Chemistry of Heterocyclic Compounds, Vol. 45, No. 10, 2009

DISPERSE DYES DERIVED FROM 2-AMINO-5-MERCAPTO-1,3,4-THIADIAZOLE

Hari R. Maradiya*

Some novel heterocyclic monoazo dyes based on 2-amino-5-mercapto-1,3,4-thiadizole have been synthesized by coupling with various N-phenylacrylamide derivatives. The dyeing performance of these dyes was assessed on polyester fabrics. IR and visible spectra of the dyes were examined. The percentage dye bath exhaustion, fixation, and various fastness properties of the dyes were also determined. These dyes were found to give brownish-orange to reddish-pink shades on dyeing with good depth, levelness, and brightness on fabric. The dyed fabric showed a good to excellent fastness to washing, rubbing, perspiration, and sublimation.

Keywords: 2-amino-5-mercapto-1,3,4-thiadizole, N-phenylacrylamide, polyester, dyeing, exhaustion, fixation.

Aminothiadiazoles were among the first heterocyclic diazo components for disperse dyes to be described in the patent literature [1]. Such heterocyclic amines have been commercially used to produce dyes that provide brilliant red shades on polyester fabrics. Depending on the substituent in the diazo component and the coupler used, brilliant in the scarlet to bluish-red dyes were obtained [2–4]. These, however, still do not quite match the brightness of the anthraquinone dyes. In spite of a great number of patent applications for structures with substituents such as sulfonamide [5], halogen [6], trifluoromethyl [7], and various substituted mercapto groups [8-12], etc. these systems have fallen short of expectations as far as their commercial exploitation is concerned. Some of the dyes produced have been used to substitute for anthraquinone red and pink dyes, which have dominated this market area for so long.

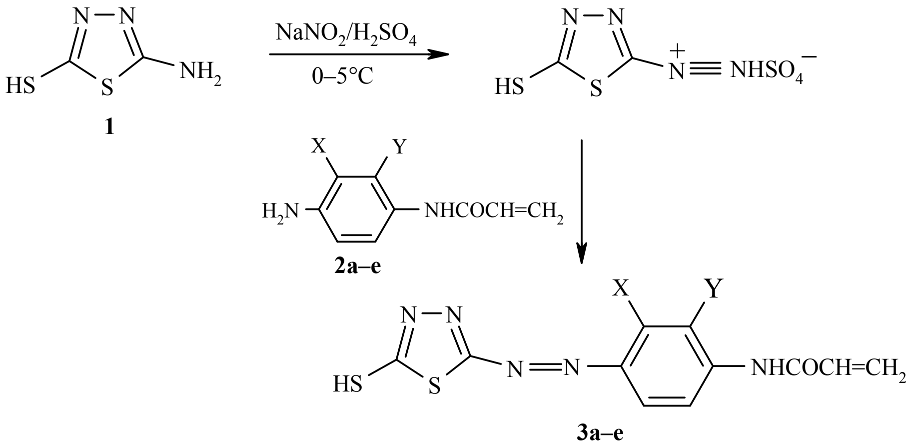
During the last two decades the level of interest as indicated by the papers published in the literature [13-22] has grown in the field of disperse thiadiazolylazo dyes. It seems that no report is available on the use of 2-amino-5-mercapto-1,3,4-thiadiazole (**1**) in the synthesis of disperse dyes by coupling with various substituted N-arylacylamides **2a–e**. Hence, it was thought worthwhile to synthesize a series of disperse dyes **3a–e** from 2-amino-5-mercapto-1,3,4-thiadiazole using various substituted N-arylacylamides **2a–e** and apply them on polyester fabrics as disperse dyes.

---

* To whom correspondence should be addressed, e-mail: mardiahariyahoo.com.

[1] V.P. and R.P.T.P. Science College, Vallabh Vidyanagar-388120 Gujarat State, India.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1558-1563, October, 2009. Original article submitted November 3, 2008.



