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Disperse Dyes Derived from 5-Substituted-3-Amino-1,2,4-Triazoles

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ABSTRACT

A series of aminoazo disperse dyes have been synthesized by coupling N,N-disubstituted anilines with diazotized 5-substituted-3-amino-1,2,4-triazoles. The dyes were applied to nylon, triacetate and polyester fibres and their properties evaluated.

1 INTRODUCTION

In a previous paper[1] we described the dyeing properties of a series of heterocyclic dyes obtained coupling substituted anilines with diazotized 3-amino-1,2,4-triazole. The simple synthesis of both amine[2] and dyes, their relatively cheapness and the presence of the triazole ring, allows a wide application of these dyes as cationic or metal-complex colourants at the azole nitrogen. However, owing to their high aqueous solubility, the fastness properties of the dyes were not high and their use in HT dyeing was unsatisfactory. In continuation of our studies on improving the fastness properties of these dyes and also on making them more suitable for HT polyester dyeing, we report here the synthesis and properties of a series of triazole azo dyes of the general formula given in Fig. 1, obtained by coupling N,N-disubstituted anilines with diazotized 3-amino 5-substituted triazoles. Comparison is made between these dyes and those derived from 3-amino triazole.[1]

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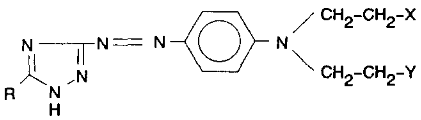
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Fig. 1. General formula for azo dyes (X = H, OH, CN; Y = H, OH, CN; R = phenyl, 3-NO_2-phenyl, 4-NO_2-phenyl.

2 EXPERIMENTAL

2.1 Coupling components

N,N-bis-(2-cyanoethyl)aniline[3] (e), N-ethyl-N-(2-cyanoethyl)aniline[4] (c) and N-ethyl-N-(2-hydroxyethyl)aniline[5] (b) were prepared as indicated in the literature. N,N-bis-(2-hydroxyethyl)aniline (d) and N,N-diethylaniline (a) were commercial products.

2.2 Diazo components

2.2.1 3-Amino-5-phenyl 1,2,4-triazole (1)

Equimolar amounts of benzoyl chloride and aminoguanidine bicarbonate in benzene were stirred at room temperature for 12 h.[6] The benzamide-guanidine hydrochloride was filtered, dissolved in water and the solution basified with Na_2CO_3 to give the free base, which was cyclized to 3-amino-5-phenyl 1,2,4-triazole by heating in an oil bath for 5 min at 200°C.

2.2.2 3-Amino-5-(3-nitrophenyl)-1,2,4-triazole (2) and 3-amino-5-(4-nitrophenyl) 1,2,4-triazole (3)

These were obtained using the method described by Grinstein & Chipen[7] by heating aminoguanidine hydrochloride with the appropriate acyl chloride. The condensation products, when refluxed for 0·5 h with KOH gave the 5-substituted triazoles.

2.3 Synthesis of dyes

The 3-amino-5-substituted 1,2,4-triazoles were diazotized at 0–5°C in aqueous sulphuric acid and coupled at pH 3–4. After coupling the reaction mixtures were neutralized with Na_2CO_3, the dyes collected, washed with water and crystallized until a constant melting point was obtained. The purity of the dyes was checked by using reversed-phase high-performance liquid chromatography (RP-HPLC) with a Waters 600 chromatograph. The detector was a Gilson 116 model, operating at 260 nm; the column a 25 cm × 4 mm Perkin-Elmer C-18 X10. The integrator was a Hewlett-

