Heterocyclic Azo Dyes. I

Azo Dyes Containing the Benzotriazole Nucleus

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Summary

The synthesis, some dyeing, and fastness properties of several new dispersed, acid, and direct dyes derived from the aminobenzotriazoles (I—IV) and 5-hydroxybenzotriazole (V) are described. The suitability of the amino derivatives (I—IV) as bases for azoic dyeing has also been studied. Several interesting observations between the properties of some synthesized dyes and the corresponding benzene or naphthalene analoges are cited.

Although the close analogy between the chemical properties of naphthylamines and naphthols and the corresponding amino- and hydroxy-derivatives of benzotriazole and its 2-aryl derivatives has been pointed out by FRIES and coworkers¹)²)³), only few attempts⁴)⁵)⁶) has been undertaken to use the latter derivatives as substitutes for the formers in dyestuff-synthesis.

In the present communication are described the synthesis and some important dyeing properties of several new dispersed, acid, and direct dyes using the benzotriazole derivatives, 4-amino- (Ia), 1-methyl-4-amino- (Ib), 5-amino- (IIa), 1-methyl-5-amino- (IIb), 2-methyl-4-amino- (III), 2-methyl-5-amino (IV), and 5-hydroxybenzotriazole (V). Moreover, the suitability of the amino derivatives (I—IV) for use as bases in azoic dyeing has also been investigated.

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1) K. FRIES and E. ROTH, Liebigs Ann. Chem. **389**, 318 (1912).

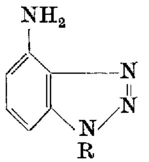
2) K. FRIES, E. SUDHOFF and A. BRETTSCHNEIDER, Liebigs Ann. Chem. **454**, 131 (1927).

3) K. FRIES, H. GÜTERBOCK and H. KUHN, Liebigs Ann. Chem. **511**, 213 (1934).

4) L. F. FIESER and E. L. MARTIN, J. Amer. chem. Soc. **57**, 1835 (1935).

5) M. SCALERA and F. H. ADAMS, J. Amer. chem. Soc. **75**, 715 (1953).

6) O. KYM and M. RINGER, Ber. dtsch. chem. Ges. **48**, 1676 (1915).



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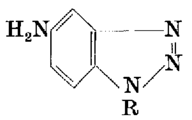
b, R = CH_3



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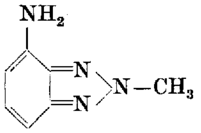

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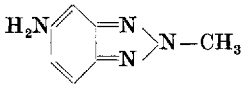

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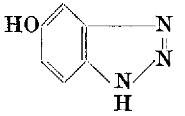

V

(i) Dispersed dyes

The preparation of the new dispersed dyes (cf. Table 1) was carried out using the usual methods of diazotisation and coupling. The aminobenzotriazoles (I—IV) were diazotized satisfactorily at 0—5° using nitrous acid. The resulting diazonium salts were generally used as soon as prepared, although undue decomposition of the salts in the cold solution was not observed. Coupling was carried out by careful addition of the diazonium salt to the coupling component. Dyes derived from 5-hydroxybenzotriazole (V) were prepared by adding the appropriate diazonium salt to a solution of the former compound.

Dyeings of dispersed dyes were made on nylon 66 fabric. The light and washing fastness properties were carried out in accordance with the standard methods for the assessment of the colour fastness of textiles⁷). The results obtained are summarized in Table 2.

It is now found from the dyeing experiments that all the synthesized dyestuffs are suitable for application as dispersed dyestuffs for nylon 66 and that they show good exhaustion on this fibre to give brilliant (yellow to bordeaux) shades. The light fastness varies considerably from 1 to 7. Those obtained from 2-naphthol show from fair to good light fastness. Dyestuffs obtained by coupling the diazonium salts with dimethylaniline, possess outstanding fastness properties. The light fastness of the dyestuffs obtained from 5-hydroxybenzotriazole (V) vary considerably and depend on the diazonium salts used.

In general however, they show poorer light fastness grading as compared with those derived from the aminobenzotriazole derivatives (I—IV). The washing fastness grading at 60° varies also between 2 and 4.

