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Disazo Direct Dyes Containing Cyclic Amido, Keto and Amino Groups

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ABSTRACT

Derived from diamines containing amino, carbonyl, carbamide and urea groups between biphenyl rings, a series of disazo dyes have been synthesised. Similar dyes have been obtained from diamines containing cyclic carbazole, fluorenone and phenanthridone systems. The effect of the molecular structure of the dyes on their colour and affinity for cellulose fibres, compared with the properties of corresponding benzidine dyes, has been studied. It has been found that 3,8-diaminophenanthridone derivatives show the most favourable properties. They are derivatives of benzidine dyes, containing additionally a cyclic amide group.

1 INTRODUCTION

The carcinogenic activity of benzidine and most of its derivatives has been known for a long time.[1] Direct dyes constitute about 17% of all dyes used for dyeing textiles and about 30% of the dyes used for dyeing cellulose fibres.[2] Benzidine dyes once constituted 30–70% of direct dyes. Direct benzidine dyes were characterised by a low price, by simplicity of use and a nearly full range of colours, including black, brown and navy blue; they were widely used for dyeing mass-produced cotton products. It has not been possible to fully replace this group of dyes by other direct dyes, e.g. urea dyes or dyes of other types such as reactive or vat dyes. Dyes of other groups are more expensive, do not cover the whole colour range and do not have the simplicity of use. Despite a lapse of twenty years since benzidine ceased to be

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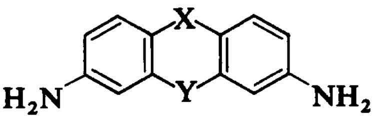
used, dye chemists are still trying to find another simple diamine as a substitute.

Thus, a number of previously known intermediates have been investigated, e.g. 4,4'-diaminodiphenylurea, 4,4'-diaminodiphenyloamino-2-sulfonic acid and others.[3] Most of these diamines give dyes of lower affinity for cellulose than benzidine based dyes, and also have a distinct hypsochromic effect. Their production is also more complicated and replacing benzidine with them would require a large investment outlay and possibly present difficulties in the supply of basic raw materials. For instance, the production of 4,4'-diaminobenzanilide and 4,4'-diaminostilbene-2,2'-disulfonic acid would require considerable amounts of toluene. Other solutions are therefore being investigated, e.g. the synthesis and properties of dyes based on new diamines such as derivatives of quinoline[4] or bipyridine[5] and similar products. As yet, these solutions are not feasible from a technological viewpoint. It has also been suggested that the benzidine problem could be resolved by use of non-carcinogenic alkyl and alkoxyl derivatives.[6,7] The use of any benzidine derivatives, however, could raise doubts of both producers and consumers, despite their non-carcinogenity.

Thus, the problem of finding a diamine that could replace benzidine in the production of direct dyes seems to be still very relevant. Such a diamine should satisfy a number of conditions. It should ensure the formation of a dye having a coplanar molecule and an extended conjugated system in order to have sufficient affinity for cellulose fibres and a sufficiently deep colour. Any amine replacing benzidine should be capable of affording asymmetric dyes, i.e. it should offer the possibility of selective coupling successively with two different coupling components in order to obtain a full colour range. For technological–economical reasons, the amine should also be characterised by simplicity of synthesis, accessibility of raw materials and a low cost. At present, no amine has been found which meets these requirements. To this end, we have therefore examined a group of simple and cyclic diamines of structure **I** and evaluated the colour and affinity for cellulose fibres of the dyes obtained from them.



