Chemistry of Heterocyclic Compounds, Vol. 39, No. 3, 2003

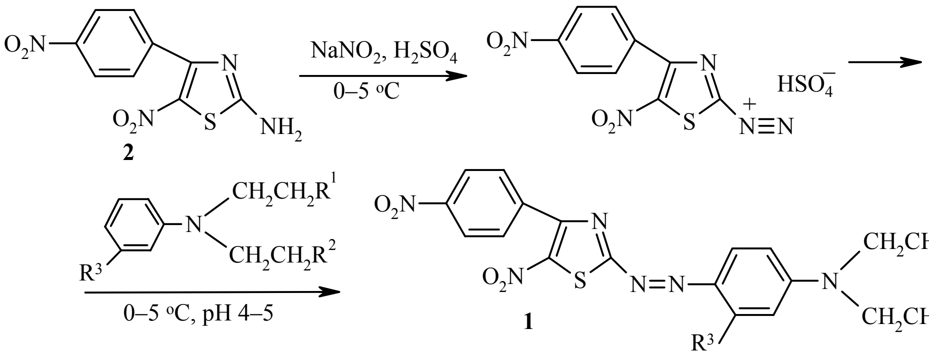
SYNTHESIS AND APPLICATION OF DISPERSE DYES BASED ON 2-AMINOTHIAZOLE DERIVATIVES

Hari Raghav Maradiya[1] **and Vithal Soma Patel**[2]

A series of novel monoazo disperse dyes based on 2-amino-5-nitro-4-(p-nitrophenyl)thiazole were prepared using various N,N-dialkylaniline derivatives as the coupling components. The spectral properties in the IR and visible range of the dyes were investigated. The dyeing performance of these dyes was assessed on nylon fabric. These dyes were found to give a wide range of color shades from reddish brown to indigo with excellent brightness, levelness, and depth on nylon fabric. The dyed fabric showed fairly good light fastness, good to excellent fastness to wash and perspiration, and excellent fastness to sublimation. The dyebath exhaustion and fixation of the dyes on nylon were found to be very good and acceptable.

Keywords: 2-amino-5-nitro-4-(*p*-nitrophenyl)thiazole, disperse dyes, nylon, dyeing, exhaustion, fixation.

The discovery of the fusion reaction between *p*-toluidine and sulfur to give dehydrothio-*p*-toluidine in 1887 constitutes the beginning of thiazole dyestuff technology. The Color Index described various basic, direct, vat, and disperse dyes possessing thiazole nucleus [1]. Before 1950, almost all the disperse blue dyes used were prepared from anthraquinone derivatives and had the limitations of poor dischargeability and sensitivity to oxides of nitrogen. Derivatives of 2-aminothiazole have a long history of use as heterocyclic diazo components for disperse dyes [2]. Blue dischargeable monoazo derivatives based on 2-amino-5-nitrothiazole caught the attention of dye chemists in the 1950's, with colorants such as C.I. Disperse Blue 339 [3] having been produced commercially [2]. 2-Aminothiazoles containing nitro groups are prized for their bathochromism and high tinctorial strength relative to their carbocyclic analogues [4]; these properties, which have aided the rise to prominence of such dyes as replacement for blue anthraquinone colorants [5], were first reported by Dickey nearly forty years ago [6].



---

[1] V. P. and R. P. T. P. Science College, Vallabh Vidyanagar 388 120, Gujarat State, India; e-mail: mardiahari@yahoo.com. [2] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat State, India. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 404-409, March, 2003. Original article submitted September 28, 2001.

2-Amino-5-nitrothiazole could be used to produce bright blue dyes with adequate light fastness combined with excellent dischargeability, gas fastness and dyeability on hydrophobic fabric. The commercial success of dyes for cellulose triacetate, which were derived from 2-amino-5-nitrothiazole, resulted in considerable interest in this class of dyes. Early dyes showed moderate light fastness on cellulose triacetate and polyesters, and light fastness on polyamides was very poor. Dyes with increased light fastness and/or sublimation fastness were prepared from aniline type coupling components bearing various substituents [7-15]. These coupler types have the advantage of providing dyes that have a neutral or green cast when exposed to artificial light, whereas the corresponding dyes from N-alkylaniline couplers have an extremely red cast. The improved fastness to light and sublimation provided by 3-acylaminoaniline type coupling components was not overlooked and dyes were patented [16-19]. Greenish blue dyes can be prepared by choosing a coupler containing electron releasing groups such as 5-acetamido-2-methoxyaniline derivatives. Additional early work on the 2-thiazolylazo dyes resulted in violet dyes from 2-amino-5-carbalkoxy-4-trifluoromethylthiazole [20], 5-alkylsulfonyl-2-aminothiazole [21], 5-formyl-4-halothiazole [22], and even more bathochromic dyes from 4-alkylsulfonyl-2-amino-5-nitrothiazole [23].

