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Dyes Derived from Aminothiophenes. Part 6: Application of Some Nitro-substituted Thiophene-based Azo Disperse Dyes to Hydrophobic Fibres

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ABSTRACT

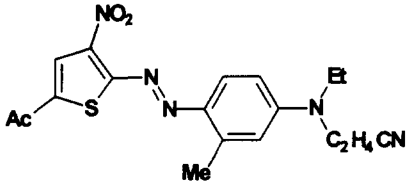
Monoazo disperse dyes prepared from 2- and 3-aminonitrothiophenes were applied to three hydrophobic fibre types, furnishing reddish-blue to green and yellow to orange dyeings, respectively. Colour yields varied greatly: the dyes exhibited marked differences in build-up on polyester as a result of only small alterations in molecular structure, while the strengths of the nylon and diacetate dyeings were generally unsatisfactory. On the whole, levels of fastness on polyester were good; trends in wet and sublimation fastness were identified. The light-fastness ratings of the thienyl-2-azo dyes on polyester and diacetate were high and superior to those of the thienyl-3-azo analogues; however, on nylon, both dye types had poor photostability. © 1997 Elsevier Science Ltd

Keywords: nitro-substituted aminothiophenes, heterocyclic azo dyes, dyeing, disperse dyes, fastness properties, photostability.

INTRODUCTION

Since the first report on the potential of nitrothienyl-2-azo dyes for the coloration of cellulose acetate appeared almost 40 years ago [1], monoazo dyes derived from aminonitrothiophenes have been commercialised as alternatives to blue anthraquinones for the coloration of polyester [2,3]. Despite, or perhaps because of, their success, few details concerning their application to, and fastness properties on, hydrophobic fibres have been published, apart from that disclosed in the patent literature. No information has appeared on their nitrothienyl-3-azo counterparts.

The synthesis [4] and spectroscopic properties [5] of some nitro-substituted thienyl-2-, thiazolyl-2- and thienyl-3-azo dyes have been reported; this paper describes their application to polyester, nylon and diacetate, as well as the colour and fastness properties of the resultant dyeings.



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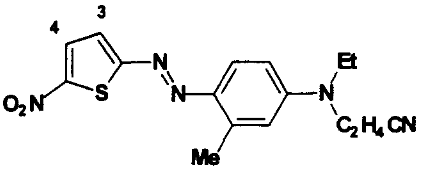
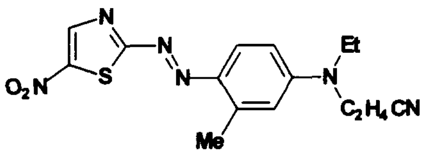


2

3 = CO_2Me, CO_2Et, CO_2Bu, NO_2
4 = H, Me



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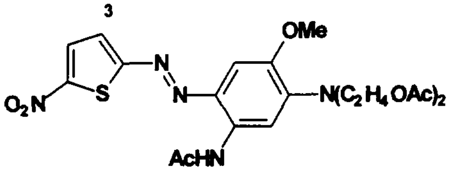

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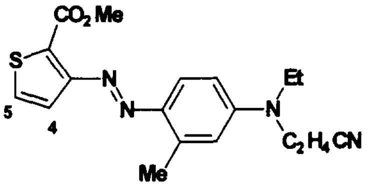
3 = CO_2Me, NO_2



5

4 = H, Me, NO_2
5 = H, NO_2

RESULTS AND DISCUSSION

Dye application

No problems were encountered in preparing satisfactory dispersions when the dyes were manually ground and treated with an ultrasonic bath before milling. Levels of exhaustion ranged from complete to very poor upon application of the dispersions to the three substrates and were reflected in the wide variation of colour yields obtained.

