ISSN 0973-3450 (Print)
JUC Vol. 14(1), 8-13 (2018). Periodicity 2-Monthly
ISSN 2319-8036 (Online)

JOURNAL OF ULTRA CHEMISTRY
An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering
website:- www.journalofchemistry.org
Estd. 2005

Synthesis and characterization of monoazo pyrazolone dyes based on 1,3,4-thiadiazole and their dyeing performance on polyester fabric

MITCHLA S. M., PATEL F. T. and MALIK G. M.*

*Department of Chemistry, Navyug Science College, Surat, Gujarat (India)
Email address of Corresponding Author: gmmalik2010@gmail.com
http://dx.doi.org/10.22147/juc/140102

Acceptance Date 05th Dacember, 2017, Online Publication Date 2nd January, 2018

Abstract

Here in this paper we report a new series of 1,3,4-thiadiazole based heterocyclic monoazo dyes which have been derived by the diazotization of N^4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine with various phenyl pyrazolone as coupling components. The structure of the synthesized dyes was characterized by elemental analysis, IR, ^{1}H NMR and UV spectroscopy with a view to determine their chemical structure. All the synthesized compounds were evaluated for their dyeing performance and fastness properties. The synthesized disperse dyes were found to possess very good dyeing properties.

Key words: Heterocyclic dyes, 5-benzyl-1,3,4-thiadiazole-2-amine, Monoazo dyes, Pyrazolone, Dyeing performance.

Introduction

Disperse dyes are very important class of dyes due to their brilliancy, wide range of hue and excellent fastness properties[1,2]. They are used for dyeing hydrophobic fibres like nylon, polyester and acrylic fibres from an aqueous dispersion[3,4]. Azo disperse dyes are cost effective and they cover the various shades and possess good fastness properties[5-7]. Now a days, heterocyclic dyes have attracted much more interest because of their greater molar extinction coefficients, brightness in colour and high chromophoric strength and fastness[8]. The heterocyclic azo dyes having sulphur, either alone or in combination with nitrogen provide commercially important azo dyes. 1,3,4-thiadiazole is a planar aromatic five member ring system which displays exceptional chemical behaviour and exhibits a broad spectrum of biocidal activities possibly due to the presence of toxophoric –N-C-S moiety[9-11]. Amino thiadiazoles are very useful compounds as intermediates in the dyestuff

industry[12, 13]. Pyrazolone based heterocyclics are important dyes and pigments. Some azo pyrazolone derivatives have various applications in the synthesis of dyes and complexes[14,15]. Recently, Arylazopyrazolone based disperse dyes is well established because of their good spectral and dyeing properties. Pyrazolones as coupling components are especially important colorants for yellow to orange dyes in industrial applications[16-21]. Amino thiadiazole based dyes incorporated pyrazolone moiety generally exhibit good tinctorial strength and brighter dyeing[22].

The purpose of the present investigation was to obtain pyrazolone dyes with good tinctorial strength, we report here the synthesis and study of the dyeing properties of the dyes based on 5-benzyl-1,3,4-thiadiazol-2-amine.

Methods and Materials

All the chemicals used were of analytical reagent grade and were used without further purification. Melting points were taken in open capillary on Stuart SMP 10 melting point apparatus and are uncorrected. The purity of all compounds was determined by thin-layer chromatography (TLC) using silica gel-G coated Al-plates (0.5 mm thickness, Merck) and spots were visualized under UV radiation. IR spectra were recorded on Perkin-Elmer 1600 FTIR in KBr pellets. ^{1}H NMR spectra were taken on a Bruker Avance II 400 NMR MHz in DMSO as solvent and TMS as internal standard and elemental analysis of "Nitrogen" was carried on Carlo Erba 1108 instrument at SAIF Central Instrumentation Laboratory, Panjab University, Chandigarh. Absorption spectra of the dyes were recorded on a Shimadzu UV-1800 spectrophotometer in DMSO and water.

Synthesis of 5-benzyl-1, 3, 4-thiadiazole-2-amine (1):

A mixture of thiosemicarbazide (0.46 g, 0.005 mol), phenyl acetic acid (1.36g, 0.01 mol), and concentrated H_2SO_4 (15 mL) was refluxed for 4 hours and cool filtrate was poured onto crushed ice. The resulting filtrate was rendered alkaline by slowly adding liquor NH_3 solution. The solid material obtained was filtered off, washed with water and dried. White solid, yield 85%, m.p. 202-203 ºC; Anal. Calcd. for $C_9H_9N_3S$, N= 21.97. Found: N= 20.22

Synthesis of N-(5-benzyl-1,3,4-thiadiazol-2-yl)-2-chloroacetamide (2) :