During the last ten years, the level of interest as indicated by the patent literature has grown in the field of thiazolylazo disperse dyes [24-26]. There has been considerable growth in the volume of the data reporting outside of the patent literature [27-34]. Earlier we had studied disperse dyes based on 2-aminothiazole derivatives [35-38]. The encouraging results prompted us to extend the study to the thiazole moiety. Hence, a series of monoazo dyes of general formula **1** were synthesized and tested as disperse dyes for nylon fabric. In addition to the characterization of the dyes, an evaluation of their technical properties and a color assessment were performed.

EXPERIMENTAL

All of the chemicals used in the synthesis of dyes **1** were of commercial grade and were further purified by crystallization and distillation. All solvents used were either of analytical grade or redistilled commercial grade.

TABLE 1. Characteristics of Compounds **1a-j** as Dyes

Compound	Substituent			Absorption maxima, λ_{max}, nm		log ε (DMF)	Nylon	
	R^1	R^2	R^3	DMF	Conc. H_2SO_4		(%*F*)*	(%*E*)*^{2}
1a	OH	OH	H	525	470	4.47	74	85
1b	OAc	OAc	H	540	465	4.69	73	90
1c	OH	OH	Me	540	475	4.60	83	86
1d	OH	OH	Cl	520	463	4.23	76	89
1e	OH	OH	NHAc	545	460	4.80	83	87
1f	OAc	OAc	Me	550	470	4.82	76	91
1g	Cl	Cl	H	510	460	4.75	84	88
1h	CN	CN	H	505	480	4.41	78	89
1i	CN	CN	Me	510	483	4.23	81	87
1j	CN	CN	Cl	500	460	4.55	84	90

---

* %*F* is fixation %.

*^{2} %*E* is exhaustion %.

TABLE 2. Physicochemical Characteristics of Compounds **1a-j**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C (DMF)	R_f	Yield, %
		C	H	N			
1a	$C_{19}H_{18}N_6O_8S$	49.60 49.78	3.75 3.93	18.20 18.34	125-127	0.81	81
1b	$C_{23}H_{22}N_6O_8S$	50.76 50.92	3.86 4.05	15.28 15.49	95-96	0.79	86
1c	$C_{20}H_{20}N_6O_6S$	50.62 50.84	4.08 4.23	17.56 17.79	124-125	0.89	78
1d	$C_{19}H_{17}ClN_6O_6S$	46.10 46.29	3.25 3.45	16.82 17.05	118-120	0.90	80
1e	$C_{21}H_{21}N_7O_6S$	51.08 51.21	4.10 4.26	18.25 18.49	113-115	0.78	79
1f	$C_{24}H_{24}N_6O_8S$	51.60 51.79	4.20 4.31	14.89 15.10	98-99	0.83	82
1g	$C_{19}H_{16}Cl_2N_6O_4S$	45.83 46.06	3.10 3.23	16.69 16.96	125-126	0.96	81
1h	$C_{21}H_{16}N_8O_4S$	52.79 52.94	3.18 3.36	22.7 22.85	140-141	0.78	85
1i	$C_{22}H_{18}N_8O_4S$	53.58 53.87	3.50 3.67	22.61 22.85	160-161	0.77	82
1j	$C_{21}H_{15}ClN_8O_4S$	49.12 49.37	2.78 2.93	21.68 21.93	127-128	0.92	76

Methods. Acetophenone was reacted overnight on a steam bath with thiourea in equimolar ratio in the presence of 1 mol bromine [39] to give 2-amino-4-phenylthiazole. The nitration of the latter with 2 mol of nitric acid gave 2-amino-5-nitro-4-(*p*-nitrophenyl)thiazole (**2**) [6]. Both thiazole derivatives obtained agreed in IR and physical properties with those reported in the literature [6, 39].

2-{4-[N,N-Bis(2-hydroxyethyl)amino]phenylazo}-5-nitro-4-(4-nitrophenyl)thiazole (1a). Synthesis of **1a** involves two steps.

(i) Diazotization of **2**.

