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Thiophene based monoazo disperse dyes for polyester fabric

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A series of monoazo disperse dyes have been prepared by coupling 2-amino-3-carbethoxy-4,5-dimethylthiophene with various *N*-arylmaleimides. The monoazo disperse dyes were characterised by IR spectral studies and elemental analysis. These dyes were applied at 2 % depth on polyester fabrics and gave light yellow to brown colour hues with fair fastness to light and very good to excellent fastness to washing, rubbing, perspiration and sublimation. The percentage exhaustion of the dyebath and fixation on the fabric were found to be very good.

Keywords: 2-amino-3-carbethoxy-4,5-dimethylthiophene, disperse dyes, exhaustion, fixation, polyester, fastness.

INTRODUCTION

Organic dye chemistry is no exception; some colorants based on heterocyclic system such as mauveine[1] are as old as the field itself, or even antedate it in cases like indigo.[2]

Heterocycles have been put to much use in the chemistry of disperse dyes 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. Systems of this kind are capable of providing red to blue disperse dyes that meet the rigorous technical and economic requirements demanded of them by both manufacturer and user.

The colours of hydrophobic monoazo dyes containing thiophene rings were investigated as long ago as 1949 by Dann.[4] A major advance was made by the research group of Dickey[5] of Eastman Kodak in the 1950s in heterocyclic azo dyes and they published a classic paper on thiophene-based disperse dyes in 1958. In the 1960s, Gewald[6] developed a simple and versatile synthetic route for 2-aminothiophenes. A recent important development is the resurgence of interest in dyes derived from 2-aminothiophene derivatives.

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The technical potential of such dyes for cellulose acetate and for polyester was noted some time ago,[5] but their manufacturer was not commercialised because of the lack of suitable economic synthetic procedures. Improvement in synthetic approaches for the synthesis of derivatives of 2-aminothiophene, stimulated by the work of Gewald,[7] sparked renewed commercial interest. The promise of Gewald's discovery signaled a steady steam of applications concerning thiophene-based azo disperse dyes over the next 20 years.[8–10] Despite, or perhaps because of, the commercial interest, few papers have been published recently,[11–13] concerning the synthesis and properties of such dyes.

Earlier we studied disperse dyes based on various *N*-arylmaleimides coupling components.[14–20] The encouraging results prompted us to extend our study to the thiophene moiety. In this paper, the synthesis of *N*-arylmaleimide base 2-aminothiophene dyes **4a-h** is reported. In the synthesis of the above compounds, 2-amino-3-carbethoxy-4,5-dimethylthiophene (**1**) was diazotised and coupled with various *N*-arylmaleimides **3a-h** to give the azo disperse dyes **4a-h**. The dyes were tested successfully as disperse dyes for polyester fabric and their percentage exhaustion, fixation and various colour fastness properties were also evaluated.

EXPERIMENTAL

Materials

All the chemicals used for the synthesis of dyes **4a-h** were of commercial grade. All solvents used were either of analytical grade or redistilled commercial grade.