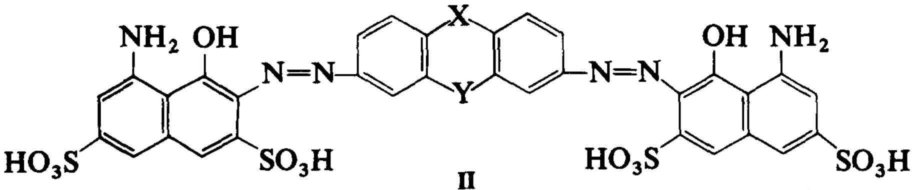
I

X = none, NH, CO, CONH, NHCONH
Y = none, NH, CO, CONH, NHCONH

2 RESULTS AND DISCUSSION

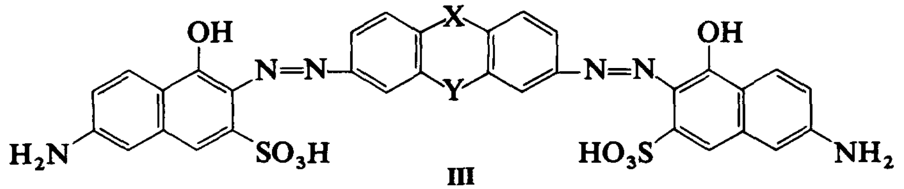
The diamines **I** contain two phenylamino rings linked in positions 3- or 4- to the amino groups by an amino (NH), carbonyl (—CO—), amide (CONH) or urea (NHCONH) bridge, or are diamines containing a cyclic system linking the phenyl rings, viz., 3,6- and 2,7-diaminocarbazole, 2,7-diaminofluorenone, 3,8-diaminophenanthridone. It was anticipated that a study of such diamines would provide information about the effect of the position and type of the bridge and linking the effect of the phenyl rings on the colour and substantivity of the dyes derived from them.

The amines **I** obtained were used as diazo components for the synthesis of disazo dyes. For simplicity, we restricted ourselves to investigating the symmetrical dyes **II** and **III** containing H-acid and J-acid as coupling component. This allowed the determination of their standard affinity by the chromatographic method[8] and comparison of their colour with analogous benzidine dyes. It was thus possible to draw general conclusions concerning the value of the diamines as potential replacements for benzidine. Some of the dyes are known and are in practical use. Their dyeing and colour properties, however, have not been determined or have been determined in different conditions, which makes comparisons impracticable.



II

X,Y = as **I**



III

The absorption maxima and affinity for cellulose are given in Table 1.

From the λ_{max} data listed in Table 1 it is apparent that the deepest colour, excluding benzidine dyes, is shown by dyes **II** and **III** based on phenanthridone (**j**), on derivatives of diphenylamine (**b**) and carbazole (**c**, **d**) Dyes **II** and **III**, **g**, **j** and **d** can be treated as cyclised derivatives of benzidine capable of direct conjugation, while dyes **b** and **c** probably have a possibility for conjugation through the nitrogen atom. The above dyes, relative to analogous benzidine dyes, show only minor hypsochromic shifts (up to 20 nm). The remaining dyes, in which the phenylazo systems are separated by a carbamido (**h**, **i**), urea (**k**, **l**) or carbonyl (**e**, **f**) group, generally show considerably greater hypsochromic shifts (up to 100 nm) compared with the analogous benzidine dyes (**IIa** and **IIIa**). The largest shifts occur in

TABLE 1
Properties of Disazo Dyes II and III

Dye	*X*	*Y*	$R_F{}^a$	$R_F{}^b$	$\Delta\mu°$ *(kJ/mol)*	λ_{max} *(nm)*
IIa	—	None	0·05	0·21	24·6	584
IIIa	—	None	0·21	0·19	30·4	521
IIb	NH	None	—	0·43	18·9	578
IIc	NH	—	—	0·42	19·0	567
IId	—	NH	—	0·24	23·6	567
IIe	CO	None	0·10	0·45	18·3	558
IIIe	CO	None	0·25	0·52	21·0	495
IIf	None	CO	0·28	0·60	13·9	496
IIIf	None	CO	0·31	0·55	20·4	486
IIg	—	CO	0·06	0·23	23·7	558
IIIg	—	CO	0·10	0·29	27·1	513
IIh	CONH	None	0·10	0·35	21·0	553
IIIh	CONH	None	0·16	0·29	27·1	513
IIi	None	CONH	0·33	0·49	17·6	533
IIIi	None	CONH	0·37	0·47	22·4	483
IIj	—	CONH	0·05	0·22	24·1	572
IIIj	—	CONH	0·10	0·23	28·9	541
IIk	NHCONH	None	0·06	0·23	23·7	564
IIIk	NHCONH	None	0·30	0·28	27·4	518
IIl	None	NHCONH	0·16	0·54	16·4	538
IIIl	None	NHCONH	0·18	0·44	22·9	483

[a] Whatman 3 paper; pyridine, *n*-butanol, H_2O (1:1:1).
[b] Whatman 1 paper; methanol, DMF, H_2O (3:1:1).
None, signifies this link is not present in the structure I.
—, signifies a direct link between the phenyl rings.

dyes in which the azo linkages are in the *m*-position to the bridge linking the phenylazo groups. Whilst the pattern of these colour shifts could be predicted qualitatively, the quantitative extent of the hypsochromic shift is not always in agreement with expectations.