Dry $NaNO_2$ (1.38 g, 0.02 mol) was slowly added with stirring to concentrated H_2SO_4 (1.2 ml) on a water bath, allowing the temperature to rise to 65°C but no higher. The solution was then cooled to 5°C and a mixture (20 ml) of AcOH–EtCOOH (17:3) was added dropwise with stirring, allowing the temperature to rise to 15°C but no higher. The reaction mixture was then cooled to 0-5°C, compound **2** (5.32 g, 0.02 mol) was added portionwise, and stirring was continued at this temperature for 2 h. The excess nitrous acid (positive test on starch-iodide paper) was decomposed with urea. The clear diazonium salt solution thus obtained was used immediately in the coupling reaction as exemplified below.

(ii) Coupling with N,N-bis(2-hydroxyethyl)aniline.

N,N-Bis(2-hydroxyethyl)aniline (3.62 g, 0.02 mol) was dissolved in AcOH (10 ml) and water (5 ml) together with NaOAc (5 g). This solution was cooled in an ice-bath and the diazonium solution previously prepared was added dropwise over 30 min with vigorous stirring. The pH was maintained between 4 and 5 by simultaneous addition of 10% NaOAc solution. Stirring was continued for 2 h, allowing the temperature to rise to ambient. The dye was then filtered off, washed with warm and cold water until acid-free, and dried at 50°C in an oven to give azo dye **1a**. Recrystallization from EtOH provided the pure dye. The same procedure was repeated for the preparation of dyes **1b-j**. The characterization data are given in Tables 1 and 2.

Dyeing of nylon fabric was carried out with the procedure reported earlier [40].

Determination of the Percentage Exhaustion and Fixation. The dyebath exhaustion percentage (%*E*) and fixation percentage (%*F*) of dyed fabric were determined according to the know method [36].

Fastness properties. The fastness to light, sublimation, and perspiration was assessed in accordance with BS:1006-1978. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961, and the wash fastness test was performed in accordance with IS:765-1979. Details of the various fastness tests are reported in the literature [36].

RESULTS AND DISCUSSION

Preparation of Diazo Component. The nitro group reduces the basicity of the compound **2** and thus efficient diazotization can only be achieved using nitrosylsulfuric acid obtained from dry solid $NaNO_2$ and concentrated H_2SO_4.

The resulting diazonium salt solution was coupled to N,N-dialkylaniline derivatives to obtain dyes. In order to determine the end point of diazotization, it was found useful to check the presence of unreacted diazo component on thin layer chromatography (TLC) by sampling the diazotization mixture and extracting with AcOEt. Thus, when unreacted diazo component no longer persisted on TLC, the diazotization was ended. The diazonium salt solution was used immediately since it decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the diazonium salt continuously to the solution of the coupling component in AcOH. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution at 0-5°C to a solution of the coupling component in AcOH, a 72-89% yield of the dye was usually obtained. To complete coupling, particularly for reactions using nitrosylsulfuric acid in the diazotization, the pH of the reaction mixture was eventually adjusted to approximately 4-5. Thus an appropriate amount of 10% AcONa solution was slowly added below 5°C.

Physical Properties of Dyes. All the solid dyes are dark brown in color. The purity of the dyes was checked by TLC using methanol–water–acetic acid (12:3:7) as the solvent system. When adsorbed onto silica chromatography plates, each dye produced a reddish-violet color spot. All the recrystallized dyes exhibited well-defined melting points characteristic of pure compounds. The purified dyes were all found to have satisfactory elemental analyses (Table 2).

Visible Absorption Spectroscopic Properties of Dyes. The visible absorption spectroscopic properties of dyes **1** were recorded in DMF and concentrated H_2SO_4 solution, and are presented in Table 1. The value of the logarithm of molar extinction coefficient (log ε) of the dyes **1** was in the range of 4.23-4.82, consistent with their high intensity of absorption. The increased intensity might be attributed to the greater planarity of the thiazole dyes, because of the lower steric interaction of a five-membered ring. The color of dyes **1a-j** is affected by substituents in the coupler constituent. The bathochromism of the dyes is an inherent property of the thiazole system itself; the bathochromism does not derive from the substituent groups. However, the greater polarizability of the thiazole system (relative to the benzene system) affects the general bathochromism of the dyes. As can be seen from the data in Table 1, additional bathochromic shifts can also be obtained by enhancing the electron donor properties of the coupler ring, e.g., by introducing an acetamido group *ortho* to the azo group, as in dyes **1e**. This dye, however, gave a shift of 20 nm relative to dye **1a**. The acetamido group is a weak electron donor, but, more importantly, it can take part in hydrogen bonding with the azo group. This enhances the planarity of the dye containing the acetamido group. When replacing the OH group in dyes **1a** and **1c** by Cl and CN groups, the resulting dyes **1g** and **1i** are absorbed at 510 nm. The hypsochromic shift is due to a decrease in the donor strength of the coupler ring.