Methods

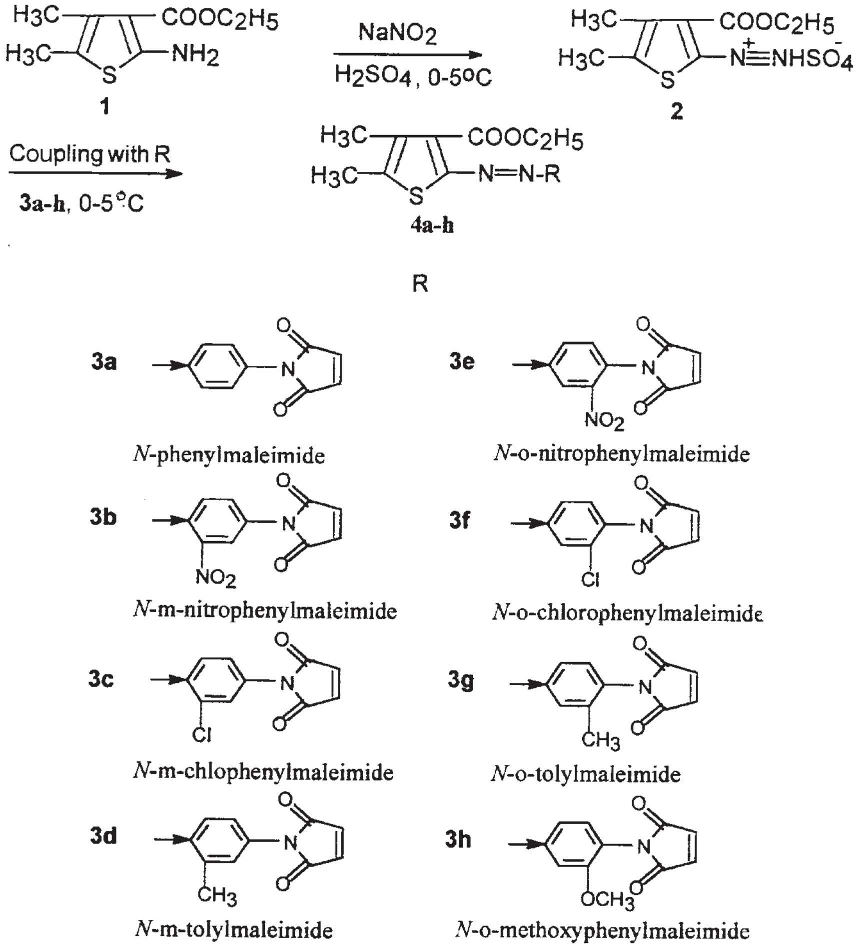
Preparation of 2-amino-3-carbethoxy-4,5-dimethylthiophene (**1**). The title compound was prepared by the method reported in the literature.[7]

Preparation of various N*-arylmaleimides* (**3a-h**). These compounds were prepared by the method reported in the literature.[21]

Diazotisation of 2-amino-3-carbethoxy-4,5-dimethylthiophene (**1**). Diazotisation was carried out with nitrosylsulphuric acid. A typical example is as follows.

Dry sodium nitrite (1.38 g, 0.02 mol) was slowly added over a period of 30 minutes with stirring to concentrated sulphuric acid (1.2 ml) which was heated on a water bath to keep the temperature at 65 ºC. The solution was then cooled to 5 ºC and a mixture (20 ml) of acetic acid-propionic acid (17:3) was added dropwise with stirring, allowing the temperature to rise to 15 ºC. The reaction mixture was then cooled to 0–5 ºC, and 2-amino-3-carbethoxy-4,5-dimethylthiophene (**1**) (3.98 g, 0.02 mol) was added portionwise and stirring was continued at this temperature for 2 h. The excess nitrous acid was decomposed with the required amount of urea. The clear diazonium salt solution **2** thus obtained was used immediately in the coupling reaction (see Scheme 1).

*Preparation of 2-(*p*-maleimidophenylazo-3-carbethoxy-4,5-dimethylthiophene* (**4a**). *N*-phenylmaleimide **3a** (3.46 g, 0.02 mol) was dissolved in acetic acid (10 ml) and then cooled in an ice-bath at 0 ºC. The diazonium solution **2** previously prepared was added dropwise over 30 min with vigorous stirring. The mixture was stirred an additional 2 h at 0–5 ºC, then sodium acetate solution (10 %) was added slowly dropwise until the pH became 4–5. The product was then filtered off, washed with warm water and then with cold water until acid-free and dried at 50 ºC in an oven to give the azo dye **4a**. It was recrystallised from DMF. The yield was 80 % and the m.p. 135 ºC. The purity of the product was checked by thin layer chromatography using ethyl acetate : benzene (1 : 4) as the solvent system. All the other dyes, **4b-h**, were prepared in a similar manner using coupling components **3b-h**, respectively. The whole process for the synthesis is shown in Scheme 1. The characterisation data of dyes **4a-h** are given in Table I.