TABLE 1
Characterization Data for the Triazole Dyes

Dye	*R*	*X*	*Y*	λ_{max} *(nm)*	*log* ε	λ_{em} *(nm)*	*RFI*[a]	*m.p. (°C)*	*RT (m)*
1a	F	H	H	466	4, 46	654	1·00	135	4·35
1b	F	H	OH	462	4, 48	652	1·29	187	3·01
1c	F	H	CN	462	4, 50	650	0·60	230	3·01
1d	F	OH	OH	459	4, 46	640	0·53	206	2·57
1e	F	CN	CN	412	4, 19	610	0·44	129	2·54
2a	MT	H	H	476	4, 62	658	0·27	154	4·87
2b	MT	H	OH	474	4, 57	660	1·46	205	3·10
2c	MT	H	CN	477	4, 53	645	1·44	138	2·90
2d	MT	OH	OH	470	4, 58	646	0·11	141	2·55
2e	MT	CN	CN	425	4, 39	628	1·04	245	2·26
3a	PT	H	H	473	4, 54	654	0·92	231	3·68
3b	PT	H	OH	472	4, 67	636	4·50	237	3·05
3c	PT	H	CN	459	4, 52	630	1·15	232	2·84
3d	PT	OH	OH	481	4, 61	660	1·46	220	2·58
3e	PT	CN	CN	425	4, 38	618	0·50	270	2·15

F, phenyl; MT, *m*-NO_2-phenyl; PT, *p*-NO_2-phenyl.

[a] Fluorescence intensity relative to dye 1a.

Packard 3393A model. The mobile phase was a methanol/water mixture 85:15 v/v; characterization data of the dyes are reported in Table 1.

2.4 General

UV/visible spectra were determined on a Hitachi 150-20 spectrophotometer using methanol as solvent. Fluorescence spectra were recorded on the solid material using an Hamamatsu GaAs fototube equipped with a Spex monochromator; the wavelength of excitation was 457·9 nm. The colour parameters of the dyed fabrics were determined with a Minolta CR 200 Chroma Meter, using the C source as illuminant. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. The IR spectra showed a broad band at 3100–3300 cm^{-1} (ν N—H bonded), and well-defined absorption bands at 1600 cm^{-1} (ν C=N, C=C), 1550 cm^{-1} (ν NO_2) and 1150 cm^{-1} (ν Ph—N). The ^1H NMR spectra showed no signal for the NH, probably because of tautomeric exchanges; only the signals of the alkyl chain protons and a multiplet at 6·7–7·4 ppm for the aromatic protons were observed. Dyeings were carried out as indicated in Ref. 1 and fastness properties were assessed according to the ISO standard procedures.[8]

3 RESULTS AND DISCUSSION

3.1 Electronic spectra

From the data reported in Table 1 it is apparent that substitution of the beta hydrogen atom in the alkyl chain of the coupling component with OH or CN groups exerts a hypsochromic effect, λ_{max} being displaced up to 50 nm. The λ_{max} of the dyes are roughly related to the inductive effects and to the number of these substituents.

Comparison of the spectra of the dyes with the triazole analogues[1] (Fig. 1, R = H) indicates that the replacement of the hydrogen in the 5 position of the triazole ring with a phenyl group produces a bathochromic shift of about 30 nm. A further bathochromic shift of about 10–20 nm is obtained with introduction of a nitro group into the 3 or 4 position of the phenyl ring. The smallness of this shift, and the fact that absorption maxima of the meta isomers are, on average, at longer wavelength than those of the corresponding para isomers, suggests that the nitro group basically acts by means of inductive effects rather than by conjugative effects.

Emission maxima for the fluorescence spectra are contained in a range of 50 nm. Both emission maxima and RFIs are roughly related respectively to λ_{max} and log ε of the absorption spectra. It appears that the same factors which influence the absorption spectra are also operative in determining the fluorescence spectra.

3.2 Colour properties

According to the dye structure and/or the fibre used, these triazole dyes give bright shades ranging from yellow to red-orange (Table 2). Considering the dominant wavelength with respect to the fibre used, it is apparent that the median of the λ_D values for nylon is higher than those for polyester and triacetate. For variations in the diazo component of the dyes, the substitution of the CH hydrogen in the triazole ring with a phenyl or a nitrophenyl group causes a general bathochromic shift of the λ_D which is more pronounced for the para isomers than for the meta isomers. The dominant wavelength is also influenced by the structure of the coupling component and the trend is similar to that observed for the absorption spectra. In fact, the medians of the λ_D values calculated for all the fibres decrease as the electron withdrawing power and the number of X and Y substituents in the alkyl chain increases. The trends of the purity values are quite different for every fibre. The chromaticity coordinates for the nylon fibres are regularly clustered along one line approximately parallel and near the spectral loci line, and the x and y values are highly

