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Synthesis, characterization and dyeing behaviour of heterocyclic acid dyes and mordant acid dyes on wool and silk fabrics

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Abstract: Novel heterocyclic acid and mordant acid dyes were synthesised by the coupling of a diazonium salt solution of different aromatic amines with 2-butyl-3-(4-hydroxybenzoyl)benzofuran. The resulting heterocyclic acid dyes were characterized by elemental analysis, IR, ^1H -NMR and ^{13}C -NMR spectral studies and UV–Vis spectroscopy. The dyeing performances of all the heterocyclic acid dyes were evaluated on wool and silk fabrics. The dyeing of chrome pre-treated wool and silk fabrics showed better hues on mordanted fabrics. The dyeing of wool and silk fabrics resulted in pinkish blue to red shades with very good depth and levelness. The dyed fabrics showed excellent to very good light, washing, perspiration, sublimation and rubbing fastness.

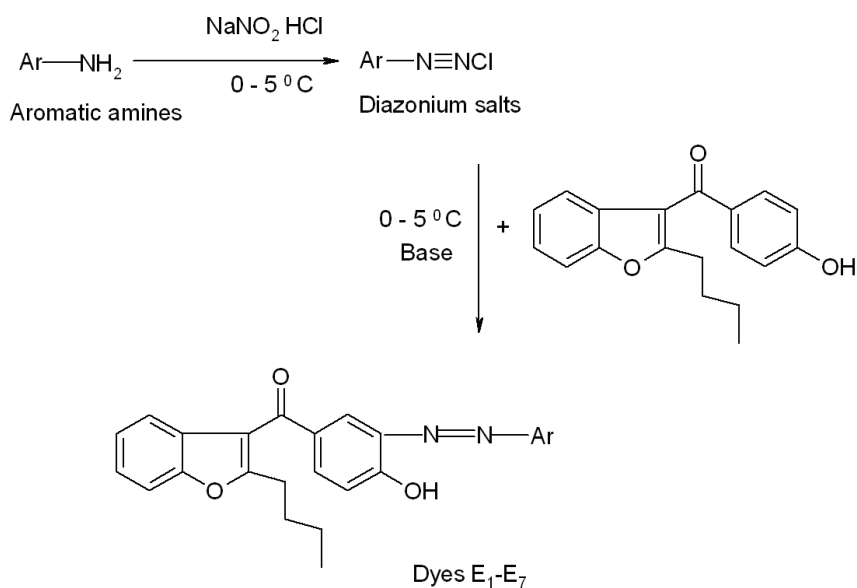
Keywords: heterocyclic acid dye; mordant acid dye; light fastness; washing fastness and rubbing fastness.

INTRODUCTION

Traditionally, heterocyclic acid dyes are the most important class of commercial dyes that contain phenols as intermediates and occupying more than half of the dye chemistry.^{1–7} If they contain sodium salts of a sulphonic acid group in addition to a phenolic group, they are referred to as an acid azo dye. All such dyes having phenolic and sulphonic acid moieties contain hydroxyl (–OH) and sulphonic (–SO₃H) groups as auxochromic groups. One such auxochromic (–OH) and chromophoric (C=O) groups containing compound, *i.e.*, 2-butyl-3-(4-hydroxybenzoyl)benzofuran, has shown wide applications as a polymer additive. It is also known for its excellent UV absorbing capacity,^{8,9} as it prevents the photo-degradation of most vinyl polymers.^{10–13} The formation of heterocyclic acid dyes and mordant acid dyes based on this compound has not been developed, except in a few patents.^{14–16} Considering the above-mentioned importance of 2-butyl-3-(4-hydroxybenzoyl)benzofuran, it was planned to explore the field of

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acid azo dyes based on this compound, which may yield dyes with good hue properties. Hence, in continuation of earlier work,^{17–21} the present communication comprises the synthesis, characterization and dyeing assessment of novel heterocyclic acid dyes and mordent acid dyes based on 2-butyl-3-(4-hydroxybenzoyl)benzofuran. The proposed synthetic route is shown in Scheme 1.



Scheme 1. Proposed synthetic route for the 2-butyl-3-(4-hydroxybenzoyl)benzofuran-based dyes E_1 – E_7 .

EXPERIMENTAL

All the employed chemicals were of analytical reagent grade. The aromatic amines shown in Table I were used for diazotization. The wool and silk fabrics were gifted by Color Tax (Pvt) Ltd., Surat, India. Melting points were determined by the open capillary method and are given uncorrected.

