

Synthesis and application of 2-aminothiadiazole disperse dyes for nylon fabrics

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Some disperse dyes based on 2-amino-5-mercapto-1,3,4-thiadiazole have been prepared by coupling with various *N*-arylacrylamides. The dyes were characterized by IR spectral studies and elemental analysis. All the dyes were applied as disperse dyes on nylon fabric. These dyes have been found to give a wide range of color shades with very good depth and levelness on fabrics. The percentage dye bath exhaustion and fixation on the fabric have been found to be very good. The dyed fabrics showed moderate to good light fastness and very good to excellent washing, rubbing, perspiration and sublimation fastness properties.

Keywords: 2-amino-5-mercapto-1,3,4-thiadiazole, disperse dyes, *N*-arylacrylamide, nylon fabric, exhaustion, fixation, fastness.

INTRODUCTION

Organic dye chemistry is nothing new: some colorants based on heterocyclic systems such as mauveine¹ are as old as the hills, or even antedate it in cases like indigo,² while today heterocycles are all-pervasive, whether or not they appear in the guise of chromophores.

Heterocycles have been put to much use in disperse dyes chemistry, which it has been claimed was the first area to foster the industrial exploitation of heterocyclic amines.³ Numerous heterocyclic dyes are now marketed to produce a full range of dispersed dyestuffs without handling colorants based on heteroaromatic diazo components. Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotisable amino group is directly attached. The ring may also possess one or more nitrogen heteroatoms and be fused to another aromatic ring. These diazo components are capable of providing red to blue disperse dyes that meet the rigorous technical and economical requirements demanded of them by both manufacturer and user.

Intensive efforts have been made in the investigation of monoazo dyes in which a heterocyclic system replaces one of the usual carbocyclic systems. Many different

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heterocyclic diazo components have been studied, especially derivatives of thiazole, thiadiazole owing to the marked bathochromic effect of such groups when compared with the corresponding benzenoid compound.⁴

Dyes derived from 2-amino-1,3,4-thiadiazole are of technical interest for the production of brilliant red shades.⁵ Commercial success has been achieved with 2-amino-5-ethylthio-1,3,4-thiadiazole in the replacement of red anthraquinone based dyes,³ a dye from this diazo component, C. I. Disperse Red 338, has the only structure of this type which has been disclosed to date.⁶ Relatively little research work has been published regarding this class compared to the other categories of dyes derived from five-membered sulphur-containing heterocycles. In addition, the level of recent patent activity has been low,⁷⁻⁹ although papers focusing exclusively on dyes derived from 1,3,4-thiadiazole have appeared.¹⁰⁻¹⁴

As no report seems to be available in the literature on the use of 2-amino-1,3,5-thiadiazole derivatives in the synthesis of azo disperse dyes by coupling with various *N*-arylacrylamides, it was thought worthwhile to synthesise some monoazo disperse dyes from 2-amino-5-mercapto-1,3,4-thiadiazole (**1**) using various substituted *N*-arylacrylamides (**3a-f**) as coupling components. The exhaustion, fixation and dyeing performance on nylon fabric of the prepared dyes have been studied.

EXPERIMENTAL

Materials

All the chemicals used were of commercial grade. They were further purified by crystallisation and distillation. The solvents used were spectroscopic grade.

Methods

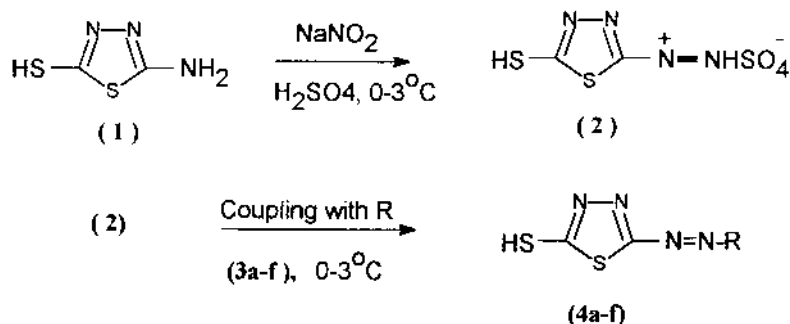
General. All melting points were determined by the open capillary method and are reported in °C. The visible absorption spectra were measured using a Carl Zeiss UV/VIS Specord Spectrometer. The IR spectra were recorded in KBr pellets, on a Perkin-Elmer 983 spectrophotometer. The C, H, N contents were estimated by means of a Carlo Erba Elemental Analyser 1108.

