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Review

Developments in azo disperse dyes derived from heterocyclic diazo components

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Dedicated to Dr. G. Hallas on the occasion of his 65th birthday by a grateful ex-student

Abstract

Advances over the last decade concerning the synthesis, properties and application of azo disperse dyes prepared from diazo components containing aromatic heterocycles are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Heterocycles are an inescapable and integral feature of numerous diverse branches of chemistry [1]. Organic dye chemistry is no exception: some colorants based on heterocyclic systems such as mauveine [2] are as old as the field itself, or even antedate it in cases like indigo [3], while today heterocycles are all-pervasive, whether they appear in the guise of chromophores, for example in phthalocyanine pigments, or functional components, such as the fibre-reactive chlorotriazine rings of certain reactive dyes [4].

Heterocycles have been put to much use in disperse dye chemistry, which it has been claimed was the first area to foster the industrial exploitation of heteroaromatic amines [5]. Numerous heterocyclic dyes are now marketed to the extent that no manufacturer can profess to produce a full range of disperse dyestuffs without handling colorants based on heteroaromatic diazo or coupling components. In addition, just as new applications have emerged for 'conventional' textile-orientated heterocyclic dyes, such as the utilisation in photodynamic therapy and lasers of thiazines and oxazines [6,7], non-textile uses of hetarylazo disperse dye types have increasingly been explored, for example, in reprographic technology, functional dye applications and non-linear optical systems [8,9].

During the last 10 years, the level of interest as indicated by the patent literature has grown in the non-textile area while commercial research activity on the textile side has seen a shift in emphasis. As anticipated [10], work by established companies has focused less heavily on novel structures than in previous decades owing to legislative requirements for product notification and testing, and also presumably the relative maturity of the field; achieving improvements in the processing, formulation and physicochemical aspects of existing dyestuffs has proved more attractive to manufacturers [11]. Despite around half a century elapsing since the commercialisation of hetarylazo dyes, the structures of many industrially produced colorants of this kind remain undisclosed and, prior to the last 10 years, relatively little information was available regarding their characteristics.

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However, since then, there has been a considerable growth in the volume of data reported outside of the patent literature. Excellent reviews concerning heterocyclic azo dyes exist but were published some time ago [5,12,13]. It is the intention of this paper to review material which has appeared since then and to discuss developments over the past decade in terms of dye preparation, properties and application.

2. General types of hetarylazo disperse dyes

Most hetarylazo 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 two nitrogen heteroatoms and be fused to another aromatic ring. Systems of this kind are therefore considered first in this review, namely

- (benzo)thiazoles (Section 2.1.1),
- (benz)isothiazoles (Section 2.1.2),
- thiadiazoles (Section 2.1.3), and
- thiophenes (Section 2.1.4),

which 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. A good general review of the synthesis and uses of certain of these diazo component types for the production of blue disperse dyes, as well as the properties of the dyes themselves, appeared several years ago [14]. Not long afterwards, a useful systematic investigation was reported in which derivatives of each of the diazo component categories were prepared using the same coupler, enabling comparisons to be made in terms of absorption characteristics as well as shade and light fastness on polyester [15]; a study of this sort is of particular value as, owing to variations in application and measurement methods, comparisons between sets of data for dye series from different sources are often difficult. (Unfortunately, in certain cases, this state of affairs is compounded through neglecting to include adequate details, which for example may entail reporting spectral characteristics of dye solutions without reference to a solvent, and giving wash fastness ratings without any indication as to the test utilised or even whether figures refer to colour change or staining!)

Commercial success of a more limited nature has also been achieved with heterocycles that contain only nitrogen heteroatoms; dyes of this type, which include those derived from imidazoles and triazoles, are the next class to be covered (Section 2.1.5). The final grouping to be contemplated is made up of diazo components of relatively minor technical importance which do not fall into the major classes mentioned above; included in this classification are relatively unexplored aminoheterocycles as well as anilines bearing aromatic heterocyclic substituents (Section 2.1.6).

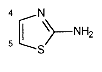
Finally, the increasingly important area of non-textile usage of hetarylazo disperse dyes is discussed from the perspective of application type, rather than structural class, for convenience (Section 2.2).

2.1. Hetarylazo dyes for textile applications

2.1.1. (Benzo)thiazolylazo dyes

Derivatives of 2-aminothiazole (**1**) and 2-aminobenzothiazole (**2**) have a long history of use as heterocyclic diazo components for disperse dyes [5]. The latter class of heterocyclic amine was the first type to be exploited and has gone on to become a source of technically important red dyestuffs for polyester, such as CI Disperse Red 177 (**3**; X = OAc, Y = H), while blue dischargeable monoazo derivatives based on 2-amino-5-nitrothiazole caught the attention of dye chemists in the 1950s, with colorants such as CI Disperse Blue 339 (**4**; X = Y = H) [16] having been produced commercially since then [5].

Given the well-established nature of (benzo)thiazole-based chromophores, it is unsurprising that the contents of recent patents have generally been confined to covering innovations in synthesis, physical form, formulation and application rather than structure. Japanese manufacturers have been active in this respect, for example, describing processes to alter the crystal forms of 5,6-(6,7-)dichloro-[17–20], 4,6-dibromo-[21] and 6-nitro-[22–24],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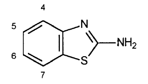
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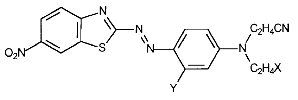
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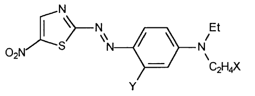
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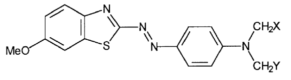
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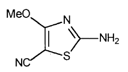
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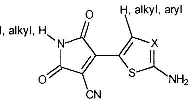
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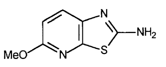
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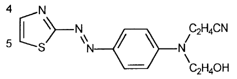
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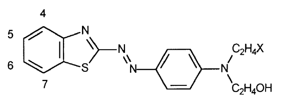
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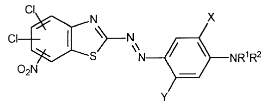
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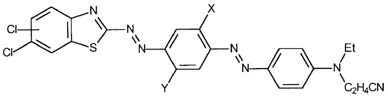
6-NO$_2$-4,5-Cl ; 6-NO$_2$-4,7-Cl ; 6-NO$_2$-5,7-Cl ;
5-NO$_2$-4,6-Cl ; 4-NO$_2$-5,6-Cl ; 4-NO$_2$-6,7-Cl

R^1, R^2 = Et, C_2H_4CN, C_2H_4OH
X = H, OMe ; Y = H, NHAc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X = H, Me, OMe, Cl
Y = H or X

benzothiazolylazo dyes as well as the preparation of mixtures with improved properties from the first type of dye [25,26] or 6-nitrobenzothiazolylazo derivatives and aminoazobenzenes [27,28]. An unusual method of crystal modification has been outlined for carbonylthiazolylazo derivatives which are converted to acetals and then hydrolysed back to the original material but in a different crystal form, for example 5-formyl dyes **5** (X = N) (Fig. 1) [29].

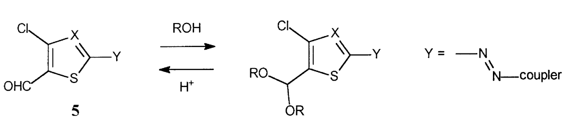


Fig. 1. Crystal modification via acetal formation.

Subjects of patents that concern synthetic methods include the purification of benzothiazolylazo dyes by treatment with acetic anhydride [30], and an alternative route to the process of conventional diazotisation and coupling in the preparation of 4,6-dinitrobenzothiazolylazo dyes, which is prone to give low yields; instead, oxidative coupling of the hydrazine analogue of the diazo component is performed [31].

While it has long been suspected that equilibria are involved in the diazotisation of aminothiazoles, it is only within the last 10 years or so that quantitative confirmation has become available [32]. Examination of diazotisation mixtures of 2-aminothiazole in nitrosylsulphuric acid by UV/visible spectroscopy has shown that the position of the diazotisation equilibrium is strongly dependent on the concentration of the aqueous sulphuric acid medium as well as that of the starting material [33]; kinetic data were consistent with a mechanism in which the aminothiazole protonated at the ring nitrogen atom (as opposed to the amino group) is nitrosated. However, investigation of the reaction at industrial concentrations using NMR spectroscopy revealed that not only the reaction rate, but also the selectivity of the reaction, is sensitive towards the acidity of the medium, whereby the maximum yield of diazotised species is determined by the competitive formation of unidentified by-products [32]. Similar analysis of the diazotisation of 2-amino-4-chloro-5-formylthiazole (**5**; X = N, Y = NH_2) in nitrosylsulphuric acid found that there was no acidity at which both diazotisation proceeded satisfactorily and the diazonium ion was sufficiently stable [32]; it was concluded that the production of dye from this diazo component must be conducted by addition of the amine in nitrosylsulphuric acid to an aqueous coupling component solution with controlled mixing so that the dilution upon addition leads to rapid diazotisation, and that coupling of the nascent diazonium ion takes place before significant decomposition can occur owing to the reduced acidity of the environment.

The diazotisation of 2-aminobenzothiazoles has also been the subject of academic enquiry: an attempt to develop a satisfactory replacement for phosphoric acid as a medium for diazotisation, focusing on the utility of haloacetic acids, found that a mixture of dichloroacetic and acetic acids could be satisfactorily used in the cases of 2-aminobenzothiazole and 2-amino-6-nitrobenzothiazole, for example in the preparation of **3** (X = OAc, Y = H) and CI Disperse Violet 52 (**3**; X = H, Y = Me), although application of this approach to the synthesis of CI Disperse Blue 106 (**4**; X = OH, Y = Me) from 2-amino-5-nitrothiazole was unsuccessful [34]. In view of the toxicity of the chlorinated acid and the lower yields obtained, the use of phosphoric acid was examined in conjunction with coagulating agents to remove the phosphate ions from effluent after collection of the presscake. Employing **3** (X = OAc, Y = H) as a model, the amount of coagulant and filtrate pH were optimised so that over 99.99% removal of phosphate could be achieved with either alum or iron (III) chloride [35].

In a study concerning the diazotisation of 2-amino-6-methoxybenzothiazole with aqueous sodium nitrite and sulphuric acid, it was found that dye **6** (X = Y = H) of very similar purity and yield to that furnished by a conventional low temperature procedure (2 h at 5°C) could be obtained by conducting the diazotisation at a higher temperature (20–25°C) over a much shorter reaction time (14–15 min) [36].

The diazotisation of 2,6-diaminobenzothiazole has been explored in connection with the synthesis of reactive disperse dyes [37]; the diazo component was prepared by reduction of 2-amino-6-nitrobenzothiazole and, contrary to previous literature reports, could be diazotised at both the 2- and 6-positions whereby a Sandmeyer-type reaction took place at the 2-position (Fig. 2). The diazonium function at the 6-position was then coupled to a naphthol, furnishing a colorant with a reactive chloro function.

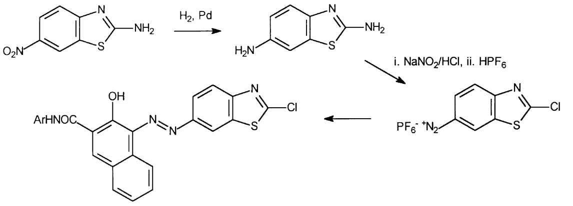


Fig. 2. Synthesis of reactive disperse dyes from 2,6-diamino-

Established diazo components, such as 2-amino-6-nitrobenzothiazole [38], have also been the focus of efforts to develop alternative synthetic routes to them, while a few novel diazo components intended for the preparation of textile dyes have been the subject of patents, for example, 5-acceptor-4-methoxy- and 5-maleimido-substituted 2-aminothiazoles, such as **7** [39] and **8** (X = N) [40], respectively, as well as 6-alkoxy-2-aminopyridino[3,2-*d*]thiazoles like **9** [41]. Numerous other novel substitution patterns in the diazo component residue have been described during the course of investigations into the properties of (benzo)thiazolylazo dyes which are discussed in the remainder of this section.

Just as information concerning the synthesis of (benzo)thiazole-based azo disperse dyes has increasingly become available, the volume of material pertaining to the properties and application of colorants of this kind has grown markedly. Whereas only fragmentary spectroscopic and fastness data have typically appeared in the past, numerous systematic studies of substituent effects in (benzo)thiazolylazo derivatives have now been published.

For example, a series of thiazolyl-2-azo systems **10** and mono- or di-substituted benzothiazolyl-2-azo derivatives **11** (X = CN) bearing a variety of functions, such as halogen, trifluoromethyl, cyano, methylsulphonyl and nitro groups in the 4-, 5- and 6-positions, has been prepared, examined spectroscopically and applied to polyester [15]. As expected, the mono-substituted benzothiazole dyes were more bathochromic ($\Delta\lambda_{max}$ 81–102 nm) than their carbocyclic analogues; this differential was reduced in the case of di-substitution with electron-acceptors as a consequence of reduced additivity compared to the azobenzene counterparts. Substituent orientation in the benzothiazolyl structures was observed to be less influential on spectroscopic properties than in the corresponding carbocyclic derivatives. The light fastness of the parent benzothiazole dye on polyester (rating 4 at 0.5% o.m.f.) was not significantly altered by the introduction of substituents except in the case of 4- and 6-nitro groups (fastness 5–6 and 5, respectively). Other investigations have tended to focus on dye series derived from a single or limited number of

Table 1
Some diazo components used in investigations into (benzo)thiazolylazo dyes

Diazo component	Substitution pattern	Reference
1	4-methyl	[42,43]
1	4-methyl/4-phenyl	[44]
1	4-methyl-5-acetyl	[45]
1	4-methyl-5-ethoxycarbonyl	[44]
1	4-phenyl-5-methyl	[44]
2	4-methoxy	[46,47]
2	4-methyl	[48]
2	4-nitro	[49]
2	5-nitro	[50,51]
2	6-bromo	[52,53]
2	6-dialkylamino	[54]
2	4-diakylamino-6-thiocyanato	[54]

diazo components with substitution patterns of relative technical unimportance (Table 1).