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7) The Society of Dyers and Colourists, "Standard Methods for the Assessment of the Colour Fastness of Textiles" Third report of the fastness tests co-ordinating committee, 19 Piccadilly Bradford, Yorkshire, 1955, p. 24 and 42.

Table 1

Azo dye	M. p. °	Solvent of crystallization	Analysis			Yield (%)
			Found N %	Formula	Requires N %	
Ia → 2-Naphthol	> 340	Ethanol	23.13	$C_{16}H_{11}N_5O$	23.42	77
IIa → 2-Naphthol	223	Methanol	23.05	$C_{16}H_{11}N_5O$	23.42	82
Ib → 2-Naphthol	254	Acetic acid	23.10	$C_{17}H_{13}N_5O$	23.10	80
IIb → 2-Naphthol	211	Ethanol	23.13	$C_{17}H_{13}N_5O$	23.10	79
III → 2-Naphthol	246	Benzene	23.11	$C_{17}H_{13}N_5O$	23.10	78
IV → 2-Naphthol	217	Acetic acid	23.62	$C_{17}H_{13}N_5O$	23.10	76
Ia → Dimethylaniline	227	Benzene	31.67	$C_{14}H_{14}N_6$	31.58	77
IIa → Dimethylaniline	217	Methanol	31.85	$C_{14}H_{14}N_6$	31.58	80
Ib → Dimethylaniline	202	Light petrol (b.p. 120—140°)-benzene	29.83	$C_{15}H_{16}N_6$	30.0	79
IIb → Dimethylaniline	235	Ethanol	30.42	$C_{15}H_{16}N_6$	30.0	78
III → Dimethylaniline	155	Methanol	29.93	$C_{15}H_{16}N_6$	30.0	79
IV → Dimethylaniline	177	Methanol	30.33	$C_{15}H_{16}N_6$	30.0	78
p-Aminoazobenzene → V	248	Ethanol	27.93	$C_{18}H_{13}N_7O$	28.59	78
5-Aminobenzofuran → V	246	Ethanol	25.12	$C_{14}H_9N_5O$	25.10	79
p-Aminodiphenyl → V	237	Ethanol	22.80	$C_{18}H_{13}N_5O$	22.32	80
p-Aminobenzenesulphonamide → V	> 340	Ethanol	26.10	$C_{12}H_{10}N_6O_3S$	26.43	79
p-Anisidine → V	260	Methanol	26.07	$C_{13}H_{11}N_5O_2$	26.04	81
o-Chloroaniline → V	248	Ethanol	26.04	$C_{12}H_8ClN_5O$	25.66	78
α-Naphthylamine → V	235	Acetic acid	23.85	$C_{10}H_{11}N_5O$	24.24	80
β-Naphthylamine → V	229	Acetic acid	24.60	$C_{10}H_{11}N_5O$	24.24	77
p-Nitroaniline → V	234	Acetic acid	29.19	$C_{12}H_8N_6O_3$	29.59	78
3-Methoxy-2-nitroaniline → V	> 340	Ethanol	26.88	$C_{13}H_{10}N_6O_4$	26.77	79

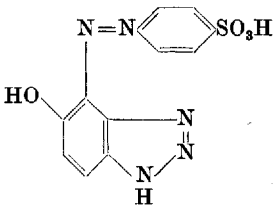
(ii) Acid dyes

A single azo group is known to be adequate for the production of useful dyes for wool and silk. In the present study the following monoazo dyes (VI, VII, VIII, and IX) containing the benzotriazole moiety were prepared