Infrared Spectra of Dyes. The C–H stretching vibrations of the aromatic ring appear at 700-820 and 1580-1595 cm^{-1}. The strong absorption band in the range 1500-1510 cm^{-1} corresponds to the C–N stretching

TABLE 3. Results of Dyeing and Various Fastness Properties of Dyes **1a-j** on Nylon Fabric*

Com-pound	Shade on nylon	Light fastness	Wash fastness	Perspiration fastness		Rubbing fastness	
				Acid	Alkaline	Dry	Wet
1a	Bluish violet	5-4	5	5	5	5	5
1b	Deep violet	5-4	5-4	5-4	5	5	5
1c	Dark violet	5	5-4	5	5	5	5
1d	Dark maroon	5-4	5-4	5	5	5-4	5
1e	Bright violet	6-7	5-4	5-4	5-4	5	5-4
1f	Dark violet	5-4	5-4	5	5-4	5	5-4
1g	Deep maroon	5-4	5-4	5-4	5-4	5	5
1h	Maroon	5	5-4	5	5	5	5
1i	Reddish orange	5	5	5	5	5	5
1j	Bright maroon	5	5	5	5	5	5

---

* Sublimation fastness 5 (**1a**–**j**).

vibration. The N–H stretching vibration is confirmed at 3400-3450 cm^{-1}. The azo and O–H group stretching vibration band appear at 1500-1525 and 3500-3600 cm^{-1} respectively. The C–H stretching vibration of alkyl group appears at 2895-2900 cm^{-1}.

Dyeing Properties of Dyes. The dispersed dyes **1** were applied at 1% depth on nylon fabric. Their dyeing properties are given in Table 3. These dyes gave a wide range of colors varying from reddish orange to bluish violet shades with good levelness, brightness, and depth on the fabric. The variations in the shades of the dyed fabric result from both the nature and position of the substituent present on the coupler ring, e.g., introduction of an acetamido group *ortho* to the azo linkage in dye **1e** results in a significant improvement in the light fastness. This may be due to the intramolecular hydrogen bond formed between the acetamido group and azo group. The dyeings showed fairly good fastness to light with very good to excellent fastness to washing, rubbing, perspiration, and sublimation. The remarkable degree of levelness after washing indicated good penetration and affinity of these dyes to the fabric.

CONCLUSION

A series of thiazolylazo disperse dyes containing various N,N-dialkylaniline residues have been synthesized by conventional methods and their color properties examined both in solution and on application to nylon fabric. The dyes provide a wide range of colors varying from reddish orange to bluish violet fast shades on fabric and offer excellent affinity and intensity of color. Their synthesis is generally convenient and economical. The small size of molecules of thiazolylazo dyes provides better dyeability. The intrinsic conjugation in the thiazolylazo structure results in excellent color strength. The outstanding property of thiazolylazo dyes is their high sublimation fastness. The compactness of structure improves sublimation fastness. The nature of the substituent in the coupling components has little influence on the visible absorption and shade of the dyeing. The heteroatom in the thiazolylazo structure results in bathochromism and leads to brightness of shades. Furthermore, these dyes show level dyeing and display excellent dischargeability (an additional dyeing property, not exhibited by the carbocyclic azo and anthraquinone disperse dye structure).