However, while red dyes obtained from mixtures of 5,6- and 6,7-dichloro-2-aminobenzothiazoles have been produced commercially for the coloration of polyester for many years and continue to attract industrial interest [20,25,55], no systematic investigation of these kinds of colorant had been reported until Peters and co-workers published a comprehensive series of papers describing the synthesis and properties of dyes from these and related diazo components earlier this decade. In the first paper, two well-established procedures were applied to the synthesis of the isomeric diazo component mixtures (Fig. 3); both furnished each isomer in roughly equal amounts [56]. The 1:1 mixtures were coupled to a variety of aniline and naphthylamine derivatives to produce bright orange-red to deep violet dyes of generally good light fastness on polyester (4–6 at 0.5% o.m.f.). Modifications to coupler substitution patterns led to the anticipated changes in absorption maximum and intensity; column chromatographic separation of the isomers, either before or after dye synthesis, revealed that orientation of the chloro groups had little influence on colour, either in solution or on polyester [57]. In addition, very little difference in build-up and light fastness was exhibited by individual isomers of a particular dye, or a 1:1 mixture of the two, so it was concluded that there was no advantage to be gained by separation of the isomers. Extension of the work to cover the remaining possible isomers (4,5-, 4,6-, 4,7- and 5,7-dichloro substitution) showed that their spectroscopic and application properties were very similar to the corresponding 5,6-(6,7-) dichloro dyes and demonstrated that the industrial manufacture of the latter colorants in a mixture is solely for reasons of cost and availability of intermediates [58].

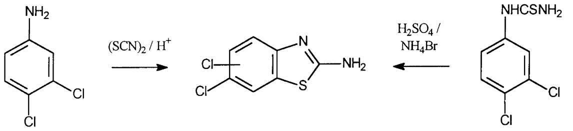


Fig. 3. Two routes to 5,6-(6,7-)dichloro-2-aminobenzothiazole mixtures.

In similar investigations, mono-nitro isomers of the commercially important 6-nitrobenzothiazolylazo class [59,60], in addition to the technically interesting 4,6-dinitro type and its 5,6- and 5,7-isomers [60], were prepared and then examined in solution and on polyester. Reasonable yields of dye were obtained upon coupling the diazotised amines to substituted anilines apart from in the case of 2-amino-4,6-dinitrobenzothiazole. The order of bathochromism was found to be 4,6 > 5,6 > 5,7 > 6 > 4 > 7 > 5 as nitro groups in

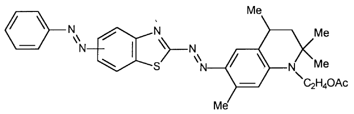
Table 2
Spectroscopic properties (λ_{max} in nm, ε_{max} in 10^{-4} dm^3 mol^{-1} cm^{-1}) and light fastness (0.5% o.m.f.) of some (di)nitro-derivatives **11** in ethanol and on polyester, respectively [60]

Dye **11**	4-NO_2	5-NO_2	6-NO_2	7-NO_2	4,6-NO_2	5,6-NO_2	5,7-NO_2
λ_{max}	522	511	527	512	560	537	531
ε_{max}	4.1	4.4	4.8	4.4	4.4	4.3	4.8
Fastness	5	5	5	5	5	6	5–6

directly conjugative positions (4- and 6-) led to greater bathochromism than those in the 5- and 7-positions (Table 2). Slightly lower than expected bathochromism in the case of the 5,6-derivatives was ascribed to steric hindrance between the adjacent nitro groups; it is notable that despite this crowding, the 5,6-dinitro-substituted diazo component was prepared by nitration of 2-amino-5-nitrobenzothiazole. Light fastness of polyester dyeings from each of the four isomers of a particular mono-nitro structure did not vary significantly, although 5,6- and 5,7-substitution tended to confer slightly higher photostability than a 4,6-pattern (Table 2). It was concluded that, while it was unlikely that any advantages were held by the 5- and 7-nitro-substituted dyes over their commercially successful 6-nitro isomers, 2-amino-5,6-dinitrobenzothiazole may be a good candidate as an alternative to its 4,6-dinitro analogue, despite the slight hypsochromism conferred by the former compared to the latter, since dye is furnished in higher yield and the required intermediates for diazo component synthesis are readily available.

Dyes **12** derived from dichloronitro-2-aminobenzothiazoles have also been proposed as possible replacements [61]. As could be anticipated from the findings related to the nitrobenzothiazolylazo dyes described above, the 6-nitro derivatives were more bathochromic than the corresponding 4-nitro isomers which in turn absorbed at slightly longer wavelengths than the 5-nitro analogues. Steric influences were observed, for example, dyes **12** (6-NO_2-5,7-Cl) were hypsochromic relative to **12** (6-NO_2-4,7-Cl) owing to increased crowding in the former derivatives. Hindrance of a nitro group in the 5-position was investigated by preparation of **11** (5-NO_2-4,6,7-Cl; X = CN) and found to be less influential.

Disazo dyes, such as **13**, prepared from a commercial 5,6-(6,7-)dichloro-2-aminobenzothiazole isomer mixture as the first component have been examined spectroscopically [62]. While methyl substitution in the middle component had little impact on λ_{max}, the introduction of methoxy or chloro groups into positions X or Y produced bathochromic shifts of 12–16 nm; synergistic bathochromism was noted when both positions were filled. Benzothiazoles have also been patented as the middle components of disazo dyes, for example **14**, which is bluish-red on polyester, but no commercial structures are known [63].



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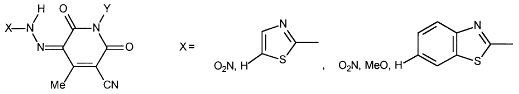

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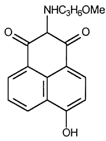

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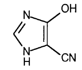

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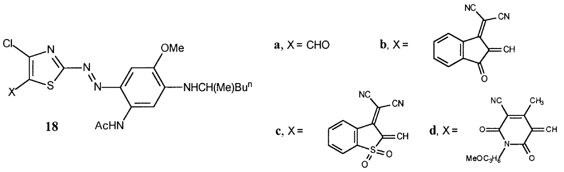

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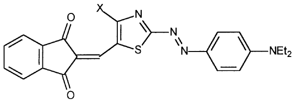

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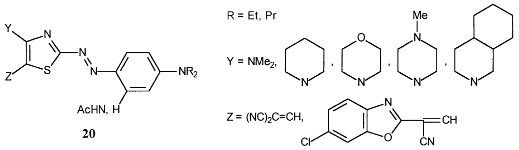

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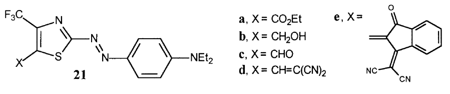

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Molecules produced by the coupling of diazotised amino(benzo)thiazoles to heterocycles, for example, diaminopyridines [64–66], continue to be researched although information concerning the synthesis and properties of (benzo)thiazolylazo dyes prepared from heterocyclic coupling components remains scarce. However, structural and spectroscopic investigations of such colorants from pyridone couplers have recently been reported in which the existence of dyes **15** (Y = Bu^n) in their hydrazone form in solid state or chloroform solution was confirmed and their solvatochromism rationalised [67]; determination of the crystal structures of the thiazolyl [68] and 5-nitrothiazolyl [69] derivatives revealed that, apart from their butyl functions, the dyes were essentially planar which was ascribed to the tautomeric form adopted and the resultant hydrogen bonding. The dissociation of the hydrazone form of the related dye **15** (X = thiazolyl-2, Y = Me) into its azo anion form in organic solvents has been studied; a lower pK value was observed than for analogous phenylazo derivatives [70].

Use of other heterocyclic couplers, *N*-3-methoxypropyl-4-hydroxy-1,8-naphthalimide (**16**) [71] and 4(5)-cyano-5(4)-hydroxyimidazole (**17**) [72], has been investigated employing typical thiazole- and benzothiazole-based diazo components in addition to substituted anilines. Whereas red dyes of good light fastness on polyester were obtained with the former coupler, those from the latter compound, while significantly more bathochromic than corresponding colorants from simple aniline couplers, proved too unstable to be of use as conventional disperse dyes.

Bathochromic structures containing thiazole rings in both the diazo and coupling components have appeared in the literature [13], although no commercial dyes of this type are known; however, their spectroscopic properties have been briefly discussed [14] and structures patented as polyester colorants [73]. Some of these derivatives are blue dyes based on the diazo component 2-amino-4-chloro-5-formylthiazole (**5**; X = N, Y = NH_2); this amine has been the subject of an account concerning both its synthesis and the impact of substituents on the colour of dyes prepared from it [14]. Such dyes have been used as intermediates for novel structures in which both the halogen and/or carbonyl functions are employed in subsequent derivatisation in order to modify absorption characteristics. In one such instance, the bathochromism of these molecules was further enhanced by condensing active methylene systems with the aldehyde function; however, the brilliant blue dyes produced in this manner suffer from the disadvantage of a lack of chemical stability [13], although the introduction of sufficiently electronegative groups and use of couplers conducive to bathochromism can push absorption into the near infra-red as well as increase intensity to very high levels (Table 3) [74,75].

Table 3
Absorption maxima and intensities of some near infra-red absorbing thiazolylazo dyes **18** in dichloromethane solution

Dye **18**	λ_{max} (nm)	ε_{max} ($dm^3\,mol^{-1}\,cm^{-1}$)
a	610	59 200
b	750	82 600
c	778	83 850
d	736	79 500

Use of a pyridone-based active methylene reagent, as in **18d**, also furnished substantial bathochromic shifts over the corresponding 5-formyl precursors ($\Delta\lambda_{max}$ 108–126 nm in dichloromethane), although the weaker electron-accepting strength of this residue compared to those used in dyes **18b** and **18c** was reflected in a lower degree of bathochromism (Table 3) [76]. Condensation of the pyridone ring to the aldehyde function was found to be deleterious to both thermal and photochemical stability of the dyes in cellulose acetate film; however, dyes of this kind have been patented as colorants for thermal transfer printing (Section 2.2.1). PPPMO calculations have been used to explore the absorption characteristics of some related derivatives such as **19** (X = Cl); λ_{max} values were predicted with reasonable accuracy in most cases [77].

An interesting recent development involves further derivatisation of this type of dye through nucleophilic substitution of the 4-chloro group with secondary aliphatic amines to give monoazo dyes **20** which are black [78]. Their colour is remarkable in view of the small molecular size of the dyes: other approaches require species of more bulk to generate multiple visible absorption bands, either through conjugation of two or more azo links, metal complexation or the non-conjugative linkage of separate chromophores. Not only does the compact nature of **20** yield potential advantages in both textile and non-textile applications, but complications associated with the use of mixtures of dyes to create blacks such as compatibility, reproducibility and fading "off tone" are obviated. Introduction of the amino group at the

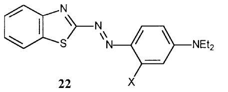
Table 4
Spectroscopic (λ_{max} and $\Delta\lambda_{\frac{1}{2}}$ in nm, ε_{max} in 10^{-4} dm^3 mol^{-1} cm^{-1}) and light fastness (2% o.m.f., polyester) data of dyes **22** [80]

Dye **22**	DMF			Light fastness
	λ_{max}	ε_{max}	$\Delta_{\frac{1}{2}}$	
a	535	5.45	96	3
b	534	6.05	96	4
c	529	3.24	97	3
d	540	4.18	104	4
e	566	4.91	94	5
f	561	2.87	114	4

4-position, made possible by the presence of the 5-acceptor function, leads to a single $\pi \rightarrow \pi^*$ visible absorption band being replaced by three such bands which together span the visible spectrum: for example, **19** (X = Cl) is blue with a single absorption band (588 nm, cyclohexane) whereas **19** (X = piperidino) is black owing to absorption maxima at 608, 493 and 424 nm in cyclohexane (ε_{max} 29 400, 26 500 and 19 900, respectively, in chloroform). PPPMO calculations correctly predict this change in the absorption spectrum and also indicate which electronic transitions are responsible for each band. The 5-acceptor and amine functions were observed not only to determine the exact shade of black obtained, but they were also seen to govern the success or failure of the nucleophilic substitution reaction: primary and secondary arylamines were too weakly electrophilic to displace the halogen, whereas primary alkylamines caused dye decomposition and too strongly electron withdrawing groups in the 5-position were attacked by the secondary alkylamines.