In a 250 mL RBF, the solution of 5-benzyl-1, 3, 4-thiadiazol-2-amine (5 g, 0.026 mol) in acetic acid (80.0 mL) was cooled to 0-5°C, chloroacetylchloride (5.9 mL, 0.052 mol) was slowly added to RBF. with continuous stirring at 0-5°C. The reaction mixture was stirred in ice-bath for 1 hour then at 15 to 20°C and it was further refluxed at 75-80°C for 1 hour and stirred for 4 hours at room temperature. The reaction mixture was finally poured in a beaker containing crushed ice and then maintaining pH 7.0 to 8.0 by the 20% sodium acetate solution. The solid residue thus obtained was filtered, washed with cold water and dried. White solid, Yield 65%.

Synthesis of N^4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine (3):

N-(5-benzyl-1,3,4-thiadiazol-2-yl)-2-chloroacetamide (1.5g, 0.006 mol) and thiourea (0.7g, 0.009 mol) in methanol (30 mL) was refluxed for 4 hours at 60-65°C. The excess of solvent was distilled off and the solid was obtained. Brown crystals, Recrystallization from ethanol: water (80: 20) m. p. = >300ºC Yield: 85.86% Anal. Calcd. for $C_{12}H_{11}N_5S_2$: N= 24.20. Found: N= 23.89; IR (KBr, cm^{-1}): 3516.35 (-NH_2), 3286 (Ar-H), 3180.72(-NH-), 1548.89 (-C=N-), 1415.80 (-CH_2-), 1153.47 (-C-N-) and 692.47 (C-S-C) ^{1}H NMR (400 MHz, DMSO-d6, δ/ppm): 1.73 (s, 2H, -CH_2), 4.36 (s,1H, CH of thiazole ring) 7.13-7.27 (m, 5H, Ar-H), 7.29 (s, 2H, -NH_2) and 8.196 (s, 1H, -NH)

Diazotization of N^4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine :

Compound (3) (2.0 g, 0.01 mol) was dissolved in acetic acid (6.0mL). It was cooled below 5°C in ice-bath. Solution of sodium nitrite (0.69 g, 0.01 mol) in concentrated H_2SO_4 (3.0 mL) previously cooled to 0°C was added over a period of 5 min. with stirring and maintained the temperature at 0-5°C. Stirring was continued, maintaining the same temperature for an

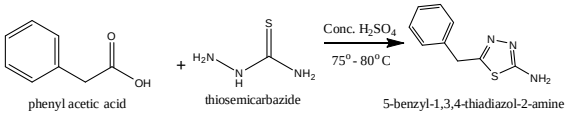
hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of urea. This clear diazonium salt solution was used for coupling reaction.

Coupling of diazotized solution with different substituted pyrazolone coupling component: Formation of Dyes (AD_1-AD_8)

Substituted pyrazolone (0.01mol) coupling component was dissolved in 10% sodium hydroxide solution (6.0 mL). The solution was cooled to 0-5°C in an ice-bath. To this well-stirred solution, the above diazonium solution was added dropwise keeping the temperature below 5°C. The reaction mass was further stirred for 2 hours at 0-5°C maintaining the pH at 8.0 by adding the required amount of 10% sodium carbonate solution. The dye was isolated by filtration, washed with cold water, dried and powdered.

Reaction Scheme

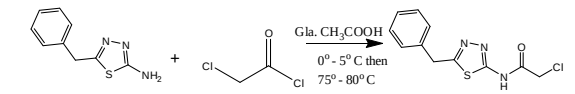
Step- 1 Synthesis of 5-benzyl-1, 3, 4-thiadiazole-2-amine



phenyl acetic acid + thiosemicarbazide → 5-benzyl-1,3,4-thiadiazol-2-amine

(1)

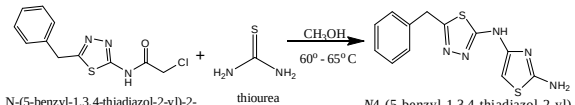
Step-2 Synthesis of *N*-(5-benzyl-1,3,4-thiadiazol-2-yl)-2-chloroacetamide



5-benzyl-1,3,4-thiadiazol-2-amine + chloro acetyl chloride → N-(5-benzyl-1,3,4-thiadiazol-2-yl)-2-chloroacetamide

(1) (2)

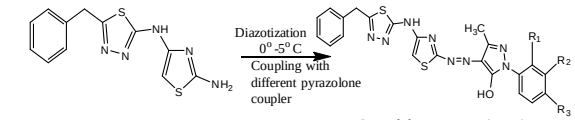
Step- 3 Synthesis of N^4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine



N-(5-benzyl-1,3,4-thiadiazol-2-yl)-2-chloroacetamide + thiourea → *N*4-(5-benzyl-1,3,4-thiadiazol-2-yl) 1,3-thiazole-2,4-diamine

(2) (3)

Step-4 Diazotization and coupling with different substituted pyrazolone coupling component: Formation of Dyes (AD_1-AD_8)



*N*4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine → General dyes structure AD_1- AD_8

Results And Discussion

Chemistry :

5-benzyl-1, 3, 4-thiadiazol-2-amine reacted with chloroacetylchloride at 0°-5°C gave solid *N*-(5-benzyl-1,3,4-thiadiazol-2-yl)-2-chloroacetamide which reacted with thiourea resulting in the formation of N^4-

Table 1. The characterization data of dyes

NO.	Substituent			Melting point (°C)	λ_{max} nm	Yield %	Nitrogen	
	R_1	R_2	R_3				Found	Calc.
AD_1	-Cl	-H	-H	142-145	445	83	22.05	22.01
AD_2	$-NO_2$	-H	$-NO_2$	168-170	462.5	80	22.89	22.77
AD_3	-H	-H	-H	92-96	407.5	78	23.53	23.61
AD_4	-H	$-CH_3$	-H	204-208	442.5	75	22.80	22.93
AD_5	-H	$-NH_2$	-H	120-124	438	65	25.60	25.75
AD_6	-H	-H	-Cl	130-135	450.5	79	22.05	22.01
AD_7	-Cl	-H	-Cl	152-154	458.5	85	20.67	20.62
AD_8	-Cl	-Cl	-H	160-163	458	80	19.11	19.02

Table 2 IR and ^{1}H NMR spectral properties of synthesized dyes

No.	IR (KBr, cm^{-1})	^{1}H NMR (400.1 MHz, DMSO-d_6, δH ppm) spectral data
AD_1	3553 (-OH), 3412 (Ar-H), 3068 (-NH), 1545.03 (-C=N), 1479.45 (N=N), 1348.44 (-CH_2), 1153.47 (-C-N), 831.35 (substituted benzene), 752.26 (C-Cl) and 692.47 (C-S-C).	2.38-2.42 (s, 3H, -CH_3), 3.42-3.62 (s, 2H, -CH_2), 5.35 (s, 1H, -NH), 7.24-8.20 (m, 10H, Ar-H) and 11.79 (s, 1H, -OH)
AD_2	3503 (-OH), 3372 (Ar-H), 3063 (-NH), 1548.03 (-C=N), 1520.05 (-N=O), 1469.45 (N=N), 1328.44 (-CH_2), 1159.47 (-C-N), 835 (substituted benzene) and 692.47 (C-S-C).	2.20-2.40 (s, 3H, -CH_3), 3.38-3.60 (s, 2H, -CH_2), 5.80 (s, 1H, -NH), 7.20-8.24 (m, 9H, Ar-H) and 11.93 (s,1H, -OH)
AD_3	3513 (-OH), 3402 (Ar-H), 3062 (-NH), 1534.03 (-C=N), 1465.45 (N=N), 1358.44 (-CH_2), 1150.47 (-C-N), and 695.47 (C-S-C).	2.18-2.36 (s, 3H, -CH_3), 3.32-3.50 (s, 2H, -CH_2), 5.75 (s, 1H, -NH), 7.20-8.14 (m, 11H, Ar-H) and 11.65 (s, 1H, OH)
AD_4	3551 (-OH), 3324 (Ar-H), 3058 (-NH), 2900 (C-H, stret. CH3 group), 1524 (-C=N), 1504 (N=N), 1344 (-CH_2) 1147 (-C-N), 867.35 (substituted benzene) and 705.47 (C-S-C)	1.99-2.10 (s, 3H, -CH3), 2.18-2.36 (s, 3H, -CH3), 3.31-3.39 (s, 2H, -CH_2), 5.70 (s, 1H, -NH), 7.14-7.86 (m, 10H, Ar- H) and 11.93 (s, 1H, -OH)
AD_5	3523.46 (-OH), 3240.52 (-NH_2), 3336.06 (Ar-H), 3052.51(-NH), 1556.61 (-C=N), 1504.22 (N=N), 1334.78 (-CH_2), 1159.26 (-C-N), 827.49 (substituted benzene) and 640.39 (C-S-C).	2.05-2.17 (s, 3H, -CH_3), 3.65-3.76 (s, 2H, -CH_2), 5.37 (s, 1H, -NH), 7.29-8.34 (m, 10H, Ar-H), 8.65 (s, 2H, -NH_2) and 11.62 (s, 1H, -OH)
AD_6	3553.24 (-OH), 3362 (Ar-H), 3068 (-NH), 1549.03 (-C=N), 1449.45 (N=N), 1335.44 (-CH_2), 1142.47 (-C-N), 829.35 (substituted benzene), 770.26 (C-Cl) and 680.47 (C-S-C).	2.32-2.40 (s, 3H, -CH_3), 3.40-3.62 (s, 2H, -CH_2), 5.05 (s, 1H, -NH), 7.14-8.10 (m, 10H, Ar-H) and 11.09 (s, 1H, -OH)
AD_7	3533.54 (-OH), 3325 (Ar-H), 3065 (-NH), 1541.03 (-C=N), 1465.45 (N=N), 1340.44 (-CH_2), 1150.47 (-C-N), 830.35 (substituted benzene), 780.26 (C-Cl) and 684.47 (C-S-C).	2.08-2.32 (s, 3H, -CH_3), 3.22-3.42 (s, 2H, -CH_2), 5.78 (s, 1H, -NH), 7.20-8.15 (m, 9H, Ar-H) and 11.65 (s, 1H, -OH)
AD_8	3525.43 (-OH), 3365 (Ar-H), 3058 (-NH), 1539.03 (-C=N), 1470.45 (N=N), 1338.44 (-CH_2), 1148.47 (-C-N), 835.35 (substituted benzene), 750.26 (C-Cl) and 630.47 (C-S-C).	2.28-2.52 (s, 3H, -CH_3), 3.42-3.60 (s, 2H, -CH_2), 5.95 (s, 1H, -NH), 7.22-8.00 (m, 9H, Ar-H) and 11.40 (s, 1H, -OH)