Preparation of 2-amino-5-mercapto-1,3,4-thiadiazole (1). The title compound was prepared by the method reported in the literature.¹⁵

Preparation of various N-phenylacrylamides (3a-f). These compounds were prepared by the method reported in the literature.^{16,17}

Diazotisation of 2-amino-5-mercapto-1,3,5-thiadiazole (1). Dry sodium nitrite (1.38 g, 0.02 mol) was added to cold concentrated sulphuric acid (1.1 ml, 0.02 mol) at such a rate that brown fumes were not evolved. After addition, the mixture was warmed gradually on a water-bath to between 60 and 65 °C, when all the sodium nitrite went into solution. The resulting solution was cooled externally to 3 °C and then treated dropwise at 5–20 °C with mixture of 17 ml of acetic acid and 3 ml of propionic acid. The resulting nitrosylsulphuric acid was cooled to 0 °C and the finely ground compound **1** (2.66 g, 0.02 mol) was added portion wise at 0–3 °C with vigorous stirring and then the liquor was stirred for 2 h, maintaining a temperature of 3 °C. The excess nitrous acid (the presence tested by starch-iodide paper) was decomposed with the required amount of urea. The thus obtained clear diazonium salt solution **2** was used immediately in the coupling reaction (see Scheme 1).

Preparation of 2-(p-N-phenylacrylamido)-azo-5-mercapto-1,3,4-thiadiazole (4a). *N*-phenylacrylamide (**3a**) (2.94 g, 0.02 mol) was dissolved in 10 ml of acetic acid and then cooled to 0 °C. The freshly prepared diazonium salt solution **2** was added sufficiently slowly at 0 °C to prevent the



Scheme 1. Synthesis of dyes **4a-f**. R is the *N*-phenylacrylamide (**3a-f**) coupling component.

liberation of nitrous gases. The coupling occurred rapidly. The reaction mixture was stirred for 1 h at 0–3 °C, maintaining the pH at 4–5 with the help of a 10 % sodium acetate solution. The product was then filtered off, washed with water until acid-free, and dried in an oven at 50 °C. The total elimination of the contaminants required two times recrystallisation.

The same procedure was used for the preparation of dyes (**4b-f**) using various *N*-aryl-acrylamides (**3b-f**). The whole process for the synthesis is shown in Scheme 1. The characterisation data of the dyes (**4a-f**) are given in Tables I and II.

TABLE I. Characterisation, % exhaustion and fixation data of dyes

Dye No.	Coupling component R	Yield %	Melting point °C	Absorption maxima in DMF nm	$\log R_f$	Exhaustion %	Fixation %	Absorption maxima in H ₂ SO ₄ nm
4a	<i>N</i> -Phenylacrylamide	80	174	445	4.65 0.83	84	90	410
4b	<i>N-m</i> -Nitrophenyl-acrylamide	85	209	430	4.42 0.91	84	89	390
4c	<i>N-m</i> -Chlorophenyl-acrylamide	75	232	450	4.44 0.90	82	92	395
4d	<i>N-m</i> -Tolylacrylamide	79	249	435	4.58 0.81	82	90	408
4e	<i>N-o</i> -Tolylacrylamide	68	240	440	4.65 0.85	86	91	410
4f	<i>o-N</i> -Acryloylaminobenzoic acid	65	248	430	4.35 0.86	78	86	405

Dyeing of nylon fabric. Dyeing of nylon fabric was performed using a procedure reported in the literature.¹⁸

Colour fastness tests. Fastness to light, sublimation and perspiration was assessed in accordance with BS: 1006 – 1978. The wash fastness was tested in accordance with IS 765-1979. The rubbing fastness was determined using a crockmeter (Atlas) in accordance with AATCC-1961. The details of the various fastness tests are given in the literature.¹⁸ The data regarding the various fastness properties are reported in Table III.

Exhaustion and fixation. The percentage dye bath exhaustion and fixation of the dyed fabric were calculated by known methods.¹⁹

TABLE II. Elemental analysis of the dyes

Dye No.	Molecular formula	Molar mass g mol ⁻¹	C %		H %		N %	
			Calcd.	Found.	Calcd.	Found.	Calcd.	Found.
4a	C ₁₁ H ₉ N ₅ OS ₂	291	45.36	45.10	3.09	2.92	24.05	23.92
4b	C ₁₁ H ₈ N ₆ O ₃ S ₂	336	39.28	39.00	2.38	2.18	25.00	24.86
4c	C ₁₁ H ₈ N ₅ OS ₂ Cl	325.5	40.55	40.15	2.45	2.30	21.50	21.36
4d	C ₁₂ H ₁₁ N ₅ OS ₂	305	47.21	47.10	3.60	3.41	22.95	22.79
4e	C ₁₂ H ₁₁ N ₅ OS ₂	305	47.21	47.06	3.60	3.46	22.95	22.85
4f	C ₁₂ H ₉ N ₅ O ₃ S ₂	335	42.98	42.68	2.68	2.46	20.89	20.60