Colour properties of the dyeings

The strengths of each dyeing, expressed as *fk*, a visually-weighted function of *K*/*S*, are listed in Table 1, along with the shade on polyester. The hues of the dyeings were consistent with the spectra of the dyes in solution [5]. Dyeings from **1**–**4** were reddish-blue to green, **2** (3-CO_2Me-4-Me) being the most hypsochromic of the thienyl-2-azo derivatives and of similar colour to the thiazole-based dye **3**. The dyes **4**, which were found to be the most bathochromic of the series [5], furnished the greenest dyeings. As anticipated from their spectroscopic properties, the thienyl-3-azo dyes **5** were considerably more hypsochromic, conferring yellow to orange shades on the substrates.

For each substrate, the depths of shade of the dyeings differed considerably at a dye application level of 0.5% o.m.f.; in the case of each dye, colour yields were highest with polyester. Although it is recognised that crystal structure, differences in dispersion quality and dye–dispersant interaction may affect depth of shade [6], the influence of molecular structure on build-up can be discerned.

Polyester

The thiazole-based dye **3** built up well, yet three thienyl-2-azo analogues, **2** (3-CO_2Me, 3-CO_2Me–4-Me and 3-NO_2), failed to build up to deep shades on

TABLE 1
Colorimetric and Fastness Properties of the Dyes **1**–**5**

Dye	*Shade on polyester*	*fk*			*WF*[c]		*SF* (*180°C*)[d]		*SF* (*210°C*)[d]	
		P[b]	*N*[a]	*D*[a]	*D*	*N*	*C*	*P*	*C*	*P*
1	Blue	42.4/189/212	32.6	32.7	3–4	4	5	4–5	4–5	3–4
2 (3-CO_2Me)	Blue	42.1/66.9/67.8	9.8	16.6	5	5	5	5	5	4–5
2 (3-CO_2Me-4-Me)	Reddish-blue	38.1/88.5/94.5	13.6	33.9	4–5	4–5	5	4–5	4–5	4
2 (3-CO_2Et)	Navy blue	47.2/205/212	36.7	27.3	4–5	4	5	4–5	4–5	3
2 (3-CO_2Bu^n)	Navy blue	36.8/254/280	32.2	13.5	4–5	4–5	4–5	4	4	2–3
2 (3-NO_2)	Sky blue	40.6/92.8/97.8	9.4	17.5	4–5	5	5	5	5	4
3	Dark reddish blue	45.1/261/269	40.6	91.7	3–4	4	4–5	4	3–4	1–2
4 (3-CO_2Me)	Turquoise	22.0/177/244	14.5	9.3	4–5	4–5	5	5	4–5	4–5
4 (3-NO_2)	Green	15.0/132/203	13.3	12.0	4–5	4–5	5	5	5	5
5 (4-Me-5-NO_2)	Dark yellow	16.5/128/189	52.7	52.7	4–5	5	4–5	4–5	4	3
5 (5-NO_2)	Orange	19.9/113/127	16.4	23.0	4–5	4–5	4–5	4–5	4	3
5 (4-NO_2)	Yellow–orange	—/103/—	—	—	4	4–5	4–5	4–5	4	3

P = polyester; N = nylon; D = diacetate; C = cotton.

[a] 0.5% o.m.f.

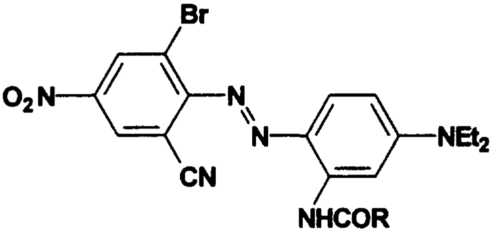
[b] 0.05%/0.5%/1.0% o.m.f.

[c] Wash fastness (ISO C06 B2S) of polyester (0.5% o.m.f.); all samples had ratings of 5 for colour change and staining of polyester, cotton and acrylic.