The synthesis and spectroscopic properties have been described of some analogous dyes **21c–e** that contain either a 5-formylthiazolyl residue or its condensation product with active methylene compounds [79]. In contrast to the synthesis of the series **18**, an indirect route to 5-formyl substitution was taken in which **21a** was prepared from the corresponding diazo component and converted via **21b** to the aldehyde **21c**; subsequent derivatisation to **21d** and **21e** brought about substantial bathochromic shifts and intensity increases in a similar manner to the 4-chloro analogues, although curiously, the 4-trifluoromethyl derivatives were hypsochromic relative to the corresponding chloro derivative, for example, **21e** and its 4-chloro analogue exhibited λ_{max} values of 680 and 700 nm, respectively, in dichloromethane.

Given the ubiquity of (benzo)thiazolylazo dyes, it is no surprise that colorants of this kind have increasingly appeared as models studied alongside carbocyclic or other heterocyclic derivatives in publications concerned with aspects of dye application and performance. For example, the suitability for the coloration of polyester microfibres of some 6-substituted-benzothiazole-based dyes **22**, in addition to a series of phenylazo derivatives, has been investigated together with their spectroscopic properties (Table 4) [80]. In addition to the anticipated bathochromic and hyperchromic shifts in absorption associated with exchanging a *m*-toluidine coupler for a *m*-acylaminoaniline



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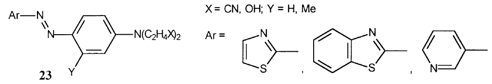
a, 6-OCH$_3$, X = NHCOCH$_3$ **d**, 5,6-(Cl)$_2$, X = NHCOCH$_3$*
b, 6-OCH$_3$, X = NHCOC$_2$H$_5$ **e**, 6-NO$_2$, X = NHCOC$_2$H$_5$
c, 6-OCH$_3$, X = CH$_3$ **f**, 6-NO$_2$, X = CH$_3$

*presumably contains 6,7-isomer

X = CN, OH; Y = H, Me



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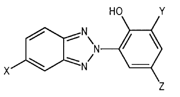

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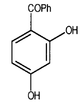

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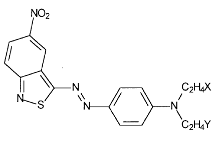

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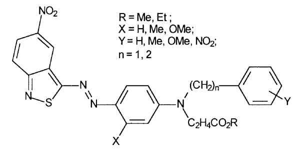
R = Me, Et;
X = H, Me, OMe;
Y = H, Me, OMe, NO$_2$;
n = 1, 2



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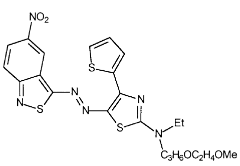

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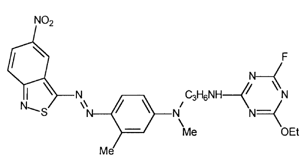

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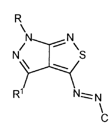

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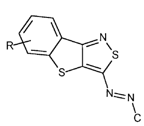

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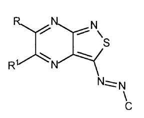

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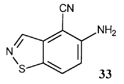
C = coupling component



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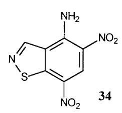

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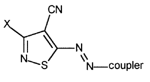

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residue, the planarity enforced by the ensuing intramolecular hydrogen-bond was also found to lead to narrower half-band widths (values of which have only been rarely reported for hetarylazo dyes) as well as increased dye uptake by the microfibre. While only moderate light fastness was observed, it was claimed that levels of washing and sublimation fastness were of a commercially acceptable standard.

The dyeing properties on silk [81] and wool [82] of related benzothiazolylazo dyes **23**, and their analogues from 2-aminothiazole and 3-aminopyridine, have been examined; the latter substrate was investigated in order to assess the feasibility of using these dyes without chemical modification of the fibre prior to dye application to increase fibre hydrophobicity and encourage disperse dye uptake. Affinities for either fibre were found to be generally lower than those for nylon at 80°C, although increasing dye hydrophobicity was observed to raise affinity: generally the benzothiazolylazo derivatives showed greater affinities than the corresponding thiazole analogues, which in turn exhibited higher affinities than their pyridyl counterparts (Table 5). The colour properties of the dyeings corresponded with absorption maxima of the dyes in solution, the positions of which were consistent with expectations. For example, bathochromic shifts were observed on fusing a benzene ring onto a thiazole system, changing terminal cyano substituents for hydroxyl functions, or locating a methyl group *meta* to the terminal amino function. The photostabilities of the cyano derivatives were slightly higher relative to those of the hydroxy-substituted dyes with moderate to good light fastness being observed; a general level of wet fastness close to that of equivalent nylon dyeings as well as that obtained with acid dyes of similar molecular size was noted.

The dyebath pH stability of a disperse dye is a property of great technical importance; however, very little published data exists concerning either carbocyclic or heterocyclic azo dyes [13], although recently the stability at pH 4, 7 and 9 of 1-naphthylamino-based dyes prepared from 2-aminobenzothiazole and its 6-nitro analogue, as well as substituted aniline diazo components, have been examined [83]. High levels of degradation were observed at each pH on heating to 125°C for 1 h in the case of both heterocyclic dyes.

Much industrial and academic interest has been shown in the employment of UV-absorbing photostabilisers as a means of raising the light fastness of dyed textiles, so inevitably their use in conjunction with hetarylazo disperse dyes has been explored. The effect of **24** (X = Y = H, Z = Me), a commercial benzotriazole-based photostabiliser, on the light fastness of polyester dyed with a red benzothiazolylazo derivative **6** ($X = CH_3$, $Y = CH_2OH$) has been investigated: depending on the depth of dyeing, mode of application of the photostabiliser and photostabiliser–dye ratio in the fibre, improvements of up to 1.5 points in light fastness were observed [84]. The increase in light fastness was favoured not only by high concentrations of stabiliser and dye as expected, but also by application of the photostabiliser to the pre-dyed fabric, as opposed to simultaneous exhaustion with dye, or the dyeing of fibre previously impregnated with stabiliser; for example, application of **24** (X = Y = H, Z = Me) to dyed (1.0% o.m.f.) polyester to give a 2:1 ratio of

Table 5
Spectroscopic (λ_{max} in nm, ε_{max} in 10^{-4} dm^3 mol^{-1} cm^{-1}), dyeing (affinity at 80°C in kJ mol^{-1}) and light fastness (silk) properties of some dyes **23** [81,82]

Dye **23**			DMF solution		Affinity			
Ar	X	Y	λ_{max}	ε_{max}	Silk	Nylon	Wool	Light fastness
2-thiazolyl	OH	H	496	3.80	8.44	10.55	7.06	3–4
2-thiazolyl	OH	Me	506	3.89	9.96	12.05	8.98	3–4
2-thiazolyl	CN	H	468	3.16	9.11	10.81	7.72	4
2-thiazolyl	CN	Me	480	2.51	10.21	10.95	8.54	4
2-benzothiazolyl	CN	H	490	4.27	8.83	15.42	8.54	4
3-pyridyl	CN	H	414	1.26	7.91	8.90	5.94	5

stabiliser:dye raised the fastness rating from 2 to 3–4, while simultaneous exhaustion furnished a value of 3. However, in an extension of the work to cover the utility of other stabilisers, **24** (X = Cl, Y = Z = Bu^t) and **25**, application method was not found to influence light fastness. Of the three stabilisers, the benzophenone **25** was seen to be the most efficient [85].

Certain 5-nitrothiazolylazo dyes have attracted attention for toxicological reasons [86]; textiles coloured with CI Disperse Blue 106 (**4**; X = OH, Y = Me) and CI Disperse Blue 124 (**4**; X = OAc, Y = Me) have been identified as the source of cases of allergic contact dermatitis [87,88], whereby the sensitising action of the dyes has been promoted by their use in heavy depths on nylon articles worn close to the skin such as hosiery, leggings and socks [89]. Despite only 1–2% of contact dermatitis cases being induced by textiles, the German Federal Institute for Health Protection of Consumers and Veterinary Medicine has advocated that the two aforementioned blue colorants, together with several other disperse dyes, should be prohibited from use in textiles that come into contact with skin [90]; it has been reported that the German government has lobbied for a ban within the European Community [91].

2.1.2. *(Benz)isothiazolylazo dyes*

Of this class, the most commercially important colorants are those derived from 3-amino-5-nitro[*2,1*]benzisothiazole, which have enjoyed success as relatively dull blues since they were developed in the mid-sixties [14]; the sole structure to be disclosed (CI Disperse Blue 148; **26**, X = CO_2Me, Y = H) was revealed just 10 years ago [92].

Dyes of similar structure have featured in the majority of the most recent publications concerning benzisothiazolylazo dyes, for example derivatives of general formula **27**, which have been examined spectroscopically (visible, IR, ^1H NMR) and applied to polyester [93–95]. Absorption characteristics and light fastness for some of these dyes are given in Table 6; anticipated trends in substituent effects on absorption maxima are evident, such as bathochromism associated with the placing of a methyl group onto the coupling component *ortho* to the azo link. From the limited light fastness data, it was claimed that a correlation between mass spectroscopic fragmentation patterns and photostability existed [93]. Analysis of the photofading of some of these dyes in ethanolic solution found that the rates of fading did not vary significantly with changes in the substitution pattern of the coupling component or correlate with the light fastness of the corresponding polyester dyeings [96]. A closer look at the photofading of the dyes on polyester reaffirmed the link between impact-induced fragmentation and light fastness [97].

Table 6
Spectroscopic properties (λ_{max} in nm, ε_{max} in 10^{-4} dm^3 mol^{-1} cm^{-1}) in ethanol and light fastness ratings on polyester of some dyes **27** [93,94]

Dye **27**				Ethanol		
R	X	n	Y	λ_{max}	ε_{max}	Light fastness
Me	H	1	H	591	4.12	5–6
Et	H	1	H	591	4.03	5–6
Me	H	1	Me	595	4.04	5
Me	H	1	OMe	604	3.84	5–6
Me	*p*-Me	1	H	585	4.18	5
Me	*m*-NO_2	1	H	569	3.05	5–6
Me	H	2	H	595	3.82	5
Et	H	2	H	595	3.92	4–5
Me	H	2	Me	609	3.64	4–5

The contribution of the 5-nitro group to the bathochromism of this type of dye can readily seen by comparing the colour of **26** (X = CN, Y = OH) (λ_{max} 570 nm in ethanol, bluish violet on polyester) with that of the dye lacking nitro-substitution (526 nm, red) [15]; however, only a small difference in light fastness was noted (5 for the former at 0.5% o.m.f. compared to 4–5 for the latter). A similar bathochromic shift was observed when the parent and 5-nitro diazo components were coupled to 4(5)-cyano-5(4)-hydroxyimidazole (**17**) [72]; like the analogous (benzo)thiazolylazoimidazole derivatives mentioned earlier (Section 2.1.1), the dyes were unstable and attempted conventional application to synthetic fibres resulted in extensive decomposition.

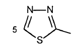
Structures in which 3-amino[*2,1*]benzisothiazoles are coupled to heterocycles have also featured in the patent literature, for example **28**, which is green on polyester [98]. However, few novel structures have been disclosed since activity has primarily concentrated on utilising known diazo components, either for the production of dye of improved physical form [99], or in the formulation of blue [100], green [101] and black [102,103] polyester dyestuffs through the combination of 5,7-dibromo or 5-nitro derivatives with other types of disperse dye. The 5-nitro-substituted diazo component has also been targeted as a synthon for reactive disperse dyes, such as **29**, for application to polyester–spandex blends alongside conventional disperse dyes [104].

Some unusual heteroannelated structures have been patented which are based on pyrazolo[*3,4-c*]- (**30**) [105], benzo[*g*]thieno[*4,5-c*]- (**31**) [106] and pyrazino[*2,3-c*]- (**32**) [107] isothiazole systems although the commercial appeal of these violet and reddish-blue dyes for conventional textile application is unclear. In another departure from conventional benzisothiazolyl-3-azo types, dyes for polyester have been claimed which are derived from diazo components that bear an amino function on the carbocyclic ring, for example, **33** [108] and **34** [109,110], which yield red and reddish-blue colorants, respectively, when coupled to anilines.

Despite extensive research, dyes based on 5-aminoisothiazoles, which are capable of producing brilliant red to violet shades [12–14], have not made much of an impact; details concerning such derivatives have remained scarce and, by and large, in the domain of the patent literature. That which has been disclosed is dominated by claims for magenta colorants intended for reprographics (Section 2.1.1). However, a few patents relating to textile applications have appeared. Red dyes **35**, derived from 5-amino-4-cyanoisothiazoles where X = 3-(2′-pyridyl) [111], 3-(aminosulphonylphenyl) [112] and 3-alkoxyalkyl [113], have been claimed for the coloration of polyester. Coupling of 5-aminoisothiazoles to 2-*N,N*-dialkylaminothiazoles furnishes violet and even blue dyes [114,115].

2.1.3. Thiadiazolylazo dyes

Dyes derived from 2-amino-1,3,4-thiadiazole (**36**) and 5-amino-1,2,4-thiadiazole (**37**) are of technical interest for the production of brilliant red shades [13]. Commercial success has been achieved with 2-amino-5-ethylthio-1,3,4-thiadiazole in the replacement of red anthraquinone-based dyes [5]; a dye from this diazo component, CI Disperse Red 338 (**38**), has the only structure of this type which has been disclosed to date [35].



