4-Hydroxy-3-arylamino-1,8-naphthalimides and 3-(and 4-) hydroxy-2-(and 5-) arylamino-7*H*-benzimidazo-(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones. Red dyes for synthetic-polymer fibres

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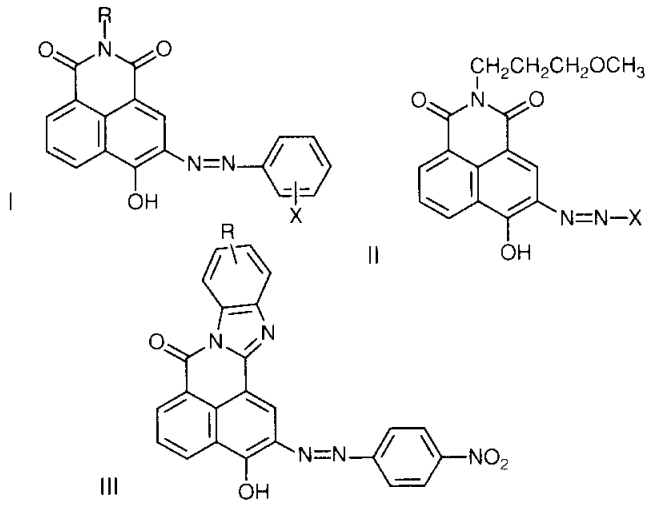
4-Hydroxy-1,8-naphthalimides and the isomer mixtures of 3- and 4-hydroxy-7H-benzimidazo-(2,1-a)-benz(d,e)-isoquinolin-7-ones were coupled with diazotised arylamines to yield orange-red to bluish-red dyes having good coloration properties and excellent fastness to light on polyester fibres. Structure–property relationships in the dyes are discussed with respect to the nature of the substituents in the imide, imidazole and arylazo moieties.

INTRODUCTION

Arylazo derivatives of 1,8-naphthalimides can be obtained by diazotisation of 3-amino- and 4-amino-1,8-naphthalimides and coupling to *N*-substituted anilines [1,2]. These dyes colour synthetic-polymer fibres in orange to scarlet hues of good fastness to light and sublimation. Phenylazonaphthalimide dyes for polyester can also be obtained by utilising 4-hydroxy-1,8-naphthalimides [3–5] or further substituted 4-hydroxy-1,8-naphthalimides, e.g. chloro or nitro substituted in the non-hydroxylated ring [6], as coupling components.

We report here the synthesis of some 3-phenylazo-4-hydroxy-1,8-naphthalimides (I), analogous thiadiazolylazo, thiazolylazo and benzothiazolylazo derivatives (II) and the isomer mixtures typified by the 2-phenyl-3-hydroxy-7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones (III). Some structure–property relationships in these dyes are also evaluated.



EXPERIMENTAL

4-Hydroxy-1,8-naphthalimides (IV)

Method A

Acenapthene was sulphonated [7,8] with chlorosulphonic acid in nitrobenzene and the resultant acenaphthene-5-sulphonic acid (67% yield) oxidised [7,8] with sodium dichromate in glacial acid to give 1,8-naphthalic anhydride-4-sodium sulphonate (68%).