[d] Sublimation fastness (ISO P01) of polyester (0.5% o.m.f.).

polyester: partitioning between dyebath and fibre could be responsible as opposed to kinetic effects. Rather than there being a kinetic control to the extent of dyeing arising from the rate of diffusion into the fibre, build-up appears to be restricted by a thermodynamic factor in these cases: the dyes had the lowest solubilities of the derivatives in organic solvents and, presumably, had low solubilities in polyester so that saturation was reached at application levels of 0.5–1.0% o.m.f., restricting depths of dyeing. Evidence of there being a thermodynamic control in these cases comes from a comparison of the dyeings of **2** (3-CO_2Me and 3-NO_2) with those of **4** (3-CO_2Me and 3-NO_2). The dyes of the latter type, which were much more soluble in organic solvents than the former derivatives, built up to much deeper depths, which suggests that the higher solubility of these dyes allows heavier depths to be achieved. Had diffusion been the determining factor, the converse would have been expected, since the molecular structures of the dyes **4** are bulkier than those of their toluidine-derived analogues. The differences in shade are probably too large to be caused by the increased intensities of the dyes **4** alone.

The influence of solubility also appears to be manifest in the cases of **2** (3-CO_2Et) and **2** (3-CO_2Bu). These dyes were much more soluble than the corresponding methyl ester and built up much more satisfactorily, giving navy blue shades at 0.5 and 1.0% o.m.f. Any lowering of the rate of diffusion was more than offset by an increase in substantivity owing to the higher solubility of the dyes in polyester. The difference in dyeing behaviour between the methyl and ethyl esters is a striking example of how a relatively small structural change (the insertion of a methylene group) can radically alter the substantivity of a colorant. The effect of small variations has been discussed previously [7,8], but only in connection with modifications to the coupling component; for example, addition of a methylene fragment to the acetyl group of **6a** produces a dye, **6b**, of improved build-up properties.



6a, R = Me
6b, R = Et

Nylon and diacetate

Application of the dyes to nylon and diacetate at 0.5% o.m.f. furnished bluer dyeings of lower depth than the corresponding polyester samples (see Table 1). The effects of molecular size and low solubility were exaggerated with these substrates. The bulk of the coupler residue in the dyes **4** limited colour yields on nylon and diacetate at 0.5% o.m.f. to lower levels than those attained at 0.05% o.m.f. on polyester. The smaller size of **3** relative to the dyes **2** could account for the greater colour strengths of the dyeings from the former colorant; the low solubilities of **2** (3-CO_2Me and 3-NO_2) may explain the very pale nature of the dyeings from these dyes. The addition of a methylene fragment to the former derivative, yielding **2** (3-CO_2Et or 3-CO_2Me-4-Me), slightly increased organic solubility, which could be the reason for the modest improvements in the depths of shade obtained from these dyes (see Table 1). However, whereas the increased solubility of the butyl ester analogue overcame the possible reduction in diffusion rate in polyester (so that build-up improved), on nylon and diacetate, the increased molecular size appears more important and the uptake of dye was restricted, the depth being of the same order as that of the methyl ester.

Fastness properties of the dyeings

The fastness of the polyester samples was generally the most satisfactory; as well as substrate type, depth of shade and dye structure were observed to influence fastness.

Wash fastness

The wash fastness ratings of the polyester dyeings (0.5% o.m.f.) were generally good (see Table 1). Nylon and diacetate were consistently the most stained components of the multifibre, presumably because of the dyes' substantivity for these materials and the fibres' accessibility at the test temperature (50°C). Ratings of 5 were obtained for the staining of the other components. In the case of polyester and acrylic, this can be ascribed to low rates of diffusion into the materials at the test temperature, whereas with cotton, the absence of staining can be explained by the poor substantivity of the dyes for this hydrophilic material.

The concentration of dye in the fibre appeared to be the most influential factor in the fastness of the dyeings. For example, the superior fastness ratings of the samples dyed with **2** (3-CO_2Me) and **2** (3-NO_2) are a result of relatively low depths of shade, whilst the samples coloured with **2** (3-CO_2Et) and **2** (3-CO_2Bu) were of greater depth and, predictably, fastness was slightly poorer.