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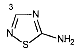

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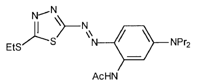

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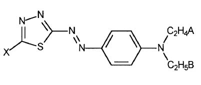

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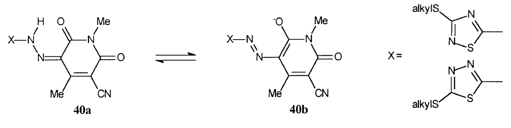

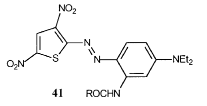

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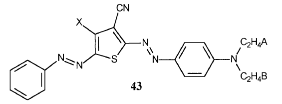

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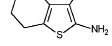

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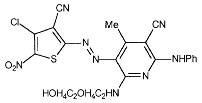

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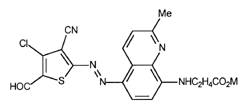

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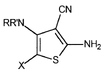

R, R′ = H, alkyl, cycloalkyl, aryl

X = CN, NO$_2$, CHO, vinyl

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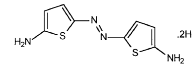

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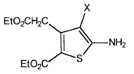

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Relatively little has been published regarding this class compared to the other categories of dyes derived from five-membered sulphur-containing heterocycles. In addition, the level of recent patent activity has been low, although papers focusing exclusively on dyes derived from 1,3,4-thiadiazole have appeared.

The dyeing properties on polyester of derivatives **39** (X = H, Me; A, B = H, OH) have been investigated with and without the use of phenol, benzoic acid and salicyclic acid as carriers [116]. While the substitution pattern in the coupling component had a surprisingly small impact on λ_{max} (498–504 nm), it was found that the most hydrophobic dyes of the series (i.e. those lacking hydroxy groups), **39** (A = B = H), possessed the highest dyeing rates and affinities with carriers generally enhancing both these properties. As has been observed in other azo dye series on polyester [117], the presence of hydroxy groups was deleterious to light fastness: **39** (A = B = OH) had the lowest ratings on polyester (5), while **39** (A = OH, B = H) and **39** (A = B = H) exhibited values of 6 and 7, respectively. Application of a chemometric approach to the prediction of the photostability of dyes of this type on polyester was undertaken using the data obtained from these derivatives to establish a quantitative relationship between light fastness and structure: predicted ratings matched observed values closely [118]. Similar studies using related series of dyes have been performed [119,120]. For example, the light fastness ratings of a "training set" on polyester (Table 7; **39a–b**, **39d–g**, **39i–j**) were used as the basis for the calculation of ratings for the 5-trifluoromethyl derivatives **39c**, **39h** and **39k**. The exceptionally high experimentally observed values were predicted accurately.

The expected trends of bathochromism resulting from increasing the electron strength of the substituent in the 5-position as well as hypsochromism arising through the placement of cyano groups onto the terminal alkyl chains can be seen in the series **39a–k** (Table 7); the former tendency can also be seen with analogous 5-alkyl(thio) dyes **39l–n** [15], whose light fastness ratings are similar to the corresponding derivatives **39a** and **39e**.

Table 7
Spectroscopic properties (λ_{max} and ε_{max} in nm and 10^{-4} dm^3 mol^{-1} cm^{-1}, respectively) and light fastness on polyester at 0.3% o.m.f. of some thiadiazolylazo dyes **39** [15,19]

Dye **39**	Substituents			DMF		
	X	A	B	λ_{max}	ε_{max}	Light fastness
a	Me	H	H	500	3.31	6
b	NHCOPh	H	H	525	3.55	4
c	CF_3	H	H	530	4.47	7
d	H	CN	H	488	4.07	7
e	SPr	CN	H	505	4.27	5
f	Br	CN	H	507	3.55	7
g	COPh	CN	H	512	5.01	7–8
h	CF_3	CN	H	522	4.37	7–8
I	Ph	CN	CN	496	4.17	5–6
j	CI	CN	CN	519	4.47	7
k	CF_3	CN	CN	507	3.98	8
l	Me	CN	OH	470[a]	2.57[a]	5–6[b]
m	SMe	CN	OH	495[a]	2.95[a]	4–5[b]
n	SEt	CN	OH	495[a]	3.02[a]	4–5[b]

[a] In ethanol.
[b] At 0.5% o.m.f.

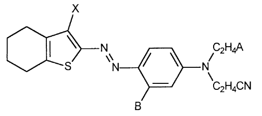
Pyridone dyes **40a** prepared from both 1,3,4- and 1,2,4-thiadiazole diazo components have been examined by NMR (^{1}H, ^{13}C) [121] and visible [70] spectroscopy which revealed that the hydrazone form of these dyes was much more acidic than analogous phenylazo dyes, and thus more liable to dissociate into the corresponding azo anion form **40b**. Further study showed that the equilibrium between **40a** and **40b** was sensitive to concentration but independent of temperature [122].

Use of a different type of heterocyclic coupling component, the hydroxynaphthalimide **16**, with 5-methylthio- and 5-ethylthio-2-amino-1,3,4-thiadiazoles produced red dyes of good light fastness on polyester (5–6 at 0.55% o.m.f.) [71].

2.1.4. Thienylazo dyes

Since they were introduced commercially two decades ago, disperse dyes derived from 2-aminothiophenes have become well established as alternatives to bathochromic anthraquinone derivatives [13,14]. Blue, green, navy and black colorants formulated from them are marketed worldwide, the first of which was CI Disperse Green 9 (**41**; R = Me), derived from 2-amino-3,5-dinitrothiophene. Other colorants based on this diazo component find use in alkali dischargeable/clearable formulations [123,124], as stand-alone blues and, more importantly, in navy or black mixtures. Blue disperse dyes have also been manufactured industrially from 3-acyl-5-nitro- and 4-chloro-3-cyano-5-formyl-2-aminothiophenes.

Dyes based on each of these diazo components have continued to feature in patents concerning formulatory or synthetic aspects as well as application properties. For example, slight variants (**41**; R = Et, Pr) of Green 9 have been claimed to possess greater dyebath stability [125], while structures based on 2-amino-3-acyl-5-nitrothiophenes have been disclosed to be of use in the production of blue [126,127] and bluish-green [128] formulations as well as for ink jet printing [129]. Dyestuffs of greater economy and levelness than Disperse Blue 56 have been reported when derivatives from



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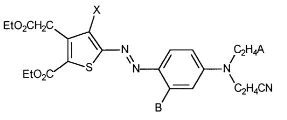

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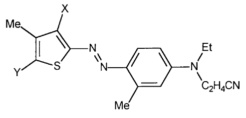

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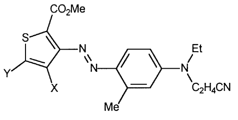

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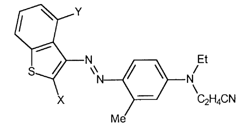

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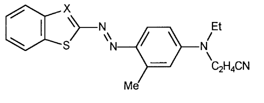

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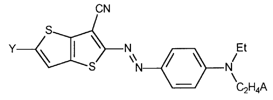

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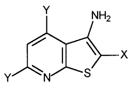

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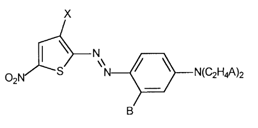
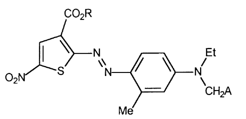
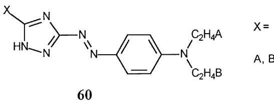


X = CO$_2$Me, NO$_2$
58 A = OAc, CO$_2$Me
B = H, NHAc



59 R = Me, Et, Bu, C$_2$H$_4$OEt
A = Me, Pr, Bu, Ph, CH$_2$Ph, C$_2$H$_4$Ph



X = H, Ph, C$_6$H$_5$NO$_2$(-*m*, *p*),
C$_6$H$_4$N(-*o*, *m*, *p*)
A, B = H, OH, CN

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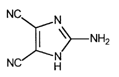

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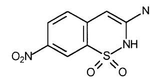

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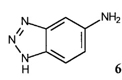

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the 5-formyl diazo component are combined with carbocyclic monoazo dyes [130].

Various topics concerning the formyl derivative **5** (X = C–CN, Y = NH$_2$) have been the subject of patents and publications. Methods of preparing this hetarylamine have been discussed [14] with improved synthetic routes claimed since then [131,132]. Detailed investigation of the diazotisation of this amine under typical industrial conditions using NMR spectroscopy has been reported [32]; competing reactions to the formation of **42**, such as hydration of the 3-cyano group, were monitored (Fig. 4) and through systematic variation of the acidity of the sulphuric acid medium, initial amine concentration, temperature and reaction time, conditions were found which minimised side reactions.

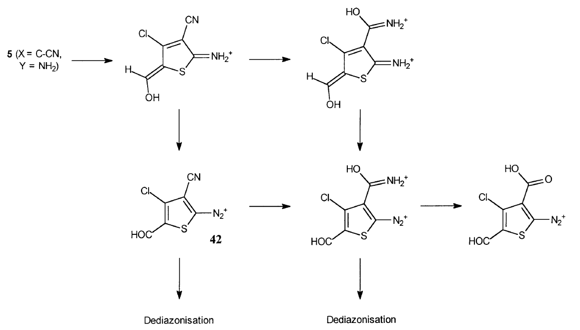


Fig. 4. Observed reactions pathways in the diazotisation of **5** (X = C-CN, Y = NH$_2$) in 85–100% sulphuric acid. [29]

An optimal yield of **42** of 99% was thus obtained by reaction of 1.0 mol kg^{-1} of **5** (X = C–CN, Y = NH$_2$) in 85% sulphuric acid with nitrosylsulphuric acid at 30°C after 40 min.

Dyes derived from 2-amino-3-cyano-5-nitrothiophene have been extensively patented in the past [13,14], and have featured in recent patents concerning the dyeing and printing of hydrophobic fabrics [133,134], for example, in the preparation of blue colorants which can be applied under alkaline conditions [135]; a dye of this kind has recently been commercialised and introduced to the Japanese market [136]. Specific crystal modifications of particular structures derived from this diazo component, as well as post-synthetic methods for obtaining them, have been claimed [137–140]. Patents covering the use of this class of dye in mixtures formulated with aminoazobenzene- and anthraquinone-based colorants have also appeared, for example, in the production of blue [141–144], as well as green, turquoise and navy dyestuffs [145].

Navy disazo dyes containing thienyl middle components have also been marketed [13,14] and structures, for example **43** (X = Cl, A = CN, B = Et) [146,147], as well as improved methods [148], have continued to be the subject of patents. The synthesis of disazo disperse dyes whereby 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophenes (**44**; X = CO$_2$Et, CN) are utilised as the first component with phenyl [149] or naphthyl [150] middle components has been described. Red-brown to blue shades were obtained on polyester; however, light fastness was found to be generally only low.

The brilliant red lightfast dyes that can be produced by coupling of diazotised thiophenamines to diaminopyridines [151], such as **45** [152], have excited commercial activity. Structures have also been claimed in which aminothiophenes have been coupled to 2,4,6-triamino-3-cyanopyridines to yield lightfast red colorants for polyester [153]. Other heterocyclic couplers explored include 8-aminoquinolines, for example, in the case of blue **46** [154], and 2-*N,N*-dialkylaminothiazoles [155,156]. Carbocyclic couplers in the form of *N*-alkoxycarbonylalkylanilines [157] and 3-aminophenol derivatives [158] have been disclosed as suitable for the manufacture of dischargeable colorants and lightfast blue dyes, respectively, from 2-aminothiophene-based diazo components.

Against the trend for utilising well-established thiophenamines, diazo components with novel structures have appeared, for example 4-amino derivatives of general type **47**, such as **47** ($R = R' = Et$, $X = CH = C(CN)_2$), produced in an analogous manner to the thiazolylazo dyes **20** (Section 2.1.1) by nucleophilic substitution of the corresponding 4-chloro derivative with a primary or secondary alkyl- or aryl-amine [159]. Other derivatives which have been disclosed either for the preparation of disperse dyes, or as colorants in their own right, include related 4-chlorothiophenamines [160], 2-aminothiophenes bearing maleimido residues in the 5-position, for example **8** ($X = C–CO_2Me$) [40], and diaminoazothiophene **48** [161].

Despite 40 years having elapsed since thienyl-2-azo dyes were first scrutinised systematically, and the continued industrial interest in them, prior to the end of the previous decade, only a very limited amount of information pertaining to the synthesis, properties and application of such dyes existed outside the patent literature. Since then, however, papers have appeared dealing with each or all of these aspects.

The first of these to appear concentrated solely on dyes from aminothiophene diazo components **44** and **49**, presumably as a result of the ease with which these compounds can be prepared in one step by the Gewald synthesis [162]. In addition to the disazo colorants mentioned earlier, monoazo derivatives were synthesised by diazotisation of **44** ($X = CN$) [163] or **44** ($X = CO_2Et$) [163–164] and attachment to carbocyclic and heterocyclic coupling components to produce yellow to red-violet dyes, such as **50** ($X = CN/CO_2Et$, $A = CN$, $B = H$), which were reported to be of poor to very good light fastness. In an analogous manner, dyes described as being yellow to blue with a similar range of properties were prepared from **44** ($X = CONH_2$) [166], **49** ($X = CN$) [167] and **49** ($X = CO_2Et$) [168]. However, discrepancies were found between the absorption characteristics and photostabilities of some of these dyes and those of a closely related series (**50**/**51**; $A = H$, $B = Me$) synthesised in a separate study [169]. For example, some of the latter dyes (**50**; $A = H$, $B = Me$) were observed to have much lower light fastness values than that of the corresponding derivatives **50** ($A = CN$, $B = H$) reported by Sabnis and co-workers, who also attributed some unusually low ε_{max} values to their dyes (Table 8). Additionally, experimental data and PPPMO calculations contradicted the assertion by Sabnis et al. that diazo components **44** ($X = CONH_2$) and **49** ($X = CN$, CO_2Et) furnish blue dyes with relatively simple aniline couplers.