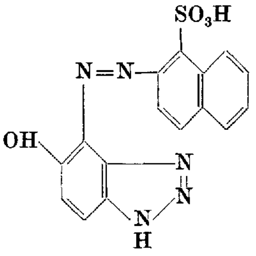
Table 2

Dye	Shade on nylon 66	Light fastness (day-light)	Washing fastness at 60°
IIa → 2-Naphthol	Bordeaux	4	3
Ia → 2-Naphthol	Orange	4	3–4
Ib → 2-Naphthol	Orange	3–4	2–3
IIb → 2-Naphthol	Orange-red	3	4
III → 2-Naphthol	Orange	4	2–3
IV → 2-Naphthol	Orange	5	3
Ia → Dimethylaniline	Orange-yellow	7	4
Ib → Dimethylaniline	Yellow	7	3–4
IIb → Dimethylaniline	Orange	6	3–4
III → Dimethylaniline	Yellow	7	4
IV → Dimethylaniline	Orange	7	2–3
p-Aminoazobenzene → V	Orange	5	4
5-Aminobenzofuran → V	Yellow	5	3
p-Aminodiphenyl → V	Orange	2	3
p-Aminobenzenesulphonamide → V	Orange	3	3–4
p-Anisidine → V	Orange	7	3
o-Chloroaniline → V	Orange	3	3
α-Naphthylamine → V	Orange	1	4
β-Naphthylamine → V	Orange	2	3
p-Nitroaniline → V	Brown	2	4–5
3-Methoxy-2-nitroaniline → V	Yellow	3	3–4

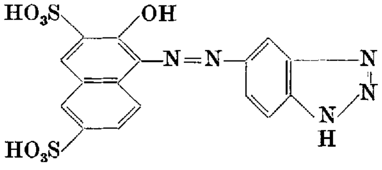
and their important dyeing and fastness properties for wool were investigated. The results are summarized in Table 3.



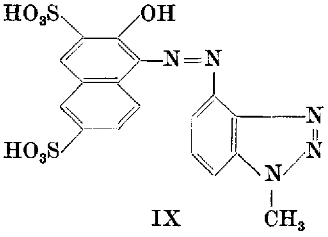
VI



VII



VIII



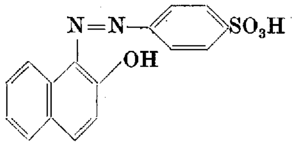
IX

Table 3

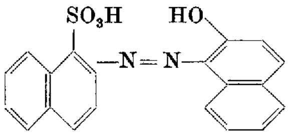
Dyestuff	Shade	Intensity of colour	Migration test	Light fastness (day-light)	Washing fastness at 40°	Washing fastness at 60°
VI	Orange	Moderate	4	5	5	3
VII	Orange	Good	3	4	5	3
VIII	Orange	Excellent	2	7	5	3
IX	Red	Excellent	1	5	5	3

It is clear from Table 3 that the above dyes show good affinity to wool giving orange to red shades with good exhaustion to the dye baths. Dyestuffs VI and VII possess very good and good migration properties, respectively, indicating their high level dyeing character. On the other hand, dyestuffs VIII and IX containing two sulphonic acid groups show poor levelling properties. In this connection it may be mentioned that levelling properties are mainly determined by the colloidal character of the dyes in solution, which is favoured by increasing molecular weight and decreasing degree of sulphonation[8][9].

The light fastness properties of these dyes are good to excellent, but their washing fastness properties are moderate presumably due to the presence of the imino group. It may be interesting to mention that the light fastness grading of dyestuffs VI and VII are better than those of the analogously substituted naphthalene derivatives X and XI, respectively.



C.I. 15510, X



C.I. 15630, XI

However, the washing fastness grading of the four dyestuffs are nearly equal.

(iii) Direct dyes

It is well known, that the presence of 4,4'-bisazodiphenyl moiety, infers substantive properties to a dye molecule. In conformity with this, it is now found that compounds (XIIa and b) obtained from the tetrazotisation and coupling of benzidine and benzidine-3,3'-dicarboxylic acid and 5-hydroxybenzotriazole (V), respectively, can be satisfactorly applied to cotton as direct dyes. The dyestuff (XIIb) containing the ortho hydroxy ortho

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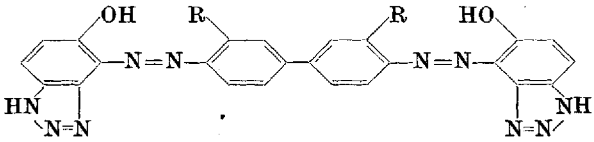
[8] LEMIN and RATTE, J. Soc. Dyers and Col. **65**, 217 (1949).

[9] SPEAKMAN and CLEGG, J. Soc. Dyers and Col. **50**, 348 (1934).

carboxy azo chelating system is the first example in the literature for such group of metal complex forming dyes of this type. It is also remarkable to mention that although dyestuff (XIIa) does not contain strong polarising groups e.g. sulphonic acid group, yet it dissolves in alkaline solutions due to the presence of the imino groups of the triazole moiety.