The dye **3** had inferior fastness relative to that shown by the **2** (3-CO_2R) series (see Table 1), presumably because of one or more of the following factors: smaller molecular size, higher substantivity for nylon and especially diacetate, as well as a deep sample shade. In the case of **1**, which also showed good substantivity for these fabrics and whose depth of shade on polyester at

0.5% o.m.f. was similar to that of the thiazole dye, fastness ratings were the same as those of **3**, suggesting that these two factors hold more import than that concerning the slight difference in molecular structure.

Like their thienyl-2-azo counterparts, the thienyl-3-azo dyes had good wash fastness on polyester.

The wash fastness ratings of the nylon and diacetate dyeings were primarily influenced by depth of shade. These substrates would be expected to have poorer wet fastness than polyester samples of the same depth, but generally, because of the relatively pale colours of the nylon and diacetate dyeings, these samples had ratings for the staining of nylon and diacetate equal to, or better than, those for the corresponding polyester samples; for example, the dyes **1** and **2** on nylon furnished identical staining ratings to those exhibited by the polyester dyeings. The relatively pale depths of the diacetate dyeings meant that staining was low and, unlike the polyester samples, which did not lose colour, colour change ratings of 3 to 4–5 were shown.

Perspiration fastness

The dyeings of five derivatives were selected for alkaline perspiration fastness testing: **2** (3-CO_2Me), **2** (3-NO_2), **3**, **4** (3-CO_2Me), **5** (5-NO_2). The dyeings from the thienylazo colorants on each substrate had excellent fastness, having colour change and staining ratings of 5. This finding can be attributed in the case of the polyester samples to the hydrophobic, crystalline nature of the material inhibiting diffusion at the test temperature; for the polyamide and acetate samples, low depths of shade restricted the occurrence of any staining. While the polyester coloured with **3** had the same excellent fastness as the samples from the thiophene-derived analogues, the corresponding nylon and acetate dyeings did cause staining, unlike the other samples: the diacetate dyeing stained acetate and nylon (ratings 3–4 and 4, respectively) as did the nylon sample (ratings 4 for both). This situation may stem from the greater depths of shade achieved on these substrates by **3** compared to the other dyes.

Light fastness

The thienylazo dyes exhibited light fastness which varied widely according to molecular structure, substrate type and depth of shade (see Table 2). The thienyl-2-azo dyes had better fastness on polyester and diacetate than the thienyl-3-azo colorants, although this was not the case on nylon.

The nitrothienyl-2-azo derivatives had better photostability on polyester and diacetate than analogous dyes bereft of nitro groups; for example, **2** (3-CO_2Me) had superior fastness to dyes with less strongly electron-withdrawing groups (see Table 3). The effect parallels that found with aminoazobenzenes, in which an increase in electron-withdrawing power of the diazo component serves to reduce electron density on the amino nitrogen atom, with photofading occurring by attack at this site by singlet oxygen [9,10]. However, the 5-nitro derivative, like the other nitro-substituted dyes, had low light fastness on nylon. The poor photostability may stem from photoreduction of the nitro substituent being promoted by the amino end groups of the polyamide chains [11].

The substituent in the 3-position of the thienylazo dyes had an indirect influence on light fastness by affecting depth of shade. While there was little difference between **2** (3-CO_2Me) and **2** (3-NO_2), the ethyl and butyl ester analogues had improved ratings on polyester at 0.5% o.m.f. (see Table 2), which can be attributed to their increased concentration in the fibre. The