TABLE 2
Colour Properties of the Dyes

Dye	x	y	Y (%)	p (%)	λ_D (nm)	L^* (%)	a^*	b^*
1a[a]	0·56	0·41	32·65	93·0	591	64·1	39·8	80·6
1a	0·54	0·41	34·01	87·5	590	65·0	34·8	73·3
1a	0·47	0·43	41·06	73·6	582	70·2	11·9	62·8
1b	0·57	0·40	30·90	92·4	592	62·4	44·1	81·7
1b	0·46	0·42	46·70	67·9	583	73·9	13·5	59·6
1b	0·53	0·43	32·71	89·1	587	64·0	26·6	76·6
1c	0·56	0·40	29·60	89·0	592	61·3	41·7	75·8
1c	0·48	0·42	41·20	71·7	585	70·3	19·5	63·2
1c	0·52	0·43	33·80	89·1	586	64·8	24·5	74·9
1d	0·55	0·42	34·00	91·2	589	65·0	37·1	86·2
1d	0·37	0·38	58·10	35·9	574	80·5	1·0	29·8
1d	0·43	0·46	52·00	64·2	580	77·2	−6·7	64·1
1e	0·48	0·47	57·90	84·9	578	80·7	4·0	92·5
1e	0·40	0·46	74·20	61·1	572	89·0	−6·2	32·4
1e	0·44	0·43	45·40	71·7	576	73·2	6·4	58·0
2a	0·57	0·40	29·04	89·0	592	60·8	43·1	77·1
2a	0·53	0·41	33·00	83·9	589	64·2	34·8	68·3
2a	0·48	0·42	31·40	70·9	586	62·5	18·7	54·3
2b	0·57	0·40	27·10	92·4	592	59·0	43·2	75·1
2b	0·45	0·41	47·70	62·3	583	74·7	13·1	39·2
2b	0·48	0·41	36·10	70·9	586	66·6	20·1	54·8
2c	0·51	0·43	27·01	85·4	585	58·9	25·3	61·9
2c	0·44	0·44	51·60	37·3	578	77·0	2·8	60·7
2c	0·37	0·39	52·90	37·3	576	77·8	−1·9	31·3
2d	0·56	0·40	23·50	89·0	592	55·6	38·2	68·9
2d	0·43	0·40	47·30	54·0	583	74·3	12·9	40·5
2d	0·47	0·42	37·00	70·4	584	67·3	17·2	55·2
2e	0·48	0·48	50·83	86·8	578	76·6	4·0	92·5
2e	0·41	0·44	61·40	61·1	574	82·6	−7·2	37·9
2e	0·43	0·45	50·10	67·9	576	76·1	−1·9	57·4
3a	0·58	0·39	26·80	91·0	595	58·8	48·4	74·6
3a	0·50	0·42	35·13	79·6	585	73·2	17·3	44·3
3a	0·47	0·40	37·00	66·7	585	67·2	22·2	47·9
3b	0·55	0·41	31·80	88·8	591	64·0	37·3	79·9
3b	0·52	0·40	33·50	83·7	589	64·6	34·0	68·0
3b	0·51	0·41	25·40	80·4	588	57·5	27·6	56·9
3c	0·57	0·39	25·20	90·0	594	57·3	45·0	68·9
3c	0·52	0·42	37·90	85·5	586	67·9	26·4	78·0
3c	0·52	0·43	35·50	87·3	585	66·1	22·4	79·9
3d	0·58	0·38	25·50	90·0	595	57·6	47·9	70·8
3d	0·50	0·40	35·10	71·4	589	73·2	29·8	56·8
3d	0·53	0·41	29·20	81·0	591	60·9	33·8	64·7
3e	0·48	0·46	50·50	86·8	580	76·4	10·4	85·2
3e	0·43	0·45	55·10	69·2	577	79·1	−1·8	63·6
3e	0·46	0·46	46·50	77·4	579	73·8	2·5	71·4

[a] The first row values of each figure refer to nylon, the second to triacetate, the third to polyester respectively.