Scheme 1. Synthesis of dyes **4a-h**.

Dyeing method.

Dyeing of polyester fabric was carried out using a procedure reported in the literature.[15]

Exhaustion and fixation study.

The percentage dyebath exhaustion and fixation of the dyed fabric were calculated by the usual method.[22]

Colour fastness tests.

The fastness to light, sublimation and perspiration was assessed in accordance with BS:1006-1978, and the wash fastness in accordance with IS:765-1979. The rubbing fastness test was carried out using a Crockmeter (Atlas) in accordance with AATCC-1961. The details of various colour tests have been described earlier.[15] The data regarding the various colour fastness tests are given in Table III.

General.

Melting points were determined by the open capillary method. The visible absorption spectra were measured using a Carl Zeiss UV/VIS Specord Spectrometer. The elemental analyses were carried out on a Carlo Erba Elemental Analyzer 1108. The IR spectra were recorded in KBr pellets, on a Perkin-Elmer model 983 spectrophotometer.

TABLE I. Exhaustion, fixation and characterisation data of the 2-aminothiophene derivatives on polyester fabric

Dye No.	Yield %	Melting point ºC	Absorption maxima λ_{max}/nm		log ε	Exhaustion %	Fixation %	R_f
			λ_{max} in DMF	λ_{max} in conc. H_2SO_4				
4a	80	135	495	395	3.53	80	85	0.85
4b	83	109	530	405	3.53	82	78	0.83
4c	78	127	520	395	3.38	78	72	0.88
4d	75	145	530	420	3.44	47	79	0.86
4e	81	103	525	400	3.52	78	84	0.89
4f	85	152	520	410	3.68	79	80	0.93
4g	88	145	520	410	3.92	75	79	0.93
4h	74	109	530	390	3.20	80	76	0.82

TABLE II. Elemental analysis of the 2-aminothiophene derivatives

Dye No.	Molecular formula	Molecular weight	C (%) Requires (Found)	H (%) Requires (Found)	N (%) Requires (Found)
4a	$C_{19}H_{17}N_3O_4S$	383	59.5 (59.4)	4.4 (4.2)	10.9 (10.7)
4b	$C_{19}H_{16}N_4O_6S$	428	53.2 (53.1)	3.7 (3.6)	13.0 (12.8)
4c	$C_{19}H_{16}N_3O_4SCl$	417.5	54.6 (54.4)	3.8 (3.7)	10.0 (9.9)
4d	$C_{20}H_{19}N_3O_4S$	397	60.4 (60.3)	4.7 (4.6)	10.5 (10.4)
4e	$C_{19}H_{16}N_4O_6S$	428	53.2 (53.0)	3.7 (3.6)	13.0 (12.8)
4f	$C_{19}H_{16}N_3O_4SCl$	417.5	54.6 (54.4)	3.8 (3.7)	10.0 (9.8)
4g	$C_{20}H_{19}N_3O_4S$	397	60.4 (60.3)	4.7 (4.6)	10.5 (10.4)
4h	$C_{20}H_{19}N_3O_5S$	413	58.1 (58.0)	4.6 (4.5)	10.1 (10.0)

RESULTS AND DISCUSSION

Synthesis of 2-amino-3-carbethoxy-4,5-dimethythiophene (1)

The Gewal reaction is a one-pot procedure which includes the condensation of ketones with active nitriles such as cyanoacetic esters and sulphur in the presence of an aliphatic amine at room temperature. 2-Amino-3-carbethoxy-4,5-dimethythiophene **1**, a versatile intermediate in the synthesis of various classes of dyes, is synthesised by the condensation of 2-butanone with ethyl cyanoacetate and sulphur in presence of diethylamine as a catalyst using Gewald's elegant method. This synthesis, based on the cyclisation of compounds containing an active methylene group to form 2-aminothiophene derivatives, has provided several crucial intermediates used as starting materials in various studies, particularly those intermediates containing an electron withdrawing substituent at the 3-position. The principal advantages of the key intermediate used here are the high yield, the short reaction time, the involvement of only one facile step, and the convenient work-up. Thus the starting material can be easily prepared. The presence of the electron withdrawing carbethoxy group adjacent to the diazotisable 2-amino group has a bathochromic influence on the hue of these dyes on polyester.