Large differences were also observed on comparing the affinity of the dyes on cellulose fibres. According to general principles, dyes containing the J-acid residue (**III**) are characterised by a greater affinity, while their analogues derived from H-acid (**II**) have a smaller affinity. The differences in the magnitude of the standard affinity between dyes **III** and **II** amount to approximately 3–5 kJ/mol. This phenomenon was predictable based on known characteristics observed in other groups of dyes.

More interesting relationships can be observed when comparing the standard affinity of the dyes with analogous benzidine based dyes (**IIa** and **IIIa**). An affinity similar to that of the benzidine dyes (**a**) is shown only by dyes **II** and **III**, which contain a phenanthridone residue (**IIj** having nearly the same value as **IIa**, whilst **IIIj** is about 1 kJ/mol higher than **IIIa**). Dyes containing the fluorenone residue (**g**) the 2,7-substituted carbazole residue (**d**) and derivatives of 4,4′-substituted diphenylurea (**k**) are characterised by fairly high standard affinity. However, the values are about 1 kJ/mol smaller than the affinity of analogous benzidine dyes. Almost all these dyes (**d, g, j**) can be regarded as cyclic analogues of benzidine dyes. It should also be noted that an increase in affinity does not always occur in conjunction with a deepening of colour.

The remaining dyes (**II** and **IIIb**, **c**, **e**, **f**, **g**, **h**, **i**, **l**) are not benzidine derivatives and show a standard affinity 3–10 kJ/mol lower than the corresponding benzidine dyes. This observation refers to dyes derived from H-acid (**II**) as a coupling component. In the case of some of the dyes based on J-acid as the coupling component, the affinity increases to an unexpectedly high level.

3 EXPERIMENTAL

3.1 Synthesis and purification of diamines I

Benzidine (**Ia**) was purified by crystallisation of its hydrochloride from water. Technical *4,4-diaminodiphenylamine* (**Ib**) was purified by crystallisation of its hydrochloride from water; coloured oxidation products were removed with activated charcoal.

3,6-Diaminocarbazole (**Ic**) was obtained by nitration of carbazole in acetic acid.[9] 3,6-Dinitrocarbazole (mp 318°C, Lit.[10] 320°C), purified by crystallisation from acetic acid was reduced with hydrazine hydrate in the presence of Raney nickel in *N*,*N*-dimethylformamide.[11] *2,7-Diaminocarbazole* (**Id**) was obtained by the method described by Porai-Koshits & Salamon[12] by nitration of benzidine sulphate, reduction and cyclisation. After recrystallisation from ethanol, pure 2,7-diaminocarbazole was obtained (mp 258–261°C).[12] *4,4-Diaminobenzophenone* (**Ie**) was obtained by oxidising 5,5-diaminodiphenylmethane with sodium polysulphide.[13] *3,3-Diaminobenzophenone* (**If**) was obtained by nitration of benzophenone[14] and reduction of the nitro-compound with hydrazine hydrate in the presence of Raney nickel.[14]

2,7-Diaminofluorenone (**Ig**) was obtained by Bechamp reduction of 2,7-dinitrofluorenone in *N*,*N*-dimethylformamide. The reduction was carried out in the manner similar to that for the reduction of 3,8-dinitrophenanthridone. *4,4-Diaminobenzanilide* (**Ih**) was obtained from *p*-nitrobenzoyl chloride and *p*-nitroaniline as previously described.[15] *3,3-Diaminobenzanilide* (**Ii**) was similarly obtained from *m*-nitroaniline and *m*-nitrobenzoyl chloride.

3,8-Diaminophenanthridone (**Ij**) was obtained by nitration of fluorenone, transformation of the 2,7-dinitrofluorenone into the oxime, Beckmann rearrangement to 3,8-dinitrophenanthridone, and reduction with iron. To obtain a satisfactory product, the synthesis conditions described in the literature had to be considerably modified (see below).