2,3 a X = Y = H; **b** X = NO$_2$, Y = H; **c** X = Cl, Y = H; **d** X = Me, Y = H; **e** X = H, Y = Me

TABLE 1. Characterization Data, Exhaustion (E), and Fixation (F) Properties of Dyes **3a-e**

Dye	Mp (DMF), °C	Absorption maxima, (λ_{max}, nm)		log ε	*E*,%	*F*,%	R_f (AcOEt–PhH)	Yield, %
		DMF	Conc. H$_2$SO$_4$					
3a	174-175	445	410	4.65	80	85	0.83	80
3b	209-210	430	390	4.42	76	83	0.91	85
3c	232-233	450	390	4.44	80	89	0.90	75
3d	249-250	435	406	4.58	76	86	0.81	79
3e	240-241	440	410	4.65	74	85	0.68	68

TABLE 2. Elemental Analysis of Dyes **3a-e**

Dye	Empirical Formula	Found, % / Calculated, %		
		C	H	N
3a	$C_{11}H_9N_5OS_2$	45.10 45.36	2.92 3.09	23.92 24.05
3b	$C_{11}H_8N_6O_3S_2$	39.00 39.28	2.18 2.38	24.86 25.00
3c	$C_{11}H_8N_5OS_2Cl$	40.15 40.55	2.30 2.45	21.36 21.50
3d	$C_{12}H_{11}N_5OS_2$	47.10 47.21	3.41 3.60	22.79 22.95
3e	$C_{12}H_{11}N_5OS_2$	47.06 47.21	2.92 3.60	23.92 22.95

TABLE 3. Dyeing and Fastness Properties of Dyes **3a-e** on Polyester Fabric

Dye	Shade on polyester	Fastness Properties						
		Light	Wash	Perspiration fastness		Subli-mation	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
3a	Light-orange	4-5	5	5	5	5	5-4	5
3b	Brown	3-4	5	5	5	5	5	5-4
3c	Reddish-pink	4-3	5	4-5	5	4-5	5	5
3d	Bright reddish-pink	4-3	5	4-5	5	5	5	5
3e	Reddish-brown	3-4	4-5	5-4	5	5	5	5

Six novel monoazo dyes were derived from diazotized 2-amino-5-mercapto-1,3,4-thiadiazole **1** and coupled with various N-phenylacrylamides **2a-e**. Diazotization in concentrated acids was used for the diazo component, since hydrolysis of the diazonium salt occurs in diluted acid. Here, the acid of choice is concentrated H_2SO_4, used in admixture with glacial AcOH. A particularly important reagent combination is nitrosylsulfuric acid ($NOHSO_4$), which is used extensively as a nitrosating agent for the diazo component. The amino compound **1** was diazotized satisfactorily at 0-5°C by nitrosylsulfuric acid in AcOH. In order to determine the diazotization end point, it was useful to check the presence of the unreacted diazo component on TLC by sampling the diazotization mixture. Thus, when the unreacted diazo component no longer persisted on TLC, the diazotization ended. The diazonium salt solution was used immediately since it decomposed on standing even when cold. Subsequent coupling reaction took place readily on adding the resulting diazonium salt continuously to the solution of the coupling component in AcOH, and good dye yields of 68-85% were usually obtained.

The purity of the dyes was evaluated by TLC using AcOEt-benzene (1:4) as the eluting system. When adsorbed onto silica chromatography plates, the dyes produced a single color spot. All the recrystallized dyes exhibited well-defined melting points. The characterization data are given in Table 1.

The visible adsorption maxima λ_{max} of dyes **3a–e** were recorded in concentrated H_2SO_4 and DMF (Table 1). Their values are directly proportional to the electronic power, and the nature and position of the substituent in the phenyl ring of a coupler moiety. The logarithm values of the molar extinction coefficient (log ε) of dyes **3a-e** were in the range of 4.42–4.65, consistent with their high absorption intensity. One reason for the increased intensity might be attributed to the greater planarity of the thiadiazole dyes because of the lower steric interaction of a five-membered ring.

The IR spectra of dyes reveal the characteristic bands around 2960-3010, 1580-1610, and 1500 cm^{-1} due to the aromatic stretching vibration of the phenyl ring, and the bands at 600–660 and 675-700 cm^{-1} (C–S–H stretching), 1070 (C–N stretching), 1200 ($NHCOCH=CH_2$ group), and 1435 cm^{-1} (S–C stretching). The bands at 800-870 (a *para*-disubstituted phenyl ring), 960-990, and 870-900 cm^{-1} are due to the out-of-plane C-H bending of the vinyl group. The azo group (N=N) indicates the stretching vibration at 1540-1560 cm^{-1}. Two strong bands observed at 1650-1690 cm^{-1} are assigned to the stretching vibration of the C=O group of the acrylamido group. The amide grouping N–H stretching vibration was observed around 3275-3350 cm^{-1}. The band at 1320-1350 cm^{-1} is due to the symmetric stretching of the NO_2 group. The bands at 620-685 and 1385-1450 cm^{-1} are due to the C–Cl and C–CH_3 stretching vibration, respectively.