REFERENCES

1. *Color Index*, Ed. Society of Dyers and Colorists, American Association of Textile Chemists and Colorists, Bradford (1971).
2. L. Shuttleworth and M. A. Weaver, in: D. R. Waring, G. Hallas (editors), *The Chemistry and Application of Dyes*, Plenum Press, New York (1990), p. 107.
3. J.-Z. Hu, P. Skrabal, and H. Zollinger, *Dyes Pigm.*, **8**, 189 (1987).
4. M. A. Weaver and L. Shuttleworth, *Dyes Pigm.*, **3**, 133 (1982).
5. R. Egli, *The Design and Synthesis of Organic Dyes and Pigments*, Eds. A. T. Peters, H. S. Freeman, Elsevier, London (1991), Chap. 1.
6. J. B. Dickey, E. B. Towne, M. S. Bloom, W. H. Moore, H. M. Hill, H. Heynemann, D. G. Hedberg, D. C. Sievers, and M. V. Ottis, *J. Org. Chem.*, **24**, 187 (1959).
7. Gosei Senryo Gijutsu Kenkyu Kumia, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 59215355; *Chem. Abstr.*, **102**, 186655 (1985).
8. Gosei Senryo Gijutsu Kenkyu Kumia, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 59170142; *Chem. Abstr.*, **102**, 26377 (1985).
9. Mitsubishi Chemical Industries Co. Ltd., Jpn. Kokai Tokkyo Koho, Jpn. Pat. 80133458; *Chem. Abstr.*, **94**, 104887 (1981).
10. Sumitomo Chemical Co., Ltd., Jpn. Kokai Tokkyo Koho, Jpn. Pat. 57161653; *Chem. Abstr.*, **98**, 73836 (1983).
11. H. Erwin, W. Matthias, R. Helmut, and G. Sabine, Ger. Offen. DE 4120362; *Chem. Abstr.*, **118**, 256596 (1993).
12. B. Parton, U.K. Pat. 2028856; *Chem. Abstr.*, **94**, 4937 (1981).
13. M. A. Weaver and J. M. Straley, US Pat. 3525733; *Chem. Abstr.*, **73**, 131958 (1970).
14. G. Modena and A. Risatsu, *Bull. Sci. Fac. Chem. Ind. Bologna*, **11**, 65 (1953).
15. Gosei Senryo Gijutsu Kenkyu Kumia, Jpn. Kokai Tokkyo, Jpn. Pat. 5920356; *Chem. Abstr.*, **100**, 211648 (1984).
16. Nippon Kayaku Co. Ltd., Jpn. Kokai Tokkyo Koho, Jpn. Pat. 8060558; *Chem. Abstr.*, **93**, 151649 (1980).
17. M. Peter, Ger. Offen. 3001945; *Chem. Abstr.*, **93**, 206144 (1980).
18. Mitsubishi Chemical Industries Co. Ltd., Jpn. Kokai Tokkyo Koho, Jpn. Pat. 80112266; *Chem. Abstr.*, **94**, 32171 (1981).
19. Gosei Senryo Gijutsu Kenkyu Kumia, Jpn. Kokai Tokkyo Koho, Jpn. Pat. 5991152; *Chem. Abstr.*, **101**, 173017 (1984).
20. E. B. Towne and H. M. Hill, US Pat. 2746953; *Chem. Abstr.*, **50**, 6058 (1956).
21. E. Merian, US Pat. 3007915; *Chem. Abstr.*, **57**, 7421 (1961).
22. R. Egli, US Pat. 4395544; *Chem. Abstr.*, **99**, 159949 (1983).
23. E. B. Towne, J. B. Dickey, and M. S. Bloom, US Pat. 2852504; *Chem. Abstr.*, **53**, 6627 (1958).
24. H. Tsien, K.-P. Chu, and H. Chang, US Pat. 5652344; *Chem. Abstr.*, **127**, 150201 (1997).
25. R. Sens and K.-H. Etzbach, Ger. Offen. DE 4426023; *Chem. Abstr.*, **124**, 204936 (1996).
26. S. Beckmann, K.-H. Etzbach, and R. Sens, PCT Int. Appl. WO 9529958; *Chem. Abstr.*, **124**, 120121 (1996).
27. K. A. Bello, C. M. O. A. Martins, and I. K. Adamu, *Colorage*, **42**, 29 (1995).
28. K. R. Desai, B. R. Modi, and B. D. Mistry, *J. Indian Chem. Soc.*, **72**, 141 (1995).
29. K. A. Bello, *Dyes Pigm.*, **27**, 45 (1995).
30. J. Griffihs and C. J. Riepl, *Chem. Commun*, 1349 (1998).
31. G. Hallas and J.-H. Choi, *Dyes Pigm.*, **42**, 249 (1999).

32. K. H. Chikhalia and K. R. Desai, *J. Inst. Chem. (India)*, **70**, 142 (1998).
33. D. W. Rangnekar, V. R. Kanetkar, G. S. Shankarling, and J. V. Malanker, *J. Indian Counc. Chem.*, **15**, 28 (1998).
34. A. D. Towns, *Dyes Pigm.*, **42**, 3 (1999).
35. H. R. Maradiya and V. S. Patel, *J. Serb. Chem. Soc.*, **65**, 773 (2000).
36. H. R. Maradiya and V. S. Patel, *Bull. Chem. Technol. Macedonia*, **20**, 51 (2001).
37. H. R. Maradiya and V. S. Patel, *Fiber Polymer* (in press).
38. H. R. Maradiya and V. S. Patel, *J. Braz. Chem. Soc.* (in press).
39. J. B. Dickey and E. B. Towns, US Pat. 2730523; *Chem. Abstr.*, **50**, 74676 (1956).
40. H. R. Maradiya and V. S. Patel, *High Perform. Polym.*, **12**, 335 (2000).