correlated with a correlation coefficient of −0·97. The dyeings on nylon thus have the highest saturation values and show the widest range of colours. The chromaticity coordinates for triacetate can still be clustered along one line parallel to the spectral loci, but the x and y values are more scattered than those for nylon. The dyeings on triacetate thus have, on average, lower purity values than those on nylon, but still gave a wide range of colours. The chromaticity coordinates for polyester fall into two different clusters. The first one includes dyes with saturation values comparable to those for nylon. All the other dyes, which gave low saturation values presumably due to dye degradation under high temperature conditions, are included in the other, although the possibility of a high aqueous solubility of the triazole dyes at this temperature cannot be overlooked. Lightness of the dyeings was higher on polyester than on triacetate and nylon. The phenyl substituted dyes had higher fastness than either the meta or para nitro analogues, and the bis-cyano dyes (1e, 2e, 3e) showed the highest ratings, and the dyes with unsubstituted alkyl chains showed the lowest.

3.3 Dyeing properties

All the dyes exhibited good build-up, levelling and migration properties. In previous work, we noted that the triazole dyes were not very fast and did not show much substantivity for polyester. In fact only the most hydro-phobic of the series gave dyeings of some practical interest on this fibre. Comparison of the retention times of these dyes with the triazole analogues (Fig. 1, R = H) indicates that the substitution of the C—H hydrogen of the triazole ring with a phenyl or nitro-phenyl group increases the hydrophobicity of the dyes and substantially improves the dyeing properties.

From the data reported in Table 1 it is observed that dye hydrophilicity is related to both the diazo and the coupling components. Increasing the number of X and Y substituents increases the hydrophilicity, CN being more active than OH in promoting dye hydrophilicity, which is also higher for the nitro analogues. Fastness to washing was very good for all fibres especially for triacetate and polyester, on which fibres the dyes also showed good stability to severe washing (Table 3).

Fastness to dry cleaning was also good on all fibres. Triazole itself is readily soluble in polar solvents and only slightly soluble in non-polar solvents. The low solubility of the triazole dyes in perchloroethylene can be explained by taking into account the tendency of the 1,2,4-triazole ring to aggregate in an intermolecular association in which the hydrogen atom of the imino group protonates the pyridine-like nitrogen of an