2,7-Dinitrofluoreneone. 63 g (0·35 mol) of fluorenone was dissolved in 490 ml of concentrated H_2SO_4 at 20°C. After cooling, a mixture of 58 ml of 65% HNO_3 and 21 ml of H_2SO_4 was added dropwise over 1 h at 20°C. The mixture was maintained below 10°C for 2 h and the product was precipitated by pouring the solution into a mixture of water and ice. After filtration, washing with water and drying, 89·3 g of 2,7-dinitrofluorenone (92% yield) (mp 293°C, Lit.[16] 293·5°C) was obtained.

2,7-Dinitrofluorenone oxime. To a solution of 21·6 g (0·08 mol) of 2,7-dinitrofluorenone in 80 ml of dimethylsulfoxide was added a solution of 6·23 g (0·09 mol) of hydroxylamine hydrochloride in 10 ml of water. The mixture was heated at 100°C for 15 min, then poured into 200 ml of water. The precipitate was filtered, washed with water and dried, giving 22·6 g of 2,7-dinitrofluorenone oxime (99% yield) (mp 284–285°C, Lit.[17] 285–286°C).

3,8-Dinitrophenanthridone. To 150 ml of polyphosphoric acid was gradually added 20 g (0·07 mol) of 2,7-dinitrofluorenone oxime at 180°C. The mixture was maintained at 220–222°C for 15 min, and after cooling to 160°C was poured into 500 ml of water and ice. The precipitate was filtered, washed with water and dried, giving 19·6 g (98% yield) of 3,8-dinitrophenanthridone of mp 370°C, Lit. 350°C,[18] 380°C[19]).

3,8-Diaminophenanthridone (**Ij**). To a suspension of 45 g of iron filings pickled with 10% HCl in 180 ml of a 3% solution of NH_4Cl was added dropwise, over 30 min at 90°C, a solution of 17·1 g (0·06 mol) 3,8-dinitrophenanthridone in 240 ml of *N,N*-dimethylformamide. The mixture was maintained at 95°C for 15 min, the residue of iron oxides was filtered and washed several times with hot *N,N*-dimethylformamide. The solvent was evaporated from the filtrate and the crude product was purified by dissolving in 500 ml of 3% HCl and reprecipitating with ammonium hydroxide. (Yield: 7·5 g (55%) 3,8-diaminophenanthridone. N—calculated: 6·2%; found: 6·1%.)

4,4'-Diaminophenylurea (**Ik**) was obtained by heating *p*-phenylenediamine with an aqueous solution of urea.[20] *3,3'-Diaminophenylurea* (**Il**) was similarly obtained using *m*-phenylenediamine.

3.2 Synthesis of dyes

Diamines I were diazotised by adding 0·1 mol 4N $NaNO_2$ dropwise to a solution of 0·05 mol diamine in 450 ml of 2% HCl at 0–5°C. On completion of diazotation (1–2 h), the diazonium solution was added dropwise to a solution of 0·1 mol H- or J-acid in 600 ml of 5% Na_2CO_3. On completion of coupling (1–2 h) the dye was separated by adding 10–20% NaCl.

Crude dyes were purified by dyeing 20 g of cotton fabric in a boiling solution of 5 g of dye in 250 ml of water for 1 h. After thorough rinsing of the dyed fabric, the dye was extracted from the cotton with a 50% boiling solution of pyridine in water (5–7 parts per 150 ml). The extract was evaporated, giving dyes free from salts.[21]

Homogeneity of the purified dyes was confirmed by chromatography on Whatman 3 paper, using pyridine, butanol and water (1:1:1) and on Whatman 1 paper using methanol, *N*,*N*-dimethylformamide and water (3:1:1).[8] The content of the disazo compound in the purified dyes was determined vanadometrically.[21] The dyes, homogeneous chromatographically, sometimes contained a small amount of starch from the fibre finish.

3.3 Dye properties

Spectra of the azo compounds **II** and **III** were determined in aqueous solutions of a concentration of about 2×10^{-2} g/l and at pH 7·5 on a Specord UV-VIS spectrophotometer.