All the dyes were applied at 2% depth on polyester fabric as disperse dyes. Their dyeing properties are given in Table 3. These dyes gave a narrow range of color varying from orange to pink with excellent levelness, brightness, and depth on fabric and a deeper shade with high tinctorial and excellent levelness. The variation in the shade of the dyed fabric results from alteration in the coupling components. The dyed fabric has good (3-4) to excellent (5) light, washing, rubbing, perspiration, and sublimation fastness properties. A remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of dyes to the fabric. The value obtained for the given colorant in any fading test depends on many factors, the most important of which are: Dye concentration and/or aggregation degree within the fabric; the nature of fabric in which it is dispersed; characteristics of the incident radiation, molecular structure, molecular size, and substantivity. The substantivity of the dyes for polyester fabric is such that they conferred almost similar depth of shade (close fixation values), which had the same rating, implying that the intrinsic photostabilities of dyes on the fabric are similar. This suggests that smaller molecular size and higher substantivity factors hold more importance than those concerning a slight difference in molecular structure of dyes.

Table 1 shows exhaustion and fixation of all the dyes on fabric. Very good exhaustion on the fabric may be expected because dye diffusion within the fabric proceeds rapidly under the dyeing condition. Hence, the diffusion rate of the dye molecules into fabric is higher, which increases the exhaustion value. Also the smaller thiadiazole dye molecule penetrates deeper into the fabric, which closes easily on fabric after dyeing and so it from sublimation. The sublimation fastness observed shows that all the dyes exhibit very good (5-4) to excellent (5) rating on fabric. The other fastness properties are found to be good to excellent (5).

The efficient diazotization of amino compound **1** can only be achieved using nitrosylsulfuric acid obtained from $NaNO_2$ and concentrated H_2SO_4. A series of thiadiazole-based disperse dyes containing various N-aryl-acrylamide residues has been synthesized by conventional methods and their color properties examined both in solution and on application to polyester fabric. A gamut of color shades narrowly by ranging from orange to pink was obtained by applying variously substituted dyes. The small size of thiadiazolylazo dyes provides good dye ability. The intrinsic conjugation in the dye structure results in very good color strength. The nature of the substituent in coupling components has little influence on the visible absorption. These dyes give very good exhaustion, fixation, and economy (as compared with anthraquinones, which could only provide up to blue shades). An outstanding characteristic feature of these dyes is that they give a level dyeing and excellent dispersability. The remarkable levelness degree after dyeing indicates good penetration and affinity of these dyes to the fabric.

The results suggest that polyester fabric dyeing with thiadiazolylazo disperse dyes may be promising for practical use, chiefly on account on facility and cheapness of the dye synthesis, the application ease, and the overall versatility of their use.

EXPERIMENTAL

All the melting points were determined by the capillary method. The visible absorption spectra were measured in a Carl Zeiss UV/VIS Specord spectrometer. The elemental analysis was carried out on a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded in the KBr pellets on a Perkin-Elmer 983 spectrometer. The solvents and reagents were obtained from commercial sources. They were further purified by a standard method [23]. The diazo component **1** was prepared as reported in the literature [24].

The coupling components **2a-e** were prepared by the method reported in the literature [25]. All the dyes were applied to polyester fabrics adopting the general dyeing method [26]. Fastness to light, sublimation, and perspiration were assessed in accordance with BS: 1006-1978 (British Standard Institute, Dictionary of Quality Standards) and the wash fastness test in accordance with IS: 765-1979. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961. The percentage dye bath exhaustion (%E) and fixation (%F) of the dyed fabric was also determined by the known method [27].

2-(N-Phenylacryamido)azo-5-mercapto-1,3,4-thiadiazole (3a). The synthesis of compound **3a** involves two steps:

a) Diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole (**1**)**.** The compound **1** was diazotized by the general method reported in the literature [17].

b) Coupling with N-phenylacrylamide (**2a**). Compound **2a** (2.94 g, 0.02 mol) was dissolved in AcOH (10 ml)and cooled to 0-5°C in an ice bath. A freshly prepared diazonium salt solution was added at 0-5°C sufficiently slowly to prevent liberation of nitrous gases. The coupling occurred rapidly. The reaction mixture was stirred at 0-5°C for 45 minutes, maintaining the pH 4.5-5.0 by adding 10% AcONa solution. The mixture was stirred further at 0-5°C for 1 h and then diluted with 100 ml water, and the solid product was filtered off, washed with water, and finally dried in an oven at 50°C. The crude product thus obtained was recrystallized from the minimum amount of DMF to provide **3a** as a brown powder.