A wider variety of 2-aminothiophenes, prepared directly by the Gewald synthesis or after subsequent derivatisation [162,170], were used to produce a range of yellow-red to green dyes [171,172]. Raising the total electron withdrawing strength of the substituents in the thiophene ring not only led to the need for increasingly acidic diazotising media through weakening of the basicity of the amino group, but also resulted in bathochromism shifts (in agreement with theory and PPPMO calculations), hyperchromism, increased positive solvatochromism and a reduction in the size of observed positive halochromic shifts (Table 9) [173,174]. The presence of two strong acceptors or a nitro group on the heterocyclic ring was sufficient to bring about negative halochromism. Half band-widths, which had not previously been reported for thienyl-2-azo dyes, were observed to be smaller than those of the corresponding phenylazo derivatives, with 3-cyano functions conferring narrower band-widths than 3-ester groups.

Dyeings on polyester were generally more satisfactory in terms of build-up and fastness than on

Table 8
Comparison of the spectroscopic properties (λ_{max} in nm, ε_{max} in dm^3 mol^{-1} cm^{-1}) in DMF solution and light fastness on polyester (1.0% o.m.f.) of some thienyl-2-azo dyes **50** and **51**

Dye	X	A = H, B = Me [169]			A = CN, B = H [163,166–168]		
		λ_{max}	ε_{max}	LF	λ_{max}	ε_{max}	LF
50	CN	531	42 300	2	525	log 3.30	4
50	CO_2Et	503	34 000	1	510	log 3.37	3
50	$CONH_2$	506	33 700	1[a]	581	30 900	5
51	CN	565	48 600	6	585	32 400	4
51	CO_2Et	536	40 700	5–6	582	40 700	5–6

[a] 0.5% o.m.f.

Table 9
Absorption maxima, intensities and half band-widths (in nm, 10^{-4} dm^3 mol^{-1} cm^{-1} and nm, respectively), halochromic shifts ($\Delta\lambda_h$, in nm for neutral and acidic ethanol), and light fastness of some thienyl-2-azo dyes **52** and **53** [169,173–177]

Dye	Substituents		Properties in DMF solution			$\Delta\lambda_h$	Light fastness at 0.5% o.m.f.		
	X	Y	λ_{max}	ε_{max}	$\Delta\lambda_{\frac{1}{2}}$		Polyester	Nylon	Diacetate
52	CN	Me	529	4.15	95	–	1–2	1	1
52	CO_2Et	Me	500	3.39	103	127	1	1	1
52	CO_2Et	CO_2Et	530	3.91	107	49	5	4	3–4
52	CO_2Me	Ac	536	3.96	108	31	5	4	3–4
52	CO_2Et	CN	546	4.27	106	22	5	4	3–4
52	CO_2Me	NO_2	589	4.36	124	−14	5	1–2	4–5
53	NO_2	H	454	2.16	123	51	4	–	–
53	H	NO_2	479	3.02	121	47	3–4	2	2
53	Me	NO_2	430	2.29	134	86	4	3	3

nylon and acetate [176,177]. Light fastness increased as the total electron withdrawing strength of the substituents on the thiophene ring was raised, although the presence of nitro groups led to very low ratings on nylon (Table 9). The above findings help explain why the more bathochromic thienylazo dyes from carbocyclic couplers have attained commercial success while those in the red sector have remained unexploited, for example, because of their fugitive nature.

Relatively low photostabilities on hydrophobic substrates (Table 9), as well as unremarkable absorption characteristics, account for the low level of recent patent activity [178] concerning disperse dyes from 3-aminothiophenes. As predicted by PPPMO calculations, three nitrothienyl-3-azo dyes **53** (X = H, Y = NO_2; X = NO_2, Y = H; X = Me, Y = NO_2) were found to be hypso- and hypo-chromic relative to their thienyl-2-azo isomers, for example, **53** (X = H, Y = NO_2) was yellow and observed to have an ε_{max} value around half that of the blue isomer **52** (X = CO_2Me, Y = NO_2) (Table 9). However, the hypsochromism of **53** (X = NO_2, Y = H) relative to **53** (X = H, Y = NO_2) was not reproduced, which was assumed to be due to steric hindrance caused by the presence in the former structure of two groups *ortho* to the azo link; this effect was also assumed to be the reason for the hypsochromism and lower intensity of **53** (X = Me, Y = NO_2) relative to **53** (X = H, Y = NO_2).

Steric effects were observed in benzo[*b*]thienyl-3-azo dyes **54** when substituents were present in both the 2- and 4-positions as in **54** (X = CO_2Me, Y = Cl, NO_2) which were hypsochromic and of lower intensity than **54** (X = CO_2Me, Y = H) [179]. As anticipated, stronger electron acceptors in the 2-position led to bathochromism so that **54** ($X = Ac$, CN, $Y = H$) were red and **54** ($X = NO_2$, $Y = H$) was violet, while PPPMO calculations correctly predicted yellow-orange **54** ($X = CO_2Me$, $Y = H$) and its ethyl homologue to be hypsochromic relative to the red benzo[*b*]thienyl-2-azo isomers **55** ($X = C–CO_2Me$, $C–CO_2Et$). The latter dyes were, as expected, bathochromic and hyperchromic compared to the tetrahydrobenzo[*b*]thiophene analogues **50** ($X = CO_2Me/Et$, $A = H$, $B = Me$); the light fastness of the former dyes on polyester, nylon and acetate (5, 5 and 4, respectively, at 0.5% o.m.f.) represented a significant improvement on that of the latter derivatives (1 on each substrate) [175]. No significant advantage was held by dyes **55** ($X = C–CO_2Me$, $C–CO_2Et$) over their benzothiazolylazo counterpart **55** ($X = N$) apart from slightly higher light fastness. Related derivatives of greater bathochromism have been synthesised from substituted 3-cyano-2-aminobenzo[*b*]thiophene diazo components [180].

Heteroannelated analogues of benzo[*b*]thienyl-2- and -3-azo dyes have also been studied. Thieno[*3,2-b*]thiophene-based dyes, such as **56** ($X = H$, $Y = CO_2Et$), have been claimed as violet to blue colorants for polyester and other hydrophobic fibres [181], while thieno[*2,3-b*]pyridines **57** ($X = CN$, $Y = Me$, Ph) [182] and **57** ($X = CO_2Et$, $Y = Me$) [183] have been linked to carbocyclic and heterocyclic couplers, giving yellow to red-violet dyes of widely varying light fastness on polyester (2–6 at 1.0% o.m.f.). In addition, the latter diazo component has been used to produce monoazo dye intermediates for fluorescent brightening agents [184] or as a synthon in the preparation of arylazopyrazole-based dyes [185].

An important commercial aspect of certain dyes derived from 2-aminothiophenes is their sensitivity towards alkali, which can destroy the chromophore, allowing discharging or clearing without the need for reducing agents [123,124]. Not only does this property confer better fastness in tests employing alkaline washing liquors, but it also permits removal of any disperse dye cross-staining the cellulosic component of polyester–cotton/viscose blends with mild alkali, improving wet fastness, brightness and productivity [186]. An alternative approach utilised with carbocyclic dyes involves hydrolysis of carboxylic acid ester groups on the coupling component to produce alkali-solubilising carboxylic acid functions [123]. An investigation has been made into combining the latter chemistry with the alkali-sensitivity of the thienylazo chromophore by the synthesis and application to polyester of the dye series **58** and **59** composed of 5-nitrothienyl-2-azo derivatives bearing ester groups on the diazo component and/or coupling component [187]. While the dyes were found to be effectively cleared by alkali, in some cases just as efficiently as by reduction clearing, the presence or absence of ester groups was not observed to make much of an impact on wash fastness, which was ascribed to various complicating factors, including the possibility that the effect of any ester hydrolysis is swamped by the decolorisation mechanism.

Thiophene-based disperse dyes have also been examined as colorants for both components of polyester–wool blends in an attempt to develop a one-stage coloration process. Dyes from **44** ($X = CN$, CO_2Et) were applied to the blend and each fibre in isolation: surprisingly, not only were the dyes reported to show higher affinity for wool than polyester, but also to exhibit very high light fastness ratings (6 to 7) [188].

2.1.5. *Triazolyl-, imidazolyl- and pyrazolyl-azo dyes*

Of the relatively little that has been published recently about dyes prepared from diazo components comprised of five-membered ring systems with two (imidazole, pyrazole) or three (triazole) nitrogen heteroatoms, most material has involved the last of these types.

Reports featuring 1,2,4-triazole-based dyes of general structure **60** have been published concerning their application to hydrophobic fibres. The parent compounds (**60**; $X = H$) [189] and their 5-methylthio analogues (**60**; $X = SMe$) [190] were found to be unsuitable for polyester in regard to substantivity and fastness. However, increasing dye hydrophobicity by substitution at the 5-position with a (nitro)phenyl group brought about improved dyeing properties (as well as a bathochromic shift of 30 nm through extension of the conjugation, augmented by around 10–20 nm with the presence of a nitro group) [191]. Light fastness ratings were generally poor for each of the dyes on polyester, triacetate and nylon unless a coupler with bis-cyano substitution was employed which led to ratings of 4 to 4–5 being observed. Similar findings were obtained with 5-pyridyl analogues [192]. The use of dyes **60** (X = A = H, B = H, CN) to produce metal complexes for application to wool and nylon has been explored [193]. *N*-Benzylated 1,2,3-triazolyl derivatives have been claimed as bright red dyes of good fastness [13], and more recently, analogous 1,2,4-triazole-based dyes have been patented [194].

The capacity of 2-amino-4,5-dicyanoimidazole (**61**) to furnish brilliant red disperse dyes of high fastness has been exploited commercially [13], but to the authors knowledge, no specific information on the synthesis and properties of dyes from imidazolyl diazo components has been published recently, although yellow dyes prepared by condensation of 2-hydrazinobenzimidazole with indol-2,3-dione and subsequent alkylation have been described [195].

Patents have appeared concerning dyes based on aminopyrazole diazo components, but in connection with non-textile applications (Section 2.2.1); an exception is a claim for dyes intended for hydrophobic fabric coloration, which are synthesised from quaternised thiadiazolylazo derivatives [196].

2.1.6. *Miscellaneous hetarylazo dyes*

This group of dyes can be split into two types, the first of which consist of structures derived from diazo components which bear the diazotisable amine function on a hetaryl ring, while the second kind are essentially azobenzenes to which have been attached heteroaromatic systems. Numerous papers have been published which feature the latter despite such structures being of no particular commercial interest. Examples include 4-(pyridyl-2)- [197], 4-(5-thio-1,3,4-oxadiazolyl-2)- [198] and 2-(benzimidazolyl-2)- [199] azobenzene series.

A substantial amount of the published material concerning unusual heterocycles for the preparation of the other type of dye relates to non-textile uses (Section 2.2). However, accounts of the application to polyester of dyes derived from 3-amino-7-nitro-2*H*-1,2-benzothiazine-1,1-dioxide **62** [200] and 5-aminobenzotriazole **63** [201] diazo components have appeared.

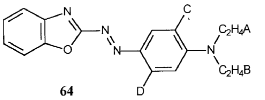
Very little data is available which pertains to disperse dyes synthesised from 5-membered heterocyclic amines containing only nitrogen and oxygen heteroatoms so a recent study in which a series of monoazo derivatives was prepared from 2-aminobenzoxazole is of interest: diazotisation and coupling to substituted anilines, furnishing **64**, and to 4-hydroxyquinolines, yielded yellow to red dyes of fair light fastness on polyester [202]. Unfortunately, spectroscopic and performance comparisons with benzothiazolyl analogues are difficult to make as absorption maxima and fastness tests are given without reference to the solvent and methods used. Curious coupling component substituent effects on λ_{max} are evident; for example, acetylation of terminal hydroxyethyl groups typically brings about modest hypsochromic shifts in aminoazobenzenes, yet **64** (A = B = OAc, C = H, D = Cl) is reported to have a λ_{max} value of 520 nm which is substantially red-shifted compared to the figure of 440 nm listed for **64** (A = B = OH, C = H, D = Cl).

2.2. *Hetarylazo dyes for non-textile applications*

Aside from the continuing research effort devoted to colorants for textiles discussed above, a substantial amount of time and money has been channelled into developing disperse dyes derived from heterocyclic diazo components for a diverse range of non-textile uses. These applications may call on the light absorption properties of such dyes for aesthetic or functional reasons, while dyes utilised in non-linear optics (Section 2.2.2) are not even required to absorb light and, within certain limits, absorption may actually be undesirable. For example, hetarylazo dyes have found use in reprographic technology (Section 2.2.1), either specifically for their colour in transfer inks or toners, or as replacements for inorganic photoconductors for which their colour is not important.