Diazotisation in concentrated acid is used for the diazo component, since hydrolysis of the diazonium salt occurs in dilute acid. Here, the acid of choice was concentrated sulphuric acid, used in admixture with glacial acetic acid. A particularly important reagent combination is nitrosylsulphuric acid ($ONHSO_4$) which is used extensively as a nitrosating agent for heterocyclic amines. The diazo component was diazotised satisfactorily at 0–5 °C by nitrosylsulphuric acid in acetic acid. In order to determine the end point of diazotisation, it was found useful to check for the presence of unreacted diazo component in the diazotisation mixture by thin layer chromatography (TLC). Thus, when unreacted diazo component was no longer detectable by TLC, the diazotisation was ended. The diazonium salt solution **2** was used immediately after preparation since it decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the resulting diazonium salt continuously to the solution of coupling component in acetic acid (see Scheme 1). Coupling was usually accompanied by some evidence of decomposition; however, by the careful addition of the diazonium salt solution **2** at 0–5 °C to a solution of the coupling component in acetic acid, 74–88 % yields of dyes were usually obtained. To complete the coupling, particularly for reactions using nitrosylsulphuric acid in the diazotisation, the pH of the reaction mixture was adjusted to approximately 4–5. Thus, an appropriate amount of 10 % sodium acetate solution was slowly added below 5 °C.

Infrared spectra of dyes

The IR spectra of dyes **4a-h** showed characteristic bands at 3085–3200 cm^{-1} (C-H stretching of *N*-phenylmaleimide ring), 1580–1595 cm^{-1}, 825–835(s) and 945–955(w) cm^{-1} (C=C conjugated with C=O). The bands at 1700–1721 cm^{-1} (stretching of C=O), 630–680 cm^{-1} (in-plane deformation vibration of C=O), 570–580 cm^{-1} (out-of- plane deformation of C=O), 820–860 cm^{-1} (para disubstituted phenyl ring), 1585–1605 cm^{-1} (–N=N–), 1480–1530 cm^{-1} (ester group), 1371(s) and 1350(s) cm^{-1} (–C–N–C asymmetrical and symmetrical stretching, respectively).

The IR spectra of some of the dyes also showed the following characteristic bands

4b and **4e** : 1320–1360 cm^{-1} (symmetric stretching due to –NO_2 group).

4c and **4f** : 640–700 cm^{-1} (C–Cl group).

4d and **4g** : 1450 and 1390 cm^{-1} (C–CH_3 group).

4h : (C–H bending of –OCH_3 group).

Physical properties of dyes

The dyes **4a-h** were dark brown coloured solids and gave deep reddish-brown coloured solution in DMF. The purity of the dyes was checked by TLC using ethyl acetate–benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, each dye produced a single colour spot. All the recrystallised dyes exhibited well-defined melting points and also had satisfactory elemental analyses (Table II). It would be unwise to attempt to explain in detail the relative values of the melting points, because of their complex dependence on a number of factors (*e.g.,* polarity, size, geometry, interaction, *etc.*).

Colour and spectral properties of dyes

The dyes are dark brown having absorption maxima between 495 and 530 nm. The data reveal that the value of the absorption maximum of the dyes depends on both the nature and the position of substitution in the aryl ring system. No proper generalisation is possible within this series of dyes. The value of the logarithm of the molar extinction coefficient (log ε) of the dyes were in the range of 3.20–3.92, indicating their good intensity of absorption. One cause of the increased intensity might be attributed to the greater planarity of the dyes, because of the lower steric interaction of a five-membered ring. The resonance theory gives the reason for the bathochromism of 2-aminothiophene dyes.[23] The first concerns the powerful electron withdrawing thiophene residue that contains sulphur as a π-excessive heteroatom. The sulfur atom, which is said to act as an additional electron withdrawing group, has unoccupied 3d orbitals available that can accommodate transferred negative charge and stabilize the excited state, resulting in a bathochromic shift. The 3d orbitals on the sulphur atom may contribute to the first excitation energy.[24] Sulfur also increases the diene character of the thiophene ring, so the π-electrons in the thiophene ring are likely to migrate more easily. This factor is responsible for the larger absorption shift.[25] But, in this dye series, the moderate electron withdrawing CO_2Et group in the thiophene ring is responsible for the comparatively small values of absorption maxima.