The above procedure was used for the preparation of dyes **3b-e** using various coupling components **2b-e**. The whole procedure for the synthesis is given in the Scheme. The characterization data of dyes **3a–e** are given in Tables 1-3.

The author thanks Professor V. S. Patel, Ex-Vice Chancellor of Sardar Patel University, for providing research facilities and valuable guidance.

REFERENCES

1. O. Annen, R. Egli, R. Hasler, B. Henzi, H. Jakob, and P. Matzinger, *Rev. Prog. Color. Relat. Top.*, **17**, 72 (1987).
2. R. R. Giles and M. A. Weaver, US Pat. 4302387; *Chem . Abstr*, **96**, 87018 (1982).
3. Sumitomo Chemical Co. Ltd., Jpn. Kokai Tokkyo Koho, JP 8200169; *Chem. Abstr.*, **96**, 164138 (1982).
4. M. R. De Giorgi, R. Carpignano, and G. Viscardi, *Melliand Textilber,* **74**, 234 (1993).
5. I. Sebe, C. Curelea, I. Novac, and C. Supuran, *Sci. Bull. Polytech. Inst. Bucharest*, *Chem. Matter Sci.*, **53**, 103 (1991).
6. P. W. Austin and B. R. Fishwick, Eur. Pat. Appl. 23386; *Chem. Abstr.*, **95**, 8792 (1981).
7. Sumitomo Chemical Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 5795381; *Chem. Abstr.*, **98**, 36075 (1983).
8. K. Bramham, A. J. Chalk, and A. W. Pitt, UK Pat. Appl. GB 2067584; *Chem. Abstr.,* **96**, 36860 (1982).
9. Mitsubishi Chemical Industries Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 8124452; *Chem. Abstr.*, **95**, 63666 (1981).
10. Sumitomo Chemical Co., Ltd., Jpn. Kokai Tokkyo Kokkyo Koho, JP 81165076; *Chem. Abstr.*, **96**, 182739 (1982).
11. M. A. Weaver, C. A. Coates, Jr., and J. G. Fisher, US Pat. 4407749; *Chem. Abstr.*, **100**, 87241 (1984).
12. Y. Ishida and J. Murata, Jpn. Kokai Tokkyo Koho, JP 08113722; *Chem. Abstr.*, **125**, 117387 (1996)
13. A. Arcoria, M. R. De Giorgi, F. Futuzzo, and M. L. Logo, *Dyes Pigment*, **21**, 67 (1993).
14. T. R. Desai and K. R. Desai, *Indian J. Fiber Text. Res.,* **23**, 185 (1998).
15. M. R. De Giorgi, R. Carpignano, and A. Cerniani, *Dyes Pigment*, **37**, 187 (1998).
16. D. W. Rangnekar, V. R. Kanetkar, G. S. Shankarling, and J. V. Malankar, *J. Heterocycl. Chem.*, **36**, 95 (1999).
17. H. R. Maradiya and V. S. Patel, *Int. J. Polym. Matter,* **48**, 99 (2000).
18. H. R. Maradiya and V. S. Patel, *Fiber Polym.*, **2**, 212 2001).
19. H. R. Maradiya and V. S. Patel, *J. Text. Assoc.*, **62**, 25 (2001).
20. H. R. Maradiya and V. S. Patel, *Int. J. Polym. Anal. Charact.*, **7**, 314 (2002).
21. H. R. Maradiya and V. S. Patel, *Polym.-Plast. Technol. Eng.,* **41**,735 (2002).
22. H. R. Maradiya and V. S. Patel, *J. Serb. Chem. Soc.*, **67**, 709 (2002).
23. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals,* Pegamon Press, New York, 1980.
24. C.-Y. Chang, S.-Y. Yang, K.-C. Cheng, J. Selmiciu, and H.-H. Lei, *Yao Hsueh Hsueh Pao*, **6** , 351 (1958); *Chem. Abstr.*, **54** (1960) 513.
25. C. E. Schildknecht, *Vinyl and Related Polymers*, John Willey and Sons, New York, 1986.
26. H. R. Maradiya and V. S. Patel, *Adv. Colour Sci. Technol.,* **7**, 29 (2004).
27. H. R. Maradiya and V. S. Patel, *Bull. Chem. Technol. Macedonia,* **20**, 51 (2001).