The UV–Vis absorption spectra were measured on a Carl Zeiss UV/Vis Specord spectrometer, and the elemental analyses were realized using a Perkin Elmer CHNS/O analyzer 2400 Series II. The infrared spectra were recorded in KBr pellets on a Perkin–Elmer Spectrum GX FT-IR model. The ^1H -NMR spectra were recorded on a Hitachi R-1500 (400 MHz) in $\text{DMSO}-d_6$ solvent, the ^{13}C -NMR spectra (75 MHz) were recorded on a Bruker Avance DPX 100 spectrometer. The purity of the dyes was checked by thin layer chromatography (TLC) on aluminium sheets pre-coated with silica gel 60 F_{254} (Merck, Germany) using a methanol–

water–acetic acid (12:3:7) solvent system. The colour spots were visualized by a UV cabinet. An HTHP dyeing machine (model LL) was used for dyeing.

Synthesis of heterocyclic acid dyes

Diazotization. Diazotization of various aromatic amines was performed by a reported method.^{22,23} Accordingly, each of the aromatic amines (0.0100 mol) was mixed with HCl (25 mL, 37 %) in a mortar, transferred to a 3-neck round bottom flask, and additional HCl (20 mL, 37 %) was added. To the resultant suspension, crushed ice (25 g) and NaNO₂ (2.5 mL, 4 M) were added. Diazotization was realized over 0.5 h at 0–5 °C under continuous stirring. The complete synthetic route is shown in Scheme 1 and the structures of the various aromatic amines and the corresponding heterocyclic acid dyes are shown in Table I.

Coupling procedure. The coupling of above mentioned diazotized aromatic amines (as shown in Table I) was performed by a method reported in the literature.^{22,23} Thus, 2-butyl-3-(4-hydroxybenzoyl)benzofuran (2.15 g, 0.010 mol) was dissolved in an aqueous sodium hydroxide (100 mL, 0.10 M) solution. The clear solution was cooled in an ice–salt bath and the diazonium salt solution of an aromatic amine was added dropwise over a period of 30 min under vigorous stirring. The pH was maintained between 2.0 and 3.0 by the simultaneous addition of 10 % w/v sodium carbonate solution. Stirring was continued for 2 h, allowing the temperature to rise to ambient. The dye was then filtered off and dissolved in distilled water. Then the heterocyclic acid dye was obtained by evaporation and subsequently dried at room temperature. The dyes were designated as heterocyclic acid dyes **E₁–E₇**.

Acid mono azo dyeing method

Wool and silk fabrics are conveniently dyed in the laboratory at 90–130 °C and at a high pressure (166–207 kPa). A model glycerine bath, high temperature beaker and a HTHP (model LL) dyeing machine were used. For this purpose, a paste of finely powdered heterocyclic acid dyes (0.060 g) was prepared with the dispersing agent dodamol (0.090 g), the wetting agent Tween-80 (0.0060 g) and water (2.0 mL) in a ball mill. Water (10 mL) was added to this paste under stirring and the pH was adjusted to 2.0–4.0 using acetic acid. This dye suspension (100 mL) was added to a container provided with a lid and a screw cap. A wetted pattern of wool or silk fabric was rolled into the beaker and the lid was placed on the beaker and the metal cap tightened.

The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerine bath and the temperature was raised to 90 °C at a rate of 2 °C min⁻¹. The dyeing was continued for 1 h under pressure. After cooling for 1 h, the beaker was removed from the bath and washed with distilled water. The dyed pattern was thoroughly washed with cold water and dried at room temperature.

Mordant dyeing method

A wool or silk fabric dye pattern obtained from the above-mentioned process was treated with 2% potassium dichromate solution equal to half of the weight of the heterocyclic acid dye. The fabric dye pattern was rolled into the container and the container was again placed vertically on the rotator carrier inside the tank and the dyeing was continued for 1 h under pressure. After cooling for 1 h, the container was removed from the bath and the fabric was washed with cold distilled water. Finally, the dyed pattern was thoroughly washed with warm water and air dried at room temperature.

Determination of the percentage exhaustion and fixation

The percentage exhaustion and fixation of the dyed fabrics were determined according to reported methods.²⁴

Fastness property

All the fastness properties of the synthesized heterocyclic acid dyes and mordanted acid dyes were assessed, *i.e.*, the light, sublimation and perspiration fastnesses according to the British standard 1006-1978, the wash fastness according to the Indian standard IS: 765-1979 and the rubbing fastness using a Crock meter (Atlas) AATCC-1961.