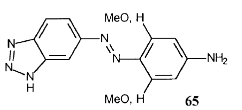
Other instances where research into heteroaromatic disperse dyes as functional colorants have continued to be pursued include pH indicators [203] and complexometric reagents for chemical analysis [204] and enhanced spectroscopy, such as benzotriazolyl dyes of type **65** [205]. The bathochromism for which certain hetarylazo dyes are renowned has sparked interest in such colorants as near infrared absorbers for use in applications like optical character recognition and security printing which employ infrared semiconductor lasers; examples of proposed systems include monoazo structures derived from thiophene diazo components and naphthylamine couplers, such as **66** (λ_{max} 830 nm in chloroform) [206], and disazo dyes containing thiazolyl or thienyl middle components [207]. Hetarylazo dyes, or their metal complexes, have also been patented very recently as absorbers of visible laser radiation for recordable compact disc information systems [208–210].

Another non-textile application where dyes from heterocyclic diazo components have received recent attention is liquid crystal display technology [8]. One pre-requisite for a successful dye is that it must be soluble in the liquid crystal host so many of the candidates which have been evaluated are modified versions of conventional non-ionic colorants; consequently, hetarylazo disperse dyes



64

A, B = H, OH, OAc, CN
C = H, OMe
D = H, Me, Cl, NHAc



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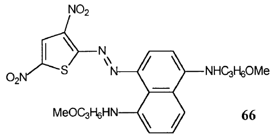

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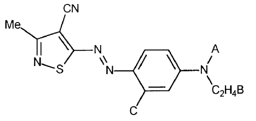

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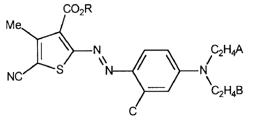

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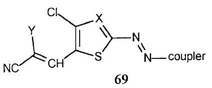

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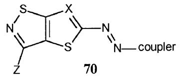

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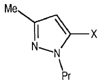

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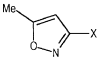
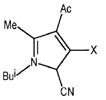


71b



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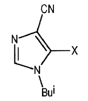

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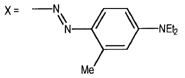

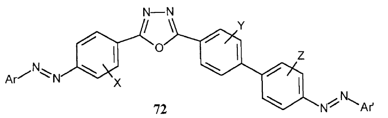

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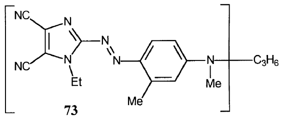

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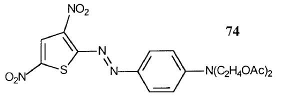

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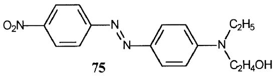

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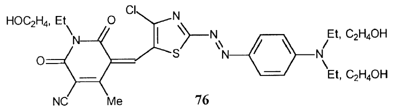

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have been well-scrutinised [211]. Interest has still been shown in them with monoazo and disazo dyes prepared from fluoroalkyl-substituted thiazole [212] and benzothiazole [213] diazo components, respectively, having been patented recently.

The remainder of this section looks at developments in reprographics and non-linear optics in more detail, focusing on the types of hetarylazo dye which have been tailored for these uses.

2.2.1. Reprography

The field of dye diffusion thermal transfer (D2T2) printing has probably been the most active non-textile area of recent research into hetarylazo dyes. The technique has attracted commercial attention because of its capacity to furnish images with continuous tones of high resolution and optical density [9]. Printing involves the application of localised heat to a colour sheet (onto which have been deposited yellow, magenta and cyan colorants by solvent coating) which causes the dyes to pass to a polymer-coated receiver sheet in a melt-state diffusion process. Disperse and solvent dye types are therefore required of high heat stability and, because the image is only a few microns thick, of high light fastness.

In the quest to identify suitable dyes, investigation into employing hetarylazo derivatives in each of the three colour areas has been found to be a "fruitful area of research" [214], especially in the magenta sector, with dyes from isothiazole and thiophene diazo components having favourable properties. While derivatives of this kind, such as 4-cyano-3-methylisothiazolyl-5-azo (**67**) and 3-alkoxycarbonyl-5-cyano-4-methylthienyl-2-azo (**68**) dyes exhibit good D2T2 performance, efforts have been directed at improving their intrinsic photostability [215].

Photodealkylated degradation products were isolated from photofaded receiver layer images, for example, **67** (A = H, B = OAc, C = Me) from **67** (A = Et, B = OAc, C = Me). The process is believed to be initiated by attack of photogenerated singlet oxygen on the terminal nitrogen atom; reduction of electron density on this centre, for example by adding electron withdrawing functions onto the pendant alkyl chains raises light fastness, a strategy which has been employed in the design of azo textile dyes for many years. However, it was also observed that incorporation of an α-methyl group onto an alkyl chain also improved photostability, for example in the case of **67** (A = CH(Me)C_2H_5, B = Et, C = Me) compared to its isomer **67** (A = Bu^n, B = Et, C = Me), contrary to expectation as, on an electronic basis, the inductive effect of the branching should tend to increase electron density on the terminal nitrogen atom. It was proposed that α-branching sterically inhibits attack by singlet oxygen such that any electronic influences are outweighed; this phenomenon and mechanism was first noted for carbocyclic and heterocyclic dyes in solution or applied to polymers [216]. Dealkylation was found to occur preferentially at non-branched chains, so that for **67** (A = CH(Me)C_2H_5, B = OAc, C = NHAc), only loss of the acetoxyethyl group was observed.

Use of couplers containing α-branched chains has been examined as a means of ameliorating light fastness with dyes of type **68** as well as aminoazobenzene and non-azo chromophores; the approach has also been applied to cyan disazo derivatives containing a thiophene middle component, i.e. of general type **43** (X = H). Monoazo thiophene-derived dyes have also been explored as cyan dyes, such as **41** (R = Me) and **69** (X = C–CN) [214], in addition to thiazole types such as **69** (X = N) [217]. Recently, numerous patents have outlined the use of benzisothiazole-based colorants from acetanilide [218], tetrahydroquinoline [219] or thiazole [220] couplers in this capacity as well as for magenta dyes when coupled to diaminopyridines [221]. Other recently examined magenta chromophores include those prepared from benzothiazole [222,223], 3-cyanopyrazole [224–226] and dicyanoimidazole (**61**) [227] diazo components as well as isothiazolylazothiazoles [228]. The synthesis of magenta dyes **70** has been claimed in which the diazo components of thiazolyl- and thienyl-azo dyes **5** are cyclised to form an isothiazole ring [229,230].

Heterocyclic diazo components have also been explored for the production of yellow dyes, for example thiadiazoles coupled to pyrazoles [214,231]. The former type of heterocycle has found use in orange [232] and red [233] colorants as well, while the latter ring system has also been employed as a diazo component [234], for example in the case of **71a** [235]; other heterocyclic systems that do not find use as acceptor rings in hetarylazo dyes for textiles, but which have been claimed as synthons for thermal transfer printing colorants, are 3-aminoisooxazoles [236], 3-aminopyrroles [237] and 5-aminoimidazoles [238], such as **71b** (yellow), **71c** (orange) and **71d** (red), respectively.

Hetarylazo dyes have also featured in other reprographic technologies like electrophotography [8,9], where such colorants may find use either as photoconductors, for example structures of type **72** [239] and related derivatives [240,241] which have been patented as charge generating agents, or in toners, with magenta colorants claimed from benzothiazole [242] and imidazole [243] diazo components, such as **73**. Azo(benzo)thiazoles complexed to metals have recently been described for use in both charge generation and toner charge control [244].

2.2.2. Non-linear optics

Non-linear optical (NLO) phenomena have been known for over a century [245], but their study has remained esoteric until relatively recently when practical applications for such effects were envisaged and NLO systems put into use [246,247]. They may be employed, for example, in second harmonic generation (SHG) to double the frequency of light or in electro-optic (EO) modulation, where the properties of electromagnetic radiation are modified in response to the application of an electric field; the former mode of operation is of use in optical data storage as a means of converting infrared light from a semiconductor laser into visible radiation, allowing a four-fold increase in the density of information which can be recorded with it, whereas the latter can be employed in telecommunications to code data onto near infrared carrier waves. While inorganic substances attracted early attention, much effort has been expended on researching organic molecular NLO materials, including those based upon hetarylazo dyes.

NLO activity is reliant upon the polarisation P induced in a material by the electric vector E of incident light not being linearly related as shown in the following equation:

$$P = aE + \beta E^2 + \gamma E^3 + ...$$

The size of the non-linear components of the interactions are determined by hyperpolarisability terms β and γ, which are the quadratic (or first) and cubic (or second) hyperpolarisabilities respectively. The former is largely responsible for second-order NLO effects like SHG and EO phenomena so it is therefore desirable to work with substances of high molecular β when attempting to design an efficient system; in addition, unless the material crystallises non-centrosymetrically, the molecules must be aligned to avoid cancellation of their NLO properties in the bulk material. This may be achieved by ordering of the molecules into Langmuir–Blodgett films, forming guest–host liquid crystalline or polymeric systems, or by copolymerisation in a "poling" electrical field. As large β values are associated with extended conjugated π-systems bearing donor and acceptor functions at each end, azo dyes have been an obvious choice for investigation, especially as they can be readily modified to facilitate incorporation into the desired assembly, which explains the interest shown by commercial organisations and academic institutions in the utilisation of hetarylazo dyes for the fabrication of NLO devices.

Findings that enhancement of β occurs through exchange of carbocyclic rings for heterocycles in the acceptor end of non-azo chromophores [248,249] have been reflected in calculations for monoazo and disazo dyes made up of heteroaromatic donors and/or acceptors [250]; thiophene systems have been noted to be especially efficacious as a result of the more facile charge conduction associated with the reduced aromaticity of the ring compared to benzene as well as the bathochromicity typical of azothiophene dyes leading to resonance enhancement. In addition, the relatively large dipole moment of the ground state (μ_g) of these structures is advantageous since the dyes will respond more efficiently to the electric field applied during poling; the effect of the conformation adopted by the 2-acetoxyethyl functions of **74** (which in another guise is a commercially successful blue alkali-clearable textile colorant) on μ_g and molecular β have been investigated [251]. Calculations showed that both properties were highly dependent on the orientation of the ester groups to the extent that it was suggested that short term reductions in SHG signals from a guest–host polymer film containing **74** may be a consequence of intramolecular conformational relaxation by conformers of high μ_g and β to those of lower NLO activity.

The NLO performance of polymeric systems prepared from several other (benzo)thiazolylazo and thienyl azo dyes has been reported and compared to those from the carbocyclic azo dye, CI Disperse Red 1 (**75**), which has often been used as a model NLO chromophore. For example, copolymerisation of **4** (X = OCOC(Me)=CH_2, Y = H) with methyl methacrylate yielded an EO polymer with higher second-order NLO activity than the corresponding material prepared from a methacrylate ester of **75** which was ascribed to the former colorant's bathochromism [252]. Similarly, SHG and relaxation behaviour of thiazolylazo dyes **76** in poly(methyl methacrylate-co-methacrylic acid) films have been found to be superior to material obtained from copolymerisation of methyl methacrylate and **75** [253].

Other (benzo)thiazolylazo systems bearing polymerisable groups have been used to prepare NLO polymers with this monomer [254], while colorants without such functions, for example CI Disperse Blue 339 (**4**; X = Y = H), have been incorporated into polymer films by poling above T_g. Hetarylazo dyes with polymerisable methacryloyloxyalkyl [255] and hydroxyalkyl [256] functions have been patented for use in the preparation of NLO polymers by co-polymerisation with methyl methacrylate and terephthalic acid respectively. Thiophene-based chromophores have attracted attention for such purposes, for example, dyes of type **56** (Y = 4-CNPh, A = OH) [257], **56** (Y = 4-CNPh, A = $CH_2OCOC(Me)=CH_2$ [258] and **69** (X = C–CN, Y = CN) [259].

Attempts to optimise the properties of NLO materials through design of the chromophore have been made. For example, long fluorinated alkyl chains were examined as a means of reducing relaxation after poling in poly(methyl methacrylate) by making use of the geometry and rigidity of the chains to inhibit re-orientation [260]: while benzothiazole derivatives **11** (6-C_4F_9, C_8H_{17}; X = H) were found to exhibit less relaxation than analogues with either no or short fluorinated functions (**11**; 6-H, Bu^n, CF_3; X = H) as expected, alignment during poling was suppressed by the longer chains, which tended to reduce NLO activity, so that **11** (6-C_4F_9; X = H) had the best compromise between the two effects.

Another balance that must be struck is that between the NLO activity of a chromophore and its robustness towards the conditions required in the processing of NLO polymers: in an attempt to improve the thermal stability of (benzo)thiazolylazo dyes, as well as carbocyclic azo and non-azo structures, alkyl chains on the terminal amino function were replaced with aryl groups which it was thought would raise decomposition temperatures at the expense of NLO activity [261]. While the former effect was achieved, in many cases increased non-linear behaviour was also noted.