TABLE III. Colour fastness properties of the dyes on nylon fabric

Dye No.	Colour hue on nylon	Light fastness	Washing fastness	Rubbing fastness		Perspiration fastness		Sublimation fastness
				Dry	Wet	Acid	Alkaline	
4a	Dark brown	4–5	5	5	5–4	5	5	5
4b	Deep brown	5–4	5	5	5	5	5	5
4c	Brown	3–4	5	5	5–4	5	5	5
4d	Dark brown	3–4	5	5	5	5	5	5
4e	Brown	4–5	5	5	5	5	5	5
4f	Reddish brown	3–4	5	5–4	5	5	5	5

RESULTS AND DISCUSSION

Diazotisation and coupling

1-Amino-5-mercapto-1,3,4-thiadiazole (**1**) was synthesized from thiosemicarbazide by reacting with carbon disulphide, either in the presence or absence of a base. The ring closure of the dithiocarboxylate salt occurs on heating under the reaction conditions. Weak amines, such as compound **1** required the use of nitrosylsulphuric acid. They can be diazotised satisfactorily at 0 °C by adding to nitrosylsulphuric acid in acetic acid and propionic acid mixture. The resulting diazonium salt solution **2** was generally used within a few hours since it decomposes on long standing, even in the cold. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution **2** at 0–3 °C to a solution of the coupler in acetic acid, 65–85 % yields of dye were usually obtained. To complete the coupling, particularly in reactions where nitrosylsulphuric acid had been used in the previously diazotisation, the pH of the reaction mixture was eventually adjusted to approximately 4–5. Thus, an appropriate amount of 10 % sodium acetate solution was slowly added below 3 °C.

In order to determine the end point of diazotisation, it was found useful to check for the presence of unreacted diazo component using TLC by sampling the diazotisation mixture and extracting with ethyl acetate. Thus, when unreacted diazo component no longer persisted on TLC, the diazotisation was ended. The subsequent coupling reaction took place readily on adding the resulting diazonium salt solution **2** continuously to a solution of the

coupling component **3a-f** in acetic acid. Frequent addition of ice flakes helped to maintain the coupling temperature below 3 °C and facilitated precipitation of the resulting dyes **4a-f**.

Physical properties of dyes

All melting points are uncorrected. All the recrystallised dyes exhibited well-defined melting points characteristics of pure compounds. It would be unwise to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors like polarity, size, geometry, interaction, *etc.* The purity of the dyes were checked by TLC using ethyl acetate–benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, the dyes produced a single colour spot.

Infrared spectra

The IR spectra of selected dyes are shown in Fig. 1. The IR spectra of dyes **4a-f** showed characteristic bands around 2960–3010, 1580–1610 and 1500 cm^{-1} . This is due to the aromatic stretching of the phenyl ring. Bands were also observed at 600–660s cm^{-1} and 675–700s cm^{-1} (–C–S–H stretching of the mercapto group), 1070s (–C–N stretching), 1200s (–NHCOCH = CH₂ group) and 1435 cm^{-1} (–S–C stretching). The bands at 800–870 cm^{-1} arise from *para*-disubstituted phenyl rings, while those at 960–990 cm^{-1} , 870–900s cm^{-1} are due to the out-of-plane C–H bending of vinyl group. The azo group (–N=N–) is confirmed at 1540–1560 cm^{-1} . The two strong bands which appear around 1659–1690 cm^{-1} are due to the C=O group. The amide grouping N–H stretching vibration is observed around 3275–3350 cm^{-1} .

The IR spectra of some of the dyes also showed the following characteristic bands: **4b**: 1320–1350 cm^{-1} (symmetric stretching due to –NO₂ group); **4c**: 620–685 cm^{-1} (C–Cl group); **4d, 4e**: 1450 cm^{-1} and 1385 cm^{-1} (C–CH₃ group); **4f**: broad peak around 3100–3400 cm^{-1} (inter- and intra-molecular H-bonding due to –COOH and –NH group).