(5-benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine in the presence of methanol. Finally diazotization of N^4-(5- benzyl-1,3,4-thiadiazol-2-yl)-1,3-thiazole-2,4-diamine and its coupling with substituted pyrazolones yielded final dyes **AD_1-AD_8**.

Spectral properties :

Visible absorption spectroscopic properties of dyes:

The visible absorption spectra of dyes were recorded in DMSO and are shown in Table 1. The colour intensity and visible absorption spectra of the dye is affected by substituents of the coupling components. The value of λmax ranges from 407-462 nm which

Table:3 Shade and fastness properties of dyes on fabrics

No.	Shade on polyester fabrics	Wash fastness	Sublimation fastness	Light fastness
AD_1	Turmeric Yellow	4	2	3-4
AD_2	Dark Orange	4-5	3	4
AD_3	Light Yellow	4-5	3	4
AD_4	Pinkish Orange	4	3	4-5
AD_5	Yellow	4-5	2	4-5
AD_6	Turmeric Yellow	4-5	3	4
AD_7	Dark Orange	4-5	3	3-4
AD_8	Dark Orange	4	2	4

Abbreviations:

Light fastness: 1-poor, 2- slight, 3-moderate, 4-fair, 5-good, 6-very good, 7-excellent. Fastness of washing, sublimation, perspiration, rubbing: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent.

depends on the coupling components used. The colour for each dye was varying i. e. light yellow, turmeric yellow, pinkish orange, dark orange due to the oscillation of electrons and the presence of additional substituents. Due to addition of electon withdrawing group such as $–NO_2$, -Cl, $-CH_3$ bathochromic effect is generated and resulted in a shift of λmax to a longer wavelength and shade of the dyes deepened.

IR and ^1H NMR spectral data :

IR spectrum of all the dyes, exhibited O-H stretching band in the region 3503-3553 cm^{-1}, C-H stretching vibrations at 3324-3412 cm^{-1}, N-H stretching vibrations at 3052-3068 cm^{-1}, -N=N stretching vibrations at 1449-1504 cm^{-1}, $-CH_2$ stretching vibrations at 1328-1358 cm^{-1} , C-N stretching vibrations at 1540-1552 cm^{-1}, C-Cl stretching vibrations at 750-780 cm^{-1}, C-S-C stretching vibrations at 630-705 cm^{-1}. The ^1H NMR spectra of the dye showed the signals as presented in Table-2.

Dyeing of fabric :

A series of disperse dyes were synthesised in order to assess their stability for dyeing polyester fabrics. The yield of these dyes ranged from 65 to 85%. The structures were identified and established based on the analytical and spectral evidences. All the dyes were applied on polyester fabrics in 2% shade according to usual procedure, pH was adjusted 7.0 using soda ash solution during HTHP dyeing method. The variation in the hues of the dyed fabric results from both the nature and position of the substituent present in the coupling components. The degree of levelness after washing indicates good dispersion and affinity of these dyes to the fabric.