RESULTS AND DISCUSSION

Physical properties of dyes

All the heterocyclic acid dyes obtained upon recrystallization from acetone were crystalline powders ranging in colour from pinkish blue to red. The purity of the dyes was checked by TLC using methanol–water–acetic acid (12:3:7) solvent system. A single spot was observed for each dye.

The analytical and spectral data of all the synthesized dyes are given in the Supplementary material to this paper.

The results of elemental analyses of each heterocyclic acid dyes were consistent with the predicted structure, given in Table I. The number of azo groups was almost one for each dye. The nitrogen content and number of azo groups for each dye were correlated with each other. The IR spectrum of each dye comprised the important features of aromatic, azo, hydroxyl, keto, sulphonic acid and carboxylic acid groups.

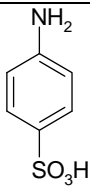
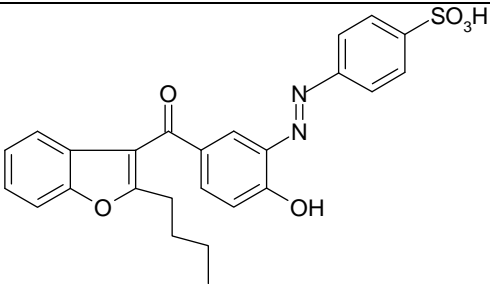
TABLE I. Structure of the aromatic amines and their corresponding heterocyclic acid dyes

Dye	Aromatic amines	Acid azo dye structure
E ₁		
E ₂		

TABLE I. Continued

Dye	Aromatic amines	Acid azo dye structure
E ₃		
E ₄		
E ₅		
E ₆		

TABLE I. Continued

Dye	Aromatic amines	Acid azo dye structure
E₇		

The $^1\text{H-NMR}$ spectra of all the heterocyclic acid dye compounds based on 2-butyl-3-(4-hydroxybenzoyl)benzofuran show important signals at their respective positions, confirming the structures of various heterocyclic acid dyes, as shown in Table I. The two OH protons in **E₁**, **E₂** and **E₃** resonated as a singlet at δ 5.35 ppm. In **E₆**, the $-\text{COOH}$ proton gave a singlet at δ 11.0 ppm. The singlet of the $-\text{SO}_3\text{H}$ proton resonated between δ 8.0 to 8.2 ppm in some of the heterocyclic acid dyes.

The visible absorption spectroscopic properties of the heterocyclic acid dyes were recorded in DMF. The absorption maxima (λ_{max}) of all the heterocyclic acid dyes fell in the range 428–472 nm in DMF and the values are given in Table II. The values of the logarithm of molar extinction coefficient ($\log \epsilon$) of all the dyes were in the range of 4.30–4.72, consistent with their high absorption intensity. Moreover, the presence of electron donating or electron withdrawing groups did not bring about any marked increase or decrease in λ_{max} in the visible region and the $\log \epsilon$ value remained nearly constant.

TABLE II. Absorption maxima in DMF (λ_{max}), intensities ($\log \epsilon$), exhaustion (E) and fixation (F) of the heterocyclic acid dyes on wool and silk fabrics

Dye	$\lambda_{\text{max}} / \text{nm}$	$\log \epsilon$	Acid azo dyeing on wool		Acid azo dyeing on silk	
			$E / \%$	$F / \%$	$E / \%$	$F / \%$
E₁	472	4.73	73	86	70	87
E₂	450	4.54	70	80	72	84
E₃	443	4.45	74	84	83	92
E₄	446	4.47	82	81	76	84
E₅	432	4.34	74	78	88	90
E₆	428	4.30	80	82	76	85
E₇	438	4.36	83	88	74	91

However, an electron withdrawing substituent, such as $-\text{SO}_3\text{H}$ and $-\text{COOH}$, in the structure of the dyes increases the polarizability and results in bathochromic shifts. This leads to a decrease in the energy between the highest

occupied molecular orbital and lowest unoccupied molecular orbital and thus the $\pi \rightarrow \pi^*$ electronic transition occurs at a lower frequency photon, resulting in a bathochromic shift of the visible absorption band.

Percentage exhaustion and fixation of the dyes

The results of the exhaustion and fixation of the dyes are given in Table II. Acid azo dyeing on wool and silk shows very good shades and if acid azo dyeing is compared with mordant azo dyeing then it clearly indicates that, due to chrome complex of dye, mordant dyeing shows better shades than acid dyeing.