3. Summary

The previous phase of innovation in the field of disperse dyes derived from heterocyclic diazo components, which has revolved around finding replacements for red and blue anthraquinoid textile colorants, is over. However, research continues unabated in response to the increased demands placed on disperse dyes as a result of the textile coloration industry seeking to add value to products and cut costs leading to the trends for finer substrate filaments, greater use of blends and finishing treatments, more exacting fastness specifications as well as more demanding application techniques. As indicated by the number of patents which have appeared dealing with synthesis, physical form, formulation, application performance and fastness, the direction taken has generally involved improving aspects of existing products and adapting them to novel processes: this shift in emphasis has been effected by use of physicochemical methods or judicious selection of dyestuff components, rather than any novelty in molecular structure, owing to the registration and testing required of new compounds as well as the diminishing returns associated with further dye design. Any adjustment to chemical constitution has typically consisted of fine tuning of existing well-known classes, often by altering the coupler with the diazo component remaining fixed as one of the "conventional" heterocyclic types, although occasionally a new substitution pattern in the latter has been described.

In the academic literature, the last 10 years have witnessed considerable growth in the amount of information published pertaining to the synthesis, properties and application of hetarylazo dyes. Prior to the start of this decade, much of the little material available on disperse dyes from five-membered heterocyclic diazo components was fragmentary; now, modern comprehensive studies have been published, furnishing data for many of these types. Such information has fleshed out extant knowledge of dyes based on well-known diazo components and helped to explain the commercial success of particular hetarylamines as well as introducing new heterocycles of either a slightly modified or radically different nature.

It is likely that the interest in the use of hetarylazo chromophores in non-textile applications will be sustained and that the constitution of the molecules investigated will differ from the dyes exploited in the textile sector. In the latter area, existing research is relatively conservative owing to the maturity of the industry with commercial colorants having evolved over several decades within cost and performance restrictions which have pared down the number of feasible colorants from the huge number of possible dyes to those which can satisfy many and varied criteria drawn from economic, synthetic, physicochemical and fastness considerations. On the other hand, the high technology applications have a different set of requirements to be fulfilled, where cost is less of a factor, so it is natural that other heterocycles, some of which may seem exotic to the textile dye chemist, are being exploited. Their development will presumably involve greater leaps in structural modification than those seen in the textile area, although it is probable that the well-established practice of taking conventional textile dyes "off the shelf", examining their utility for a new application and re-engineering them accordingly will continue.

Statements on the future of disperse dye research made at around the end of the last decade ring equally true today [8,13,123,124]. Textile dye chemists are still looking for brighter, more cost-effective colorants which can add value to substrate as well as meet the ever-increasing demands placed on them by consumers, dyers and legislators. The promise of non-textile applications, which has attracted interest from those in a wide range of disciplines and businesses, is not lost on dye manufacturers. It can therefore be seen that there is no shortage of motivating factors to drive hetarylazo dye research into the next millennium: without doubt, whether approached from an industrial or academic perspective, disperse dyes from heterocyclic diazo components will be the subject of investigation for years to come.

References

[1] Pozharskii AF, Soldatenkov AT, Katritzky AR. Heterocycles in life and society. Chichester (UK): John Wiley, 1997.

[2] Meth-Cohn O, Smith MJ. Chem Soc Perkin Trans I 1994;5.

[3] Grözinger G. J Soc Dyers Colourists 1996;112:220.

[4] Shore J, editor. Colorants and auxiliaries, vol. 1, Bradford (UK): SCD, 1990.

[5] Shuttleworth L, Weaver MA. In: Waring DR, Hallas G, editors. The chemistry and application of dyes. New York: Plenum, 1990 [chapter 4].

[6] Sternberg E, Dolphin D. In: Matsuoka M. editor. Infrared absorbing dyes. New York: Plenum, 1990 [chapter 15].

[7] Hallas G, Towns AD. In: Ansell MF, editor. Rodd's chemistry of carbon compounds, vol. IV. 2nd ed. Amsterdam: Elsevier [chapter 45].

[8] Gordon PF. In: Waring DR, Hallas G, editors. The chemistry and application of dyes. New York: Plenum, 1990 [chapter 8].

[9] Gregory P. Rev Prog Coloration 1994;24:1.

[10] Griffiths J, Hallas G. In: Griffiths J, editor. Developments in the chemistry and technology of organic dyes. Critical reports in applied chemistry, vol. 7. Oxford: Blackwell, 1984.

[11] Leaver AT, Cunningham AD. 17th IFVTCC Congress Conference Papers, Vienna, 1996. p. 59.

[12] Weaver MA, Shuttleworth, L. Dyes and Pigments 1982;3:81.

[13] Annen O, Egli R, Hasler R, Henzi B, Jakob H, Matzinger P. Rev Prog Coloration 1987;17:72.

[14] Egli R. In: Peters AT, Freeman HS. Colour chemistry: the design and synthesis of organic dyes and pigments. London: Elsevier, 1991 [chapter 1].

[15] Peters AT, Gbadamosi A. J Chem Tech Biotechnol 1992;53:301.

[16] Hu J-Z, Skrabal P, Zollinger H. Dyes and Pigments 1987;8:189.

[17] Mitsubishi, Japanese patent 62 158 763, 1987 Chem Abs; 107:219142j.

[18] Mitsubishi, Japanese patent 62 158 764, 1987 Chem Abs;107:219141h.

[19] Mitsubishi, Japanese patent 63 132 970, 1988 Chem Abs;109:212369w.

[20] Nippon Kayaku, Japanese patent 06 136 283, 1994 Chem Abs;121:257927r.

[21] Sumitomo, Japanese patent 63 210 172, 1988 Chem Abs;110:77499s.

[22] DyStar Japan, Japanese patent 09 03 352, 1997 Chem Abs;126:200661y.

[23] Nippon Kayaku, Japanese patent 03 115 467-8, 1991 Chem Abs;115:210201k–2m.

[24] Nippon Kayaku, Japanese patent 03 157 458, 1991 Chem Abs;115:234684w.

[25] Hoechst Mitsubishi, European patent 519, 459, 1992.

[26] Nippon Kayaku, Japanese patent 05 255 601, 1993 Chem Abs;120:109411g.

[27] Hoechst Mitsubishi, Japanese patent 06 16 962, 1994 Chem Abs;121:37586p.

[28] Nippon Kayaku, Japanese patent 07 258 570-1, 1995 Chem Abs;124:90176t–7u.

[29] BASF, 1993 German patent 4 215, 495.

[30] Mitsui Toatsu, Japanese patent 08 12 660, 1996 Chem Abs;124:317145h.

[31] Bayer, West German patent 3 618 752, 1987.

[32] Rys P. In: Peters AT, Freeman HS, editors. Physicochemical principles of colour chemistry. Glasgow: Blackie, 1996 [chapter 1]. p. 1.

[33] Diener H, Güleç B, Skrabal P, Zollinger H. Helv Chim Acta 1989;72:800.

[34] Sokolowska-Gajda J, Freeman HS. Dyes and Pigments 1992;20:137.

[35] Sokolowska-Gajda J, Freeman HS, Reife A. In: Reife A, Freeman HS, editors. Environmental chemistry of dyes and pigments. New York: John Wiley, 1996 [chapter 10]. p. 239.

[36] Penchev A, Simov D, Gadjev N. Dyes and Pigments 1991;16:77.

[37] Désilets D, Hamer GK. Dyes and Pigments 1993; 22:183.

[38] Jirman J, Cermák J. Dyes and Pigments 1989;10:239.

[39] Agfa-Gevaert, European patent 687 674, 1995.

[40] Eastman Kodak, US patent 5 179 207, 1993.

[41] Mitsubishi, Japanese Patent 05 17 699, 1989 Chem Abs;119:74601u.

[42] Modi BR, Mistry, BD. J Inst Chem (India) 1993;65:63.

[43] Desai KR, Modi BR, Mistry, BD. J. Indian Chem Soc 1995;72:141.

[44] Bello KA, Martins CMOA, Adamu IK. Colourage 1995;42(8):29.

[45] Rangnekar DW, Kazemi GJ, Puro SS. In: Yoshida Z, Shirota Y, editors. Proceedings of 2nd International Symposium on the Chemistry of Functional Dyes. Tokyo: Mita, 1993. p. 816.

[46] Dalal MM, Desai KR. Orient. J Chem 1995;11:71.

[47] Dalal MM, Desai KR. Indian J Fibre Text Res 1996;21:161.

[48] Desel HE, Desai KR. Orient J Chem 1996;12:193.

[49] Modi BR, Desai KR. Proc Nat Acad Sci, India, Sect A 1993;63:595.

[50] Malankar UV, Desai KR. Orient J Chem 1994;10:301.

[51] Desai V, Desai KR. J Inst Chem (India) 1995;67:141.

[52] Modi BR, Desai KR. J Inst Chem (India) 1994;66:22.

[53] Modi BR, Desai KR. Indian J Fibre Text Res 1994;19:46.

[54] Rangnekar DW, Chaudhari MB. Dyes and Pigments 1989;10:173.

[55] Sandoz, US patent 5 101 021, 1992.

[56] Peters AT, Gbadamosi NMA. Dyes and Pigments 1992;18:115.

[57] Peters AT, Tsatsaroni E, Ma Xisai. Dyes and Pigments 1992;20:41.

[58] Peters AT, Taebi A, Yang SS. J Soc Dyers Colourists 1993;109:397.

[59] Malinowski W, Szadowski, J Pol J Appl Chem 1993; 37:127.

[60] Peters AT, Yang SS, Chisowa E. Dyes and Pigments 1995;28:151.

[61] Peters AT, Yang SS. Dyes and Pigments 1996;30:291.

[62] Peters AT, Chisowa E. Dyes and Pigments 1996;31:131.

[63] Mitsubishi, Japanese patent 62 39 663, 1987 Chem Abs;107:116951t.

[64] Hoechst Mitsubishi, European patent 659 841, 1995.

[65] Mitsubishi, Japanese patent 03 02 275, 1987 Chem Abs;115:51852e.

[66] BASF, German patent 3 938 093, 1991.

[67] Ertan N, Eyduran, F. Dyes and Pigments 1995;27:313.

[68] Temel S, Özbey S, Ertan N. Dyes and Pigments 1996;32:237.

[69] Özbey S, Kendi E, Ertan N. Dyes and Pigments 1997;33:251.

[70] Peng Q, Li M, Gao K, Cheng L. Dyes and Pigments 1991;15:263.

[71] Peters AT, Mehdi Shahab Dekhordi M. J. Soc Dyers Colourists 1990;106:275.

[72] Peters AT, Wu CT, Viscardi G, Barni E. Dyes and Pigments 1995;29:103.

[73] BASF, European patent 390 027, 1990.

[74] Bello KA. Near infrared absorbing dyes. Ph.D. thesis, University of Leeds (UK), 1986.

[75] Bello KA, Griffiths JJ. Chem Soc Chem Commun 1986;1639.

[76] Bello KA. Dyes and Pigments 1995;27:45.

[77] Bello KA. J Soc Dyers Colourists 1997;113:361.

[78] Griffiths J, Riepl CJ. Chem Commun 1998;1349.