Exhaustion and fixation study of the dyes

Table I shows that the level of exhaustion and fixation of all the dyes **4a-h** on fabric ranges from good to very good. The polyester fabric is much more compact, hydrophobic and crystalline in structure and, consequently, diffusion of the dye within the fabric proceeds slowly under the given dyeing condition. Hence the rates of diffusion of the dyes molecules into the fabric are lower, which affects the exhaustion value. These dyes have good affinity and compatibility with polyester fabric.

Dyeing properties of the dyes

The disperse dyes **4a-h** were applied at 2 % depth on polyester fabric. These dyes gave deeper yellowish brown hues with excellent brightness, levelness and high tinctorial strength. The variation in the hues of the dyed fabric result from an alteration in the coupling components.

TABLE III. Dyeing properties of the 2-aminothiophene derivatives on polyester fabric

Dyes no.	Colour hue on polyester	Light fastness	Wash fastness	Rubbing fastness		Perspiration fastness		Sublimation fastness
				Dry	Wet	Acid	Alkaline	
4a	Yellowish cream	2–3	5	5	5	5	5	5
4b	Yellowish cream	2–3	5–4	4	5	5	5	4
4c	Yellowish cream	2–3	5	5	5	5	5	5
4d	Light brown	2–3	5	5	4	5	5	5
4e	Light brown	2–3	5–4	5	5	5	5–4	4
4f	Cream	2–3	5–4	5	4	5–4	5	5
4g	Yellowish cream	2–3	5	4	5	5	5–4	5
4h	Yellowish cream	2–3	5	5	4	5	5	4

The function of a dispersing agent is to promote levelling and, in particular, to prevent surface deposition of a dye, which results in poor fastness to rubbing. All the fastness properties shown in Table III are inter-related since they depend, among other things, on the rate of diffusion of dye in the fabric. This rate is a function of the geometry of the dye molecule. Fastness to rubbing depends on the presence of loose dye particles on the fabric surface. The rubbing fastness is to a certain extent dependent on the substantivity of the dye for the fabric. The substantivity of the dye, which determines its tendency to partition in favour of the fabric, depends on factors such as molecular size, geometry and, in particular, the polarity of the molecule.

The disperse dyes **4a-h** have a good solubility in the polyester fabric, which allows heavier depths to be achieved. The fastness ratings of the polyester dyeing was primarily influenced by the depth of the hue. All the dyes have the same rating of light fastness even though they have different substituents, since the substituents and their position are alike in this series of dyes. Structure compactness improve the sublimation fastness. Thus, it was found that differences in the orientation of the substituents in the dyes has no effect on the sublimation fastness.

CONCLUSION

The diazo component produced using the Gewald reaction can be used to make light yellow to brown disperse dyes. The weakly basic heterocyclic diazo component required nitrosylphulfuric acid for satisfactory diazotisation and no unreacted diazo component was found after diazotisation. The sulphur atom containing five membered ring possesses structural advantages over conventional substituted aniline diazo components because of the small molecular size and intrinsic property of the thiophene ring, and the electron withdrawing character of the appropriately substituted carbethoxy group which is useful for better dispersability, dyeability and intrinsic conjugation in structure leading to the very good to excellent colour strength. The small molecules penetrate deeper into the fabric structure which closes in on them on drying after dyeing, and so disables their sublimation. These properties have contributed to the rise in prominence of such components as replacements for blue anthraquinone colorants.