Dyeing properties of dyes

The heterocyclic acid dyes were applied at a 2 % depth on wool and silk fabrics. Their dyeing properties are given in Tables III–VI. These dyes gave a wide range of colours varying from pinkish blue to red shades with good levelness, brightness and depth on the fabrics. The variation in the shades of the dye fabric results from both the nature and position of the substituent present on the diazotized compound. The dyeing showed excellent fastness to light, with very good to excellent washing, perspiration, rubbing and sublimation fastnesses.

TABLE III. Results of heterocyclic acid dyeing and their various fastness properties on wool fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Dye	Colour shade on wool	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
E ₁	Pinkish blue	5	4	4	5	5	4	3
E ₂	Pinkish blue	5	4	4	4	4	3	4
E ₃	Reddish brown	4	5	5	4	4	4	4
E ₄	Yellowish pink	5	4	4	4	5	3	3
E ₅	Chocolate brown	4	4	4	5	4	4	4
E ₆	Red	5	5	5	4	4	3	3
E ₇	Red	5	4	4	5	4	4	3

TABLE IV. Results of heterocyclic acid dyeing and their various fastness properties on silk fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Dye	Colour shade on silk	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
E ₁	Pinkish blue	4	4	4	4	4	4	3
E ₂	Pinkish blue	5	5	4	4	4	3	3
E ₃	Reddish brown	4	4	4	5	5	4	4
E ₄	Yellowish pink	4	4	4	4	4	3	3
E ₅	Chocolate brown	4	5	4	4	4	4	4
E ₆	Red	4	5	4	5	4	4	4
E ₇	Red	5	4	5	4	5	3	3

A remarkable degree of smoothness after washing was observed. This may be attributed to the good penetration into and affinity of the dye molecule for the structure of the fabrics. The most prominent feature of these dyes is that the dye patterns treated with Cr(III) salt solution afforded an excellent shining shade of dyes. This might be due to chrome complex formation on the fabric matrix.

TABLE V. Results of mordant heterocyclic acid dyeing and their various fastness properties on wool fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Dye	Colour shade on wool	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
E ₁	Pinkish blue	4	4	5	4	5	4	3
E ₂	Pinkish blue	5	5	4	4	4	4	4
E ₃	Reddish brown	4	4	5	5	5	4	4
E ₄	Yellowish pink	5	4	4	4	4	4	4
E ₅	Chocolate brown	4	4	4	4	4	3	4
E ₆	Red	4	4	5	4	4	4	4
E ₇	Red	4	4	4	5	5	4	3

TABLE VI. Results of mordant heterocyclic acid dyeing and their various fastness properties on silk fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Dye	Colour shade on silk	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
E ₁	Pinkish blue	4	4	4	4	5	4	4
E ₂	Pinkish blue	4	5	4	4	4	3	3
E ₃	Reddish brown	4	4	5	4	5	4	4
E ₄	Yellowish pink	5	4	4	4	4	4	3
E ₅	Chocolate brown	4	4	5	5	4	3	4
E ₆	Red	5	5	4	4	4	4	5
E ₇	Red	4	4	5	4	5	3	4

CONCLUSIONS

All newly synthesized heterocyclic acid dyes and mordant acid dyes exhibited very good to excellent fastness to light, sublimation, perspiration and rubbing. The remarkable degree of levelness after dyeing indicates good penetration into, and affinity of these dyes for the fabric matrix. They gave deep and bright hues with levelling dyeing. The nature of the substituent in the coupling component has little influence on the UV–visible absorption and shade of the dyeing. A comparison of the heterocyclic acid dyes and the mordant acid dyes revealed that the mordant acid dyes had better shades than the heterocyclic acid dyes.

SUPPLEMENTARY MATERIAL

Analytical and spectral data of the synthesized compounds are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ХЕТЕРОЦИКЛИЧНИХ КИСЕЛИНА И МОЧИЛСКИХ БОЈА И ЊИХОВЕ СПОСОБНОСТИ БОЈЕЊА ВУНЕНИХ И СВИЛЕНИХ ТКАНИНА

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Синтетисане су нове хетероцикличне киселине и мочилске боје купловањем диазонијум соли различитих ароматичних амина и 2-бутил-3-(4-хидроксibenзоил)бензофурана. Добијене хетероцикличне киселине карактерисане су елементалном анализом, ИС, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ и UV-Vis спектроскопијом. Способност бојења испитана је на вуненим и свиленим тканинама. Боље нијансе приликом бојења постижу се на вуни и свили које су претходно третирана хромом. Добијене су роза-плаве до црвене нијансе добре дубине и уједначености. Бојене тканине су постојане према светлу, прању и хабању.

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