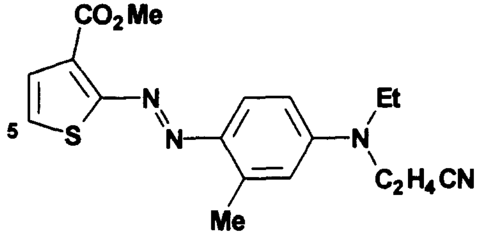
TABLE 2

Light Fastness Ratings of the Nitrothienyl Dyes on Hydrophobic Substrates

Dye	*Polyester* 0.05%	*Polyester* 0.5%	*Polyester* 1.0%	*Nylon* 0.5%	*Diacetate* 0.5%
1	5–6	5–6	6	1–2	5
2 (3-CO_2Me)	5–6	5–6	5–6	1–2	5
2(3-CO_2Me-4-Me)	4–5	5	5	1–2	4–5
2 (3-CO_2Et)	6	6–7	6–7	2	5
2 (3-CO_2Bu)	6	6–7	7	1–2	5
2 (3-NO_2)	5–6	5–6	5–6	1	5
3	6	6–7	7	2	5
4 (3-CO_2Me)	5	5	5–6	1	4
4 (3-NO_2)	5	5	5–6	1	4
5 (4-Me-5-NO_2)	4	4	4–5	3	3
5 (5-NO_2)	3–4	3–4	4	2	2
5 (4-NO_2)	—	4	—	—	—

TABLE 3

Effect of Substitution in the 5-Position on the Light Fastness Ratings of Some Thienyl-2-azo Dyes **7** on Polyester, Nylon and Diacetate at 0.5% o.m.f.



7

Dye	*Polyester*	*Nylon*	*Diacetate*	*Ref.*
7 (5-Me)	2	2	1–2	[12]
7 (5-Ph)	3–4	3–4	3	[12]
7 (5-Ac)	5	4	4	[12]
7 (5-NO_2)	5–6	1–2	5	

substantivities of the dyes **2** for diacetate were such that they conferred similar depths on the sample which had the same rating (5), implying that the intrinsic photostabilities of the dyes in the series on this substrate are similar.

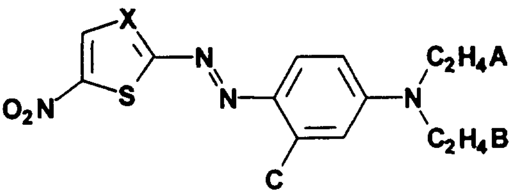
Data published by Peters and Gbadamosi [13] include two examples of 5-nitrothienyl-2-azo derivatives being more fast to light than a thiazolylazo analogue on polyester (see Table 4). However, **3** had a higher rating than **2** (3-CO_2Me) or **2** (3-NO_2) on polyester and nylon, attributable to the poorer substantivity (and thus lower depth of shade) of the thiophene-based dyes. The dyeing of the dinitro dye of Peters and Gbadamosi on polyester at 0.5% o.m.f. was recorded as being deep blue [13], which suggests that the improved fastness rating relative to **2** (3-NO_2) may, in part, be because of a higher concentration of dye on the fibre.

Dyeings of **2** (3-CO_2Et and 3-CO_2Bu), which were of similar depth to **3** at 0.5% o.m.f. on polyester, had ratings of 6–7, indicating that these dyes have photostabilities on the substrate close to that of the thiazole dye. The similarity was also demonstrated on diacetate, all the relevant dyes having a rating of 5 at 0.5% o.m.f. (and, as mentioned above, all having poor ratings on nylon).

It is evident that the presence of a nitro group *ortho* to the azo link does not appear to be deleterious to photostability on polyester for both Peters and Gbadamosi's dyes and those prepared in this study (see Table 4), unlike 4-aminoazobenzene systems [14–16]. An improvement in light fastness on polyester was observed on replacing the methoxycarbonyl group in **7** (5-Ac), which had a rating of 5 at 0.5% o.m.f. [12], with a nitro group to give **1**, which had a rating of 5–6. A slight increase in fastness on diacetate occurred (from 4 to 5), whereas the rating dropped from 4 to 1–2 on nylon, in line with previous observations on the deleterious effects of nitro groups on the stability of nylon dyeings.

TABLE 4

Light Fastness Ratings of Some 5-Nitrohetarylazo Dyes on Polyester at 0.5% o.m.f.