[79] Tanaka K, Nomura K, Oda H, Yoshida S, Mitsuhashi KJ. Het Chem 1991;28:907.
[80] Chao YC, Chen SS. Dyes and Pigments 1994;24:205.
[81] Seu G. Dyes and Pigments 1993;23:267.
[82] Seu G, Mura L. Am Dyestuff Rep 1996;85(3):44.
[83] Tsatsaroni EG. Dyes and Pigments 1996;31:301.
[84] Kehayoglou AH, Tsatsaroni EG. Dyes and Pigments 1993;23:53.
[85] Kehayoglou AH, Tsatsaroni EG, Eleftheriadis IC, Loufakis KC, Kyriazis LE. Dyes and Pigments 1997;34:207.
[86] Shenai VA. Text Dyer Printer 1998;31(3):11.
[87] Elsner P. Textilveredlung 1994;29:98.
[88] Hatch KL, Maibach HI. Text Chem Colorist 1998;30(3):22.
[89] Clarke EA, Steinle D. Rev Prog Coloration 1995;25:1.
[90] Platzek T. Melliand Textilber 1996;77:774 (E165).
[91] Ragharan V. Colourage 1998;45(3):19.
[92] Zollinger H. Melliand Textilber 1988;69:644.
[93] Kraska J, Sokolowska-Gajda J. Dyes and Pigments 1987;8:345.
[94] Sokolowska-Gajda J. Dyes and Pigments 1991;15:239.
[95] Sokolowska-Gajda J. Dyes and Pigments 1992;18:103.
[96] Sokolowska-Gajda J. Dyes and Pigments 1992;19:149.
[97] Sokolowska-Gajda J. Dyes and Pigments 1994;26:69.
[98] BASF, European patent 400 451, 1990.
[99] DyStar Japan, European patent 751 187, 1997.
[100] Nippon Kayaku, Japanese patent 05 163 442-3, 1993 Chem Abs;120:10319–20.
[101] Bayer, European patent 736 576, 1996.
[102] Nippon Kayaku, European patent 678 560, 1995.
[103] Kiwa Kagaku Kogyo, Japanese patent 08 217 987, 1986 Chem Abs;125:303249d.
[104] Asahi Chemical, Gunsen KK. Japanese patent 05 279 971, 1993 Chem Abs;120:220312q.
[105] Ciba-Geigy, European patent 335 834, 1989.
[106] Ciba-Geigy, European patent 385 938, 1990.
[107] Ciba-Geigy, German patent 4 213 395, 1992.
[108] BASF, European patent 569 759, 1993.
[109] BASF, German patent 4 339 270, 1995.
[110] BASF, European patent 390 024, 1990.
[111] BASF, European patent 335 234, 1989.
[112] BASF, German patent 3 723 884, 1989.
[113] BASF, German patent 3 816 698, 1989.
[114] BASF, European patent 362 708, 1990.
[115] BASF, German patent 3 833 443, 1990.
[116] Arcoria A, De Giorgi MR, Fatuzzo F, Longo ML. Dyes and Pigments 1993;21:67.
[117] Hallas G. J Soc Dyers Colourists 1979;95:285.
[118] De Giorgi MR, Carpignano R. Melliand Textilber 1993;74:234 (E108).
[119] De Giorgi MR, Carpignano R, Cerniani A, Cesare F. Ann Chim (Rome) 1995;85:543.
[120] De Giorgi MR, Carpignano R, Cerniani A. Dyes and Pigments 1998;37:187.
[121] Peng Q, Li M, Gao K, Cheng L. Dyes and Pigments 1990;14;89.
[122] Peng Q, Li M, Gao K, Cheng L. Dyes and Pigments 1992;18:271.
[123] Leadbetter PW, Leaver AT. Rev Prog Coloration 1989;19:33.
[124] Leaver AT, Glover B, Leadbetter PW. Text Chem Colorist 1992;24:18.
[125] Zeneca, European patent 580 284, 1994.
[126] ICI, European patent 297 710, 1987.
[127] ICI Brazilian patent 87/15 192, 1989 Chem Abs; 111:98959c.
[128] Zeneca, European patent 588 489, 1994.
[129] Zeneca, British patent 2 312 436, 1997.
[130] Bayer, European patent 708 152, 1996.
[131] BASF, West German patent 3 738 910, 1989.
[132] BASF US patent 4 814 465, 1989.
[133] Sumitomo, European patent 727 464, 1996.
[134] DyStar Japan, Japanese patent 09 87 538, Chem Abs 1997;127:19452m.
[135] Hoechst Mitsubishi, European patent 518 133, 1992.
[136] Hihara T, Takahashi Y, Himeno K. International Symposium in Wakayama on Dyeing and Finishing of Textiles Conference Proceedings, Wakayama (Japan), November–December 1998. p. 186.
[137] Hoechst Mitsubishi, European patent 673 977, 1995.
[138] Hoechst Mitsubishi, Japanese patent 06 322 285, 1994 Chem Abs;122: 108664w.
[139] Hoechst Mitsubishi, Japanese patent 07 304 989, 1995 Chem Abs;124: 234856q.
[140] DyStar Japan, Japanese patent 08 311 364, 1995 Chem Abs;126:158745b.
[141] Sumitomo, Japanese patent 10 53 717, 1998 Chem Abs;128:218329x.
[142] Sumitomo, Japanese patent 10 53 718, 1998 Chem Abs;128:231581t.
[143] DyStar Japan, European patent 714 956, 1996.
[144] DyStar European patent 771 856, 1997.
[145] Hoechst Mitsubishi, European patent 684 290, 1995.
[146] BASF, West German patent 3 622 297, 1988.
[147] Hoechst Mitsubishi, Japanese patent 07 252 427, 1995 Chem Abs;124:90171u.
[148] Nippon Kayaku, Japanese patent 01 266 167, 1989 Chem Abs;113:61298b.
[149] Rangnekar DW, Chitale RS. Indian J Fibre Text Res 1990;15:81.
[150] Rangnekar DW, Jhaveri PV. Indian J Fibre Text Res 1990;15:26.
[151] Hoechst Mitsubishi, European patent 579 192, 1994.
[152] BASF, German patent 4 138 550, 1993.
[153] Ciba-Geigy, European patent 699 718, 1996.
[154] BASF, European patent 534 296, 1993.
[155] BASF, German patent 3 639 942, 1988.
[156] BASF, German patent 3 833 442, 1990.
[157] BASF, German patent 3 718 565, 1988.
[158] Sumitomo, German patent 19 727 442, 1998.
[159] BASF, US patent 5 064 962, 1991.
[160] Clariant, US patent 5 679 800, 1997.

[161] Osaka Gas Co., Japanese patent 05 125 074, 1993 Chem Abs;119:162377f.
[162] Gewald K, Schinke E, Böttcher H. Chem Ber 1996; 99:94
[163] Sabnis RW, Rangnekar DW. Dyes and Pigments 1989;10:295.
[164] Amine MS, Serb J Chem Soc 1992;57:503.
[165] Deleted in proof.
[166] Sabnis RW, Rangnekar DW. Indian J Fibre Text Res 1992;17:58.
[167] Sabnis RW, Rangnekar DW. J Chem Tech Biotechnol 1990;47:39.
[168] Sabnis RW, Kazemi G, Rangnekar DW. Bull Chem Soc Jpn 1991;64:3768.
[169] Hallas G, Towns AD. Dyes and Pigments 1996;31:273.
[170] Gewald K. Chem Ber 1965;98:3571.
[171] Hallas G, Towns AD, Dyes and Pigments 1996;32:135
[172] Hallas G, Towns AD, Dyes and Pigments 1997;33:319.
[173] Hallas G, Towns AD, Dyes and Pigments 1997;33:205.
[174] Hallas G, Towns AD, Dyes and Pigments 1997;34:133.
[175] Towns AD. Synthesis and coloration properties of novel heterocyclic azo dyes. Ph.D. thesis, University of Leeds (UK) 1995.
[176] Hallas G, Towns AD. Dyes and Pigments 1997;33:215.
[177] Hallas G, Towns AD. Dyes and Pigments 1997;35:45.
[178] BASF, European patent 315 899, 1989.
[179] Hallas G, Towns AD. Dyes and Pigments 1997;35:219.
[180] Bayer, West German patent 3 637 223, 1988.
[181] BASF, West German patent 3 622 136, 1988.
[182] Ho YW, Wang IJ. Dyes and Pigments 1995;29:117.
[183] Rangnekar DW, Kamat PY. Indian J Fibre Text Res 1991;16:223.
[184] Rangnekar DW, Kamat PY. Indian J Fibre Text Res 1992;17:95.
[185] Ho YW, Wang IJ. Dyes and Pigments 1995;29:295.
[186] Leadbetter PW, Dervan S. J Soc Dyers Colourists 1992;108:369.
[187] Choi J-H, Hong S-H, Towns AD. J Soc Dyers Colourists 1999;115:32.
[188] Afifi TH, Sayed AZ. J Soc Dyers Colourists 1997;113:256.
[189] Seu G, Mura L. Ann Chim (Rome) 1992;82:185.
[190] Seu G, Mura L, Massacesi M. Am Dyestuff Rep 1997;86(9):57.
[191] Seu G. Dyes and Pigments 1992;20:247.
[192] Seu G. Melliand Textilber 1993;74:651 (E254).
[193] Seu G, Diaz A. Ann Chim (Rome) 1993;83:413.
[194] Sandoz, British patent 2 258 658, 1993.
[195] Sharma K, Jain R. Asian J Chem. 1994;6:273.
[196] Bayer, German patent 4 343 454, 1995.
[197] Viscardi G, Savarino P, Quagliotto P, Alberti G, Loi A. Dyes and Pigments 1992;19:291.
[198] Rahman MA, Shakra S, Ghattas AA, Ghany HA, Mostafa HM. Am Dyestuff Rep 1993;83(2):44
[199] Malankar UH, Desai KR. Orient J Chem 1994;10:77.
[200] Rajagopal R, Seshadri S. Dyes and Pigments 1990;13:93.
[201] Daud J, Saxena SB. J Soc Dyers Colourists 1994;110:154.
[202] Desai TR, Desai KR. Asian J Chem 1997;9:677
[203] Boehringer Mannheim, European patent 457 184, 1991.
[204] Martinez R, Arteaga P, Mancera C. J Het Chem 1996;33:489.
[205] Graham D, McLaughlin C, McAnally G, Jones JC, White PC, Smith WE. Chem Commun 1998;1187.
[206] ICI, British patent 2 237 804, 1991.
[207] ICI, European patent 280 434, 1988.
[208] Mitsui Toatsu, Japanese patent 10 58 828, 1998 Chem Abs;128:250725j.
[209] Mitsui Toatsu, Japanese patent 10 181 201, 1998 Chem Abs;129:115679.
[210] Mitsui Toatsu, Japanese patent 10 181 203, 1998 Chem Abs;129:115680w.
[211] Gray GW. Chimia 1980;34:47.
[212] Nippon Oil and Fats Co., Japanese patent 04 279 556, Chem Abs 1992;118:168979e.
[213] Mitsubishi, Japanese patent 10 60 445, 1998 Chem Abs;128:251018t.
[214] Bradbury R. In: Peters AT, Freeman HS, editors. Modern colorants: synthesis and structure. Glasgow: Blackie, 1995 [chapter 6].
[215] Bradbury R. Colour Science 98 Conference Proceedings, Colour Science 98, Harrogate (UK) March–April 1998.
[216] Murray SG. Solution and polymer photochemistry of azo dyes. Ph.D. thesis, University of Leeds (UK), 1985.
[217] BASF, European patent 442 360, 1991.
[218] Ciba-Geigy, German patent 4 200 739, 1992.
[219] Ciba-Geigy, German patent 4 218 688, 1992.
[220] Mitsui Toatsu, Dainippon, Japanese patent 06 206 383, 1994 Chem Abs;122:42797h.
[221] Mitsui Toatsu, Dainippon, Japanese patent 06 206 382, 1994 Chem Abs;122:119056a.
[222] Nippon Kayaku, Japanese patent 08 207 456, 1996 Chem Abs;125:288864e.
[223] Nippon Kayaku, Japanese patent 09 255 884-5, 1997 Chem Abs;127:332786y–7z.
[224] Eastman Kodak, US patent 5 079 213, 1992.
[225] Eastman Kodak, US patent 5 126 314, 1992.
[226] Eastman Kodak, European patent 492 444, 1992.
[227] Eastman Kodak, US patent 5 126 312, 1992.
[228] BASF, German patent 4 426 023, 1996.
[229] Agfa-Gevaert, European patent 701 906, 1996.
[230] Agfa-Gevaert, European patent 788 891, 1997.
[231] Fuji Photo Film Co., Japanese patent 06 106 862, 1994 Chem Abs;121:303223h.
[232] Mitsubishi, Japanese patent 08 113 722, 1996 Chem Abs;125:117387x.
[233] Ciba-Geigy, German patent 4 139 684, 1992.
[234] Eastman Kodak, US patent 5 126 314, 1992.
[235] Mitsubishi, Japanese patent 06 145 543, 1994 Chem Abs;121:303051a.
[236] Mitsubishi, Japanese patent 06 145 541, 1994 Chem Abs;121:233070e.
[237] Mitsubishi, Japanese patent 06 145 544, 1994 Chem Abs;121:282311t.

[238] Mitsubishi, Japanese patent 06 145 542, 1994 Chem Abs;121:233071f.
[239] Mita, Japanese patent 05 107 786, 1994 Chem Abs;119:82901g.
[240] Dainippon, Japanese patent 05 150 523, 1993 Chem Abs;119:259520k.
[241] Dainippon, Japanese patent 05 188 607, 1993 Chem Abs;119:259507m.
[242] Mitsubishi, Japanese patent 08 166 689, 1996 Chem Abs;125:208403r.
[243] Orient Chemical Ind., Japanese patent 04 13 664, 1992 Chem Abs;116:257371b.
[244] Sharp, Japanese patent 10 36 692, 1998 Chem Abs;128:193735m.
[245] Burland DM. Chem Rev 1994;94:1.
[246] Chemla DS, Zyss J, editors. Nonlinear optical properties of organic molecules and crystals, vol. 1. London: Academic Press, 1987.
[247] Zyss J, editor. Molecular nonlinear optics. London: Academic Press, 1994.
[248] Varanasi PR, Jen AK-Y, Chandrasekhar J, Namboothiri INN, Rathna A. J Am Chem Soc 1996;118:12443.
[249] Hutchings MG, Ferguson I, McGeein DJ, Morley JO, Zyss J, Ledoux I. J Chem Soc Perkin Trans 2 1995;171.
[250] Morley JO, Pugh D. J Chem Soc Faraday Trans 1991;87:3021.
[251] Morley JO, Hutchings MG, Zyss J, Ledoux, I. J Chem Soc Perkin Trans 2 1997;1139.
[252] Watanabe T, Amano M, Tomaru S. Japan J Appl Phys 1994;33:L1683.
[253] Matsui M, Kushida M. Funabiki K, Shibata K, Muramatsu H, Hirota K, Hosoda M, Tai K. Dyes and Pigments 1998;37:283.
[254] Xin Zhong, Huang Deyin, Abstracts of the Third International Symposium on Functional Dyes, University of California at Santa Cruz, Santa Cruz (CA), 1995. p. 69.
[255] BASF, European patent 535 490, 1993.
[256] BASF, European patent 625 553, 1994.
[257] BASF, German patent 4 339 712, 1995.
[258] BASF, German patent 19 525 304, 1997.
[259] BASF, European patent 748 853, 1996.
[260] Matsui M, Marui Y, Kushida M, Funabiki K, Muramatsu H, Shibata K, Hirota K, Hosoda M, Tai K. Dyes and Pigments 1998;38:57.
[261] Moylan CR, Twieg RJ, Lee VY, Swanson SA, Betterton KM, Miller RD. J Am Chem Soc 1993;115:12599.