TABLE 3
Fastness Properties of the Dyes

Dye no.	*Washing*[b]									*Perspiration*	*Dry cleaning*[c]			*Light*
	40°C			*60°C*			*95°C*							
1a[a]	5	4–5	5	4–5	4	4–5	2–3	2–3	3	5	5	4–5	4	2–3
1a	5	5	5	5	5	5	5	4–5	5	5	4	5	4–5	3
1a	5	5	5	5	5	5	4–5	4–5	4–5	4–5	4–5	5	4–5	2–3
1b	5	4–5	4–5	4–5	4	4–5	4–5	5	4–5	5	5	5	5	3
1b	5	5	5	5	5	5	5	5	4–5	4–5	4	5	5	3
1b	5	5	5	5	5	5	5	4–5	5	4–5	4	5	5	2
1c	5	5	5	4–5	4	4–5	2–3	2	3	5	5	5	5	3
1c	5	5	5	5	5	5	5	4–5	4–5	5	4	5	5	3
1c	5	5	5	5	5	5	5	4–5	5	4–5	4–5	5	5	3
1d	5	4–5	5	4–5	3–5	4–5	2	2	2–3	5	5	5	5	2–3
1d	5	5	5	4–5	5	4	4	4–5	4–5	5	5	5	5	2–3
1d	5	5	5	5	5	5	5	5	5	4–5	5	5	5	2–3
1e	5	5	5	5	4–5	5	2	2–3	3	4–5	5	5	5	4
1e	5	5	5	5	5	5	5	5	4–5	4–5	5	5	5	4–5
1e	4–5	5	5	4–5	5	4	5	5	4–5	4–5	5	5	5	4–5
2a	5	5	5	5	4–5	5	2	2	2–3	5	5	4	4–5	3
2a	5	5	5	5	5	5	5	4–5	4–5	5	4–5	5	5	3–4
2a	5	5	5	5	5	5	5	4–5	5	4	4	5	4–5	2–3
2b	5	5	5	5	4–5	5	2–3	2	2–3	5	5	4–5	5	3
2b	4–5	5	5	4–5	5	4	4	4–5	4–5	5	4	5	5	3
2b	5	5	5	5	5	5	5	4–5	5	5	4–5	5	5	2–3
2c	5	4–5	5	4–5	4	4–5	3	3	3–4	4–5	5	5	5	4
2c	4–5	5	5	4–5	5	4–5	4–5	5	4–5	5	5	5	5	4
2c	5	5	5	5	5	4–5	4–5	4–5	4–5	4–5	5	5	5	3–4
2d	5	5	5	5	4	5	2	1–2	2–3	5	5	5	5	3
2d	4–5	5	5	4–5	5	4–5	4–5	5	5	5	4–5	5	5	2–3
2d	5	5	5	5	5	4–5	4–5	4–5	5	4	4–5	5	5	2–3
2e	5	5	5	5	4–5	5	2	2–3	4	5	5	5	5	4
2e	5	5	5	5	5	4–5	4–5	5	4–5	5	5	4–5	5	4–5
2e	5	5	5	5	5	4–5	4–5	4–5	4–5	4–5	4–5	5	5	4–5
3a	5	4–5	5	4–5	4	4–5	1–2	1–2	2	5	5	5	5	3
3a	5	5	5	4–5	5	4–5	4–5	4–5	4–5	4–5	4	5	5	3
3a	5	5	5	5	5	4–5	4–5	4–5	4–5	4–5	5	5	5	3
3b	5	4–5	5	5	4	5	2	2	2–3	5	5	5	5	2–3
3b	5	5	5	5	5	5	5	4–5	5	5	4–5	5	4–5	3
3b	5	5	5	5	5	4–5	4–5	4	4	4–5	3	5	5	2–3
3c	5	4–5	5	4–5	4	4–5	2	1–2	3	5	5	4	5	4
3c	5	5	5	5	5	5	5	4–5	5	5	4	5	5	4
3c	5	5	5	5	5	5	5	5	4–5	4–5	4	5	5	3–4
3d	5	5	5	5	4–5	5	3	3	3–5	5	5	4	4–5	2–3
3d	4–5	5	5	4–5	5	4	4	4	4	5	3	4–5	5	3
3d	5	5	5	5	5	4–5	4–5	4	4–5	5	3	5	5	3
3e	5	5	5	4–5	4	4–5	2	2	2–3	5	5	5	5	4
3e	5	5	5	5	5	5	5	5	4–5	5	5	5	5	4–5
3e	5	5	5	5	5	4–5	4–5	4–5	5	5	5	5	5	4–5

[a] The first row of figures in each column refers to fastness on nylon, the second on triacetate and the third on polyester.

[b] The first column under each temperature refers to changes in colour of the specimens, the second to staining on the same kind of fibre and the third to staining on cotton.

[c] The first column refers to changes in colour of the specimens, the second to staining on cotton and the third to change in colour of solvent.

adjacent dye molecule.[1] The appearance in the solid state infrared spectra of the dyes of two peaks at about 3250 cm^{-1} and 3150 cm^{-1}, indicates the presence of an associated NH group[9] and appears to confirm this hypothesis.

Unfortunately, the light fastness of the dyes was not as good as the washing fastness and ranged from poor to moderate. Dyes containing a nitro group in the para position generally showed fastness similar to the meta substituents analogues. Lightfastness was lower on triacetate than on nylon, and was enhanced by the presence of electron attracting substituents (CN) in the alkyl chain of the coupling component.

CONCLUSIONS

Disperse dyes derived from 3-amino-1,2,4-triazole dyes are cheap and simple to make. They are also easy-levelling dyes that can be advantageously used for the dyeing of nylon articles whenever end-use requirements do not necessitate high fastness. The substitution of the C—H hydrogen of the triazole ring with a phenyl or nitro-phenyl group makes these dyes more hydrophobic fast and suitable also for dyeing polyester fibres. Light fastness is still not as good as washing fastness. Appropriate substitution in the triazole ring or in the coupling component could improve the dyeing properties. Further studies will be reported on the synthesis and use of triazole dyes in the dyeing of hydrophobic fibres.

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