Fastness properties of dyed fabric :

The fastness ratings are shown in Table-3. The light fastness properties were assessed in accordance with BS: 1006-1378 and the wash fastness test in accordance with IS: 765-1979. The light fastness of all the dyes exhibited the rating 4-5 for polyester which showed that light fastness was fair to good. The wash fastness of all the dyes had the rating 4-5 for polyester which indicated that wash fastness was good to excellent and the sublimation fastness of all the dyes had the rating 2-3 for polyester which showed sublimation fastness was good.

Conclusion

Synthesis of N^4-(5-benzyl-1,3,4-thiadiazol-2-yl)-1, 3-thiazole-2,4-diamine based pyrazolone disperse dyes by using various substituted phenyl pyrazolone coupling components has been described. The value of λ_{max} was in range from 407-462 nm, which is in the range of yellow to orange. These dyes gave yellow,

pinkish orange, dark orange colour on polyester fabrics. The fastness properties were found to be good to very good.

Acknowledgement

The authors thankful to Principal Dr. A. S. Patel, Navyug Science College, Surat for providing necessary research facility, SAIF Chandigarh for NMR data and Colourtex surat for IR spectral data and Atul Ltd, Valsad for dyeing and fastness properties. Mitchla S M is thankful to the authorities of UGC for the award of Maulana Azad National Fellowship.

Patel F T is also thankful to the authorities of UGC for the award of NFOBC Fellowship.

References

1. Metwally M A, Abdel-Galil E, Metwally A and Amer F A, *Dyes and Pigments*, *92*, pp 902- 908 (2012).
2. Annen O, Egli R, Hasler R, Henzi B, Jakob H and Matzinger P, *Review of Progress in Coloration and Related Topics*, *17,* pp 72- 85 (1987).
3. Zadafiya S. K., Malik G. M., *Fiber and Polymer*, *14(6),* pp 904-908 (2013).
4. Patel D R, Patel N B, Patel B M and Patel K C, *Journal of Saudi Chemical Society*, *18*, pp 902-913 (2014).
5. Zadafiya S. K. and Malik G. M., *Der pharma Chemica*, *1(3),* pp 15-21 (2010).
6. Otutu J O, Efurhievwe E M, Ameru S U and Ossai E K, *Chemistry and Materials Research*, *6(4),* pp 44-52 (2014).
7. Karabacak Atay E, Gökalp M, Kart S E and Tilki T, *Journal of Molecular Structure*, *1141*, pp 237-244 (2017).
8. Qian H F, Wang Y G , Chen X C, Ruan W G and Huang W, *Dyes and Pigments*, *99*, pp 489- 495 (2013).
9. Ramasamy S, Guria T, Singha T, Roy P, Sahu B P, Naskar J, Das A and Maity T K,, *Der Pharma Chemica*, *8(4),* pp 185-191 (2016).
10. Keerthi Kumar C T, Keshavayya J, Rajesh T N, Peethambar S K and Shoukat Ali A R, *Organic Chemistry International*, Article ID 370626, 7 pages (2013).
11. Mavrova A T, Wesselinova D, Tsenov Y A, and Denkova P, *European Journal of Medicinal Chemistry*, *44(1):* pp 63–69 (2009).
12. Karci F and Ertan N, *Dyes and Pigments*, *64*, pp 243 (2005).
13. Hallas G and Choi J H, *Dyes and Pigments*, *42(3),* pp 249- 265 (1999).
14. Naik C G and Malik G M,(2010) *Oriental Journal of Chemistry*, *26(1),* pp 113-116.
15. Malik G M, Patel P C, Tailor J H and Zadafiya S K, *IRJNAS*, 1(6) (2014).
16. Malik G M, Patel P C, Tailor J H and Naik C G, *International Journal of chemistry*, *4(3),* pp 284-294 (2015).
17. Singh A, Choi R, Choi B and Koh J, *Dyes and Pigments*, *95*, pp 580-586 (2012).
18. Koh J, *Dyes and Pigments*, *69(3),* pp 233-238 (2006).
19. Ertan N, *Dyes and Pigments*, *44(1),* pp 41- 48 (2000).
20. Schwander H R, *Dyes and Pigments*, *3(2-3),* pp 133-160 (1982).
21. Rusul Yahya Alabada, *American Journal of Applied Chemistry*, *5(2),* pp 24-27 (2017).
22. Gouda M A, Eldien H F, Girges M M and Berghot M A, *Journal of Saudi Chemical Society*, *20*, pp 151–157 (2016).