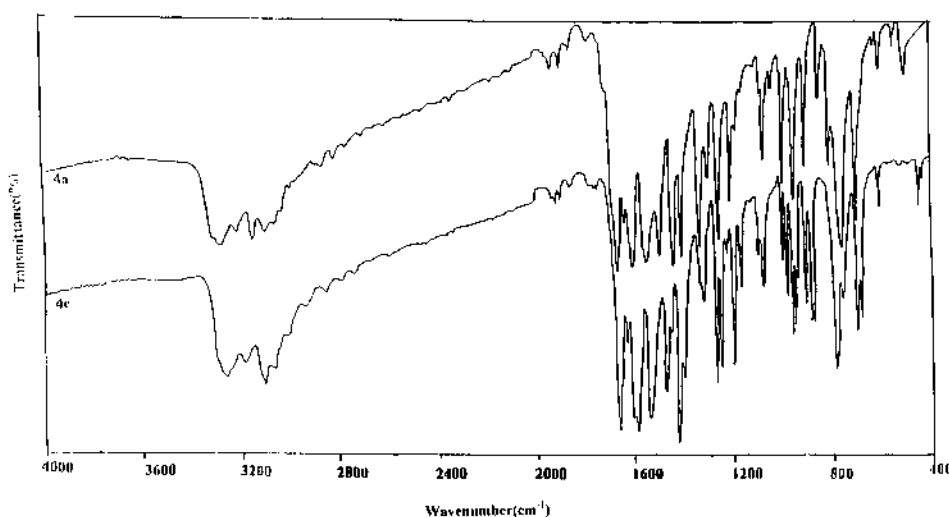


Fig. 1. IR Spectra of dyes **4a** and **4c**.

Dyeing properties of dyes

The disperse dyes **4a–f** were applied at 2 % depth on nylon fabrics. Their dyeing properties are given in Table III. These dyes gave reddish-brown to deep brown hues with brighter and deeper shades with high tinctorial strength and excellent levelness on the fabric. The variation in the hues of the dyed fabric result from the alteration in the coupling components. The dyeing showed moderate (3–4) to good (4–5) light fastness, very good (4–5) to excellent (5) washing, rubbing, perspiration and sublimation fastness properties. The remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of these dyes to the fabric.

Colour and spectral properties of dyes

The absorption maxima of the dyes **4a–f** recorded in DMF solution and concentrated sulphuric acid are shown in Table I. The absorption maxima values λ_{max} , are directly proportional to the electronic power of the substituents in the *N*-arylacrylamides ring system. The dyes, listed in Table I, are reddish-brown to deep brown with absorption maxima between 430 to 450 nm. The values of logarithm of the molar extinction coefficient ($\log \epsilon$) of the dyes were in the range of 4.35–4.65, indicating their good absorption intensity. The introduction of electron-donating or electron-attracting groups at a suitable position in the coupler ring affect the absorption characteristics of the dyes.

Exhaustion and fixation properties of the dyes

Table I shows that exhaustion and fixation of all the dyes on fabric is very good. The higher exhaustion on the nylon fabric may be expected due to the relatively open structure. Consequently, diffusion of the dye within the fabric proceeds rapidly under the given dyeing conditions. Hence, the rate of diffusion of the dye molecules into the fabric are higher, which increases the exhaustion value.

CONCLUSION

Nitrosylsulphuric acid was needed for the satisfactory diazotization of 2-amino-5-mercapto-1,3,4-thiadiazole. Disperse dyes containing the thiadiazole moiety have been prepared from various *N*-arylacrylamides as the coupling component. A gamut of colour hues ranging from reddish-brown to deep brown was obtained by applying the variously substituted dyes **4a–f**. These dyes provide a narrow range of colour hues, excellent affinity and intensity of colour. Outstanding characteristics of these dyes are that they give level dyeing, excellent dispersability and dyeability (an additional dyeing properties, not exhibited by the carbocyclic azo and anthraquinone disperse dye structure). Exhaustion and fixation of these dyes are very good. This indicates that the dyes have good affinity and solubility with the fabric.

The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes to the fabric. The small size of such diazo components provides better dyeability. The intrinsic conjugation in the diazo structure results in very good colour strength. The compactness of the structure provides excellent sublimation fastness. It is these properties which have aided the rise to prominence of such diazo components as replacement for benzenoid colorants on nylon fabrics.

ИЗВОД

СИНТЕЗА И ПРИМЕНА 2-АМИНОТИАДИАЗОЛ-ДИСПЕРЗНИХ БОЈА НА ТКАНИНЕ ОД НАЈЛОНА

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Добијене су дисперзне боје купловањем 2-амино-5-меркапто-1,3,4-тиадиазола са различитим *N*-арил акриламидима. Боје су карактеризоване ИР спектроскопијом и елементалном анализом. Све боје су примењене као дисперзне, за бојење најлонских тканина. Нађено је да ове боје дају читав низ тонова уз врло добру продорност и уједначеност при бојењу тканине. Обојене тканине показале су умерену до добру постојаност на светлост и врло добру постојаност на прање, трљање, зној и сублимацију.

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