XIIa, R = H
b, R = COOH

The results of the important dyeing properties of dyestuffs (XIIa and b) are summarized in Table 4. The improvement of the light fastness properties when the dyeings are after-treated with copper sulphate and acetic acid deserves special attention.

Table 4

Dyestuff	Shade on cotton	Migration test	Light fastness (day-light)	Washing fastness	
				at 60°	at 100°
XIIa	Bordeaux	3	3	5	4
XIIa with after-treatment	Red-brown	2	5	6	5
XIIb	Bordeaux	3	3	2	1
XIIb with after-treatment	Red-brown	1	7	3	2

(iv) Use of aminobenzotriazole derivatives as bases for azoic dyes

It seemed also interesting to investigate the behaviour of aminobenzotriazole derivatives (I—IV) as bases for azoic coupling. 2-Hydroxy-3-naphthanilide was used as a coupler. The dyeing and soaping was carried out in the usual way (see experimental). The latter after-treatment was found to cause dullness in the shade in the case of dyes obtained from 4-amino- and 5-amino-benzotriazole. The shade and fastness gradings of the dyes are given in Table 5.

All the shades are generally red except in case of 2-methyl-4-aminobenzotriazole (III) which gives a bordeaux shade. Light fastness gradings are in general good to excellent and the dyeing have good dry rubbing fastness but the wet rubbing fastness are poor.

Table 5

Amine	Shade on cotton	Light fastness (day-light)	Dry rubbing fastness	Wet rubbing fastness
Ia	Red	6	4	3
IIa	Red	5	4	2
Ib	Red	6	3	2
IIb	Red	6	3	2
III	Bordeaux	7	4	2
IV	Red	7	3	2

Experimental

General method for diazotization of the aminobenzotriazole derivatives (I—IV)

The aminobenzotriazole (0.01 mole) was dissolved in 18% hydrochloric acid (6 ml.). The mixture was cooled to 0—5°, and diazotized with a solution of sodium nitrite (0.01 mole in 5 ml. water). The diazonium salt solution was stirred for about 15 minutes and then coupled with either 2-naphthol or dimethylaniline as follows:

(i) Coupling with 2-naphthol

The diazonium salt solution was added dropwise to a cold solution of 2-naphthol (0.01 mole) in 10% aqueous sodium hydroxide solution (12 ml.). The mixture was stirred at 0—5° for 30 minutes, acidified with dilute acetic acid (pH = 6), and the precipitated dye thus formed, was then filtered off and crystallized from the proper solvent.

(ii) Coupling with dimethylaniline

The diazonium salt solution, prepared as mentioned above, was added to a cold solution of dimethylaniline (0.01 mole) in 2N hydrochloric acid (12 ml.). The reaction mixture was stirred at 0—5° for 30 minutes, and then treated with sodium acetate solution (pH = 6). The azo dye, thus formed, was filtered off and crystallized from the proper solvent.

(iii) Coupling with 5-hydroxybenzotriazole

Solutions of the diazotized amines were added to 5-hydroxybenzotriazole in alkaline solution and the reaction was completed as described above.

Sulphanilic acid → 5-hydroxybenzotriazole (VI)

Sulphanilic acid (1.73 g.) was diazotized with nitrous acid (0.69 g. sodium nitrite), in the usual manner. The diazonium compound was added to a stirred solution of 5-hydroxybenzotriazole (1.35 g.) in 10% sodium hydroxide solution (15 ml.) and the reaction mixture was stirred at 0—5° for 30 minutes. Acidification of the reaction mixture (pH = 6) gave an orange precipitate (2.7 g., yield 75%), which was crystallized from ethyl alcohol to give the azo dye (VI) in orange crystals. (VI) is sparingly soluble in most organic solvents and gives an orange colour with concentrated sulphuric acid. It dissolves readily in aqueous sodium hydroxide solution with a red colour.

2-Naphthylamine-1-sulphonic acid → 5-hydroxybenzotriazole (VII)

This azo dye was prepared from 2-naphthylamine-1-sulphonic acid (2.45 g.), and 5-hydroxybenzotriazole (1.35 g.) in the usual manner. (VII) was crystallized from ethyl alcohol in red crystals (2.7 g., yield 78%). It is readily soluble in water, gives a violet colour with concentrated sulphuric acid and a red colour with aqueous sodium hydroxide solution.