Standard affinity of the dyes for cellulose ($\Delta\mu^\circ$) was calculated on the basis of the chromatographic measurements carried out under the conditions described above (Whatman 1 paper; MeOH, DMF, H_2O, 3:1:1).[8] The calculations were performed according to the formula:

$$-\Delta\mu^\circ = \frac{b - R_m}{a} \cdot 4186{\cdot}8 \ [\mathrm{J/mol}] \qquad (1)$$

where $R_M = \log[(1/R_F) - 1]$, R_F is the chromatographic constant and a and b are experimentally determined parameters characteristic of the coupling component. For disazo dyes containing H-acid as coupling component, $a = 0{\cdot}336$, $b = -1{\cdot}391$; and for dyes containing J-acid as a coupling component, $a = 0{\cdot}292$, $b = -1{\cdot}499$.[8]

4 CONCLUSIONS

The results of this investigation indicate that the most advantageous way to obtain disazo dyes which have an affinity for cellulose fibres similar to that of benzidine based dyes is to introduce a cyclic secondary amine, amide or carbonyl system into the molecule, thus creating good conditions for association. To achieve a deep colour of dye, this cyclic system should be placed in the molecule so that the azo groups are in the *para* position of the biphenyl residue. The disazo dyes can then achieve a coplanar structure with a long conjugated system and, at the same time, they are capable of intermolecular interactions. The most favourable properties, with respect to both colour and affinity, are shown by dyes based on 3,8-diaminophenanthridone. This intermediate is not readily available under technical conditions. Metal–complex dyes derived from 3,8-diamino-5-oxy-6-phenanthridone have recently been patented,[22] but they have not been utilised industrially. It seems worthwhile therefore to continue investigations to establish an economical method for the synthesis of phenanthridone derivatives.

REFERENCES

1. Sax, N. I. *Cancer Causing Chemical.* DC9625000, New York, VNR, 1981.
2. Brook, F., *J. Soc. Dyers Colour.*, **103** (1987) 297.
3. Venkataraman, K., *The Chemistry of Synthetic Dyes.* Academic Press, New York, 1952, 1970. Vol. I, pp. 508, 628; Vol. III, p. 280.
4. Krishnan, R., Sekar, N. & Seshardi, S., *Dyes & Pigments*, **7** (1986) 457.
5. Calergo, F., Freeman, H. S., Esancy, J. F., Whaley, W. M. & Dabney, B. J., *Dyes & Pigments*, **8** (1987) 431.
6. Hoechst. GFR Pat. 3511545 (1986).
7. Casella. GFR Pat. 3534634 (1987).
8. Alberti, G. & Giorgi, M. R., *Ann. Chim. (Rome)*, **73** (1983) 315.
9. BASF. Ger. Pat. 46438 (1889). *Frdl.*, **2** (1890) 447.
10. Ziersch, P., *Ber.*, **42** (1919) 3799.
11. Organikum, Berlin, DVD 1972.
12. Porai-Koshits, B. A. & Salamon, G. S., *Zh. Obsh. Khim.*, **14** (1944) 1019.
13. BASF, Ger. Pat. 289108 (1915). *Frdl.*, **12** (1917) 207.
14. Barnett, E. B. & Matthews, M. A., *J. Chem. Soc.*, **125** (1924) 767.
15. CIBA, Ger. Pat. 221433 (1910). *Frdl.*, **10** (1913) 912.
16. Schultz, G., *Ann.*, **203** (1880) 104.
17. Schmidt, J. & Bauer, K., *Ber.*, **38** (1905) 3737.
18. Pan, H. L. & Flecher, T. L., *J. Med. Chem.*, **12** (1969) 822.
19. Arcus, C. L., Coombs, M. M. & Evans, J. V., *J. Chem. Soc.*, (1956) 1498.
20. Szadowski, J. & Niewiadomski, Z., *Przegl. Włók.*, **27** (1973) 36.
21. Venkataraman, K., *The Analytical Chemistry of Synthetic Dyes.* Academic Press, New York, 1977.
22. Zaitsev, B., Migachev, G. *et al.*, SU Pat. 1388408 (1988). *Chem. Abstr.*, **109**, (1988) 112064.