X	*A = CN, B = H, C = Me*	*A = CN, B = OH, C = H13*
N	6–7	4–5
C-CO_2Me	5–6	5–6
C-NO_2	5–6	6–7

The thienyl-3-azo dyes had poorer photostability on polyester and diacetate than their thienyl-2-azo isomers, although fastness on nylon was slightly better (see Table 2). Shifting the nitro group of **5** (5-NO_2) to the 4-position brought about a small improvement on polyester (from 3–4 to 4 at 0.5% o.m.f.); again, no deleterious effect on polyester was apparent with the introduction of a nitro group *ortho* to the azo link, as was noted with **1** and **2** (3-NO_2), in contrast to aminoazobenzene derivatives.

Sublimation fastness

Polyester samples from each dye at 0.5% o.m.f. had good to excellent fastness to heat (see Table 1). As was noted for an analogous series of thienyl-2-azo dyes [12], staining of polyester was found to be greater than that of cotton at a particular temperature. The nitro-substituted dyes had better fastness than related dyes without such groups, presumably because of the increased polarity of the former; for example, while **7** (5-Ac) had ratings of 4 and 3–4 for the staining of cotton and polyester, respectively, at 180°C and ratings of 3–4 and 2–3 for the same materials at 210°C [12], **1** had superior ratings, the corresponding values being one point higher (see Table 1).

The poorer fastness of **3** relative to **2** (3-CO_2Me) can be ascribed to the greater depth of the former dyeing at 0.5% o.m.f. and to the increased bulk of the latter colorant. Samples dyed with the ethyl and butyl ester derivatives had deeper shades than the methyl ester analogue, and consequently the staining was slightly greater, albeit still not as much as that of the dyeing from the thiazole dye.

Differences in substituent orientation between isomeric thienyl-2-azo dyes have been found not to affect heat fastness significantly [12]; results within the nitrothienylazo dye series are in accord with this finding. Exchanging the positions of the azo link and the alkoxycarbonyl group of **2** (3-CO_2Me) to give **5** (5-NO_2) slightly lowered the heat fastness of the resultant dyeing (see Table 1), although this may be partly because of the paler shade of the dyeing with the former colorant. Shifting the nitro group of the latter to the 4-position, or introduction of a methyl group into this position, made no apparent difference to the ratings.

As expected for such polar and relatively bulky molecules, the heat fastness ratings of the dyes **4** were excellent.

EXPERIMENTAL

The synthesis of the dyes **1**–**5** has been described previously [4]. Details of the milling, application and colour measurement procedures have been related elsewhere [12]. Wash (ISO 105 C06), alkaline perspiration (ISO 105 E04), light (ISO 105 B02) and sublimation (ISO 105 P01) fastness tests [17] were used in a manner which has already been reported [12].

CONCLUSIONS

Application of some nitrothienylazo disperse dyes to hydrophobic fabrics met with mixed success. Build-up on nylon and diacetate was generally poor; deep shades could be achieved on polyester although, in some instances, depth was restricted by the low solubility of the dye in the fibre.

The polyester dyeings had good overall fastness, variations in which could be related to dye structure and depth of shade. Nitro substitution was found to raise light and sublimation fastness on polyester; substitution *ortho* to the azo group was not found to be deleterious to photostability, contrary to observations with aminoazobenzene derivatives. However, as previously noted with carbocyclic azo dyes, nitro substitution significantly reduced light fastness on nylon.

While the thienyl-3-azo dyes had reasonable performance, the thienyl-2-azo colorants showed more promise. Compared to their red and violet counterparts, which lack nitro substitution, blue nitrothienyl-2-azo dyes are superior in terms of preparation, absorption intensity and fastness; while the former colorants were found to be generally unsatisfactory from a commercial perspective, it is unsurprising in view of the results of this study that dyestuffs containing blue thiophene-based monoazo dyes have been marketed, such as Zeneca's Dispersol Blue C-RN [18] and Dispersol Navy C-MS [19] products.

ACKNOWLEDGEMENT

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