5-Aminobenzotriazole → 2-naphthol-3,6-disulphonic acid (VIII)

(VIII) was prepared from the aminobenzotriazole (1.34 g.) and the 2-naphthol (3.48 g.) in the usual manner. The azo dye was separated by salting out and was crystallized from methyl alcohol in red powder (3 g., yield 72%). It gives a pink colour with concentrated sulphuric acid and dissolves in aqueous sodium hydroxide solution with a red colour.

1-Methyl-4-aminobenzotriazole → 2-naphthol-3,6-disulphonic acid (IX)

1-Methyl-4-aminobenzotriazole (1.4 g.) was diazotized and coupled with an alkaline solution of 2-naphthol-3,6-disulphonic acid (3.48 g.) to give the azo dye (IX) in red powder (from methyl alcohol).

5-Hydroxybenzotriazole ← benzidine → 5-hydroxybenzotriazole (XIIa)

A solution of tetrazotized benzidine (1 mole) is mixed with an alkaline solution of 5-hydroxybenzotriazole (2 mole) at about 0—5°. The reaction mixture was stirred for several hours and the precipitated dye was filtered off and repeatedly extracted with boiling distilled water and ethyl alcohol. (XIIa) was obtained as orange-red powder, m.p. > 340°, yield 82%. Found: N 29.60. $C_{24}H_{16}O_2N_{10}$ requires N 30.06%. It is sparingly soluble in common organic solvents and gives a violet colour with concentrated sulphuric acid and a pink colour with aqueous sodium hydroxide solution.

5-Hydroxybenzotriazole ← benzidine-3,3′-dicarboxylic acid → 5-hydroxybenzotriazole (XIIb)

Similarly prepared from the benzidine dicarboxylic acid and 5-hydroxybenzotriazole. It was obtained as orange-red crystals m.p. > 340°, yield 80%. Found: N 24.84. $C_{26}H_{18}O_7N_{10}$ requires N 24.50%.

It is sparingly soluble in most organic solvents and gives a violet colour with concentrated sulphuric acid and a pink colour with aqueous sodium hydroxide solution.

Dyeing Experiments

(i) Use as dispersed dyes

Dyeings were made on 10 g. samples of nylon 66. Dispersion of the dyes were prepared in the usual manner[10]. The previously wetted out yarns were introduced and dyeing was continued for one hour with the necessary agitation, and the yarn was then rinsed and air dried. No finish was used.

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[10] The Society of Dyers and Colourists, "Recent advances in the Colouring of Man Made Fibres", 19 Piccadilly, Bradford, Yorkshire, 1957, p. 15.

(ii) Use as acid wool dyes[11])

Dyeings were made on wool serge. The amount of dye used is sufficient to yield a dyeing of medium depth. The previously wetted out fabric was entered into the dye liquor at about 40°. The temperature was allowed to rise to the boiling in 30 minutes and then kept thereat for one hour, after which the fabric was removed.

(iii) Use as direct cotton dyes[11])

The cotton fabric was dyed in 1% shade in a dye bath containing the calculated amount of the dye and 20% of common salt in distilled water. The liquor:goods ratio was 30:1. The fabric was entered at the boiling and kept thereat for 30 minutes, then squeezed and dried.

After-treatment of the dyed fabric was carried out in 50:1 bath with 2% copper sulphate and 1% acetic acid at 60—70° for 20 minutes.

(iv) Use as bases for azoic dyes

Bleached cotton fabric was impregnated with Naphthol AS on a laboratory padder (2 Bowl-Svetema) at 90—95°, with an expression of 100% and a speed of 12 m/min. The dried naphtholated fabric was then developed using the cold diazonium salt solutions of the aminobenzotriazoles (I—IV), prepared in the usual manner, on the padder. The developed fabric was then soaped, rinsed and dried.

All fastness properties and migration test were carried out in accordance with the standard methods for the assessment of the colour fastness of textiles[7]).

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[11]) The Society of Dyers and Colourists, "Report of the Committee on the Dyeing Properties of Direct Cotton, Vat, and Wool Dyes", 19 Piccadilly, Bradford, Yorkshire, 1952, p. 1, 8, 15 and 19.

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