The dyed fabrics have fair (2–3) light fastness, very good (5–4) to excellent (5) washing, perspiration, rubbing and sublimation fastness properties. The remarkable degree of levelness and brightness after washing is indicative of good penetration and the excellent affinity of these dyes for the fabric.

The application of sulphur atom containing thiophene disperse dyes to polyester fabric met with mixed success. The dyes are superior in terms of preparation, absorption intensity (brightness), levelness and sublimation fastness.

ИЗВОД

ТИОФЕНСКЕ МОНОАЗО ДИСПЕРЗНЕ БОЈЕ ЗА ПОЛИЕСТАРСКЕ ТКАНИНЕ

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Купловањем 2-амино-3-карбетокси-4,5-диметилтиофена са различитим *N*-ариламидима добивен је низ моноазо дисперзних боја. Боје су какрактерисане IR спектрима и елементарном анализом. Полиестарске тканине су бојене са 2 % боје, и добијене су светложуте до браон нијансе уз добру стабилност на светлост и добру до одличну стабилност на прање, трење, зној и сублимацију. Степен исцрпљивања купатила за бојење и фиксација за тканину били су врло добри.

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REFERENCES

1. O. Meth-Cohn, M. J. Smith, *J. Chem. Soc. Perkin Trans.* **1** (1994) 5
2. G. Grozinger, *J. Soc. Dyers Colour.* **112** (1996) 220
3. D. R. Waring, G. Hallas, *The Chemistry and Application of Dyes,* Plenum Press, New York, 1990, Chap. 4, p. 107
4. O. Dann*, Chem. Ber.* **82** (1949) 72
5. J. B. Dickey, E. B. Towne, M. S. Bloom, W. H. Moore, B. H. Smith, D. G. Hedberg, *J. Soc. Dyers Colour.* **74** (1958) 123
6. K. Gewald, E. Schinke, H. Bottcher, *Chem. Ber.* **99** (1966) 94
7. K. Gewald, *Khim. Getero. Soedin.* (1976) 1299
8. J. F. Dawson, *Rev. Prog. Coloration* **9** (1978) 25
9. M. A. Weaver, L. Shuttleworth, *Dyes Pigm.* **3** (1982) 81
10. O. Annen, R. Egli, R. Hasler, B. Henzi, H. Jakob, P. Matzinger, *Rev. Prog. Coloration* **17** (1987) 72
11. J.–H. Choi, S.–H. Hong, A. D. Towns, *J. Soc. Dyers Colour.* **115** (1999) 32
12. A. D. Towns, *Dyes Pigm.* **42** (1999) 3
13. D. W. Rangnekar, V. R. Kanetkar, G. S. Shankarling, J. V. Malanker, *J. Heterocycl. Chem.* **36** (1999) 15
14. H. R. Maradiya, V. S. Patel, *Man-Made Text. India* **43** (2000) 554

15. H. R. Maradiya, V. S. Patel, *High Perform. Polym.* **12** (2000) 335
16. H. R. Maradiya, V. S. Patel, *Int. J. Polym. Mater.* (in press)
17. H. R. Maradiya, V. S. Patel, *Int. J. Polym. Mater.* **48** (2000) 99
18. H. R. Maradiya, V. S. Patel, *Indian J. Chem. Tech.* **8** (2001) 140
19. H. R. Maradiya, V. S. Patel, *J. Serb. Chem. Soc.* (in press)
20. H. R. Maradiya, V. S. Patel, *Adv. Color Sci. Technol.* (in press)
21. E. S. Norman, US 2444536 [*C.A.* **42** (1948) 7340 c]
22. H. R. Maradiya, V. S. Patel, *Bull. Chem. Technol. Macedonia* (in press)
23. P. F. Gordon, P. Gregory, *Organic Chemistry in Colour*, Springer-Verlag, Heidelberg 1983, p. 134
24. K.–W. Schulte, A. Schweig, *Theory Chim. Acta* **33** (1974) 19
25. J. Griffiths, *Colour and Constitution of Organic Molecules*, Academic Press, London 1985, p. 186.