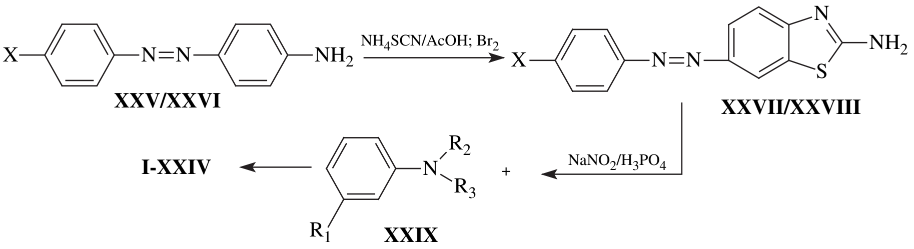
It is well known that benzothiazolyl azo dyes with negative substituent in the 6th position of the benzothiazole ring have improved light fastness and exhibit a strong bathochromic shift of λ_{max} in comparison with the unsubstituted analogue [18,19]. The typical examples are **XXX** and **XXXI** with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

Download English Version:

https://daneshyari.com/en/article/177751

Download Persian Version:

https://daneshyari.com/article/177751

Daneshyari.com