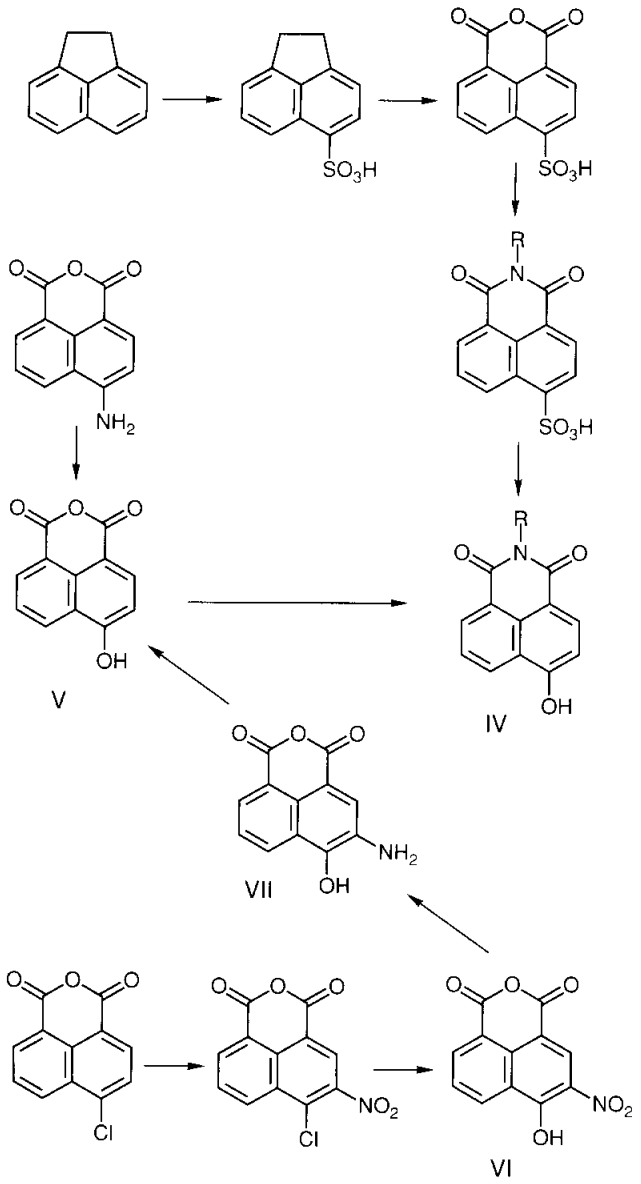
This (3g, 0.01 mol) was stirred under reflux with 3-methoxypropylamine (1.8 g, 0.02 mol) in 2-methoxyethanol (50 ml) for 3 h. The cold reaction liquor was filtered and the cream residue of *N*-3-methoxypropyl-1,8-naphthalimide-4-sodium sulphonate filtered (3.12 g, 84%) and washed with a little 50% aq. ethanol. The dry imide was refluxed for 20 h in 10% aq. potassium hydroxide (35 ml) and the cooled liquor stirred slowly into ice-cold 10% aq. hydrochloric acid (100 ml). The resultant cream-brown precipitate was filtered, washed neutral and recrystallised from 20% aq. 2-methoxyethanol (Norit) to give *N*-3-methoxypropyl-4-hydroxy-1,8-naphthalimide as off-white prisms (1.83 g, 79%), m.p. 226-227°C\($C_{16}H_{15}NO_4$ requires: C 67.1, H 5.25, N 4.9; found: C 66.8, H 5.0, N 4.7%) (P^+ at *m/e* 286).

Other derivatives of structure IV (Scheme 1) were similarly prepared, i.e. R = H, m.p. >350°C (lit. m.p. >300°C [9]); R = Me, m.p. 328–330°C (lit. m.p. 325–327°C [9]); R = Pr, m.p. 240–242°C; R = CH_2Ph, m.p. 262–264°C; R = $CH_2CH_2CH_2OH$, m.p. 216–218°C; R = C_6H_{11}, m.p. 237–238°C; and R = Ph, m.p. 274–276°C.

Method B (via 4-hydroxy-1,8-naphthalic anhydride)

4-Amino-1,8-naphthalic anhydride (2 g) was diazotised by adding to nitrosulphuric acid (prepared from sodium nitrite (0.66 g) and conc. sulphuric acid (3 ml) and dilution of the cooled liquor with glacial acetic acid (6 ml)]. After stirring for 2 h at 10°C, the diazo liquor was run slowly into ice-water (100 ml), the temperature then raised to 55°C, maintained for 30 min and then raised slowly to 90°C. The grey-white residue deposited was filtered and recrystallised twice from 2-methoxyethanol (Norit) to give 1.18 g (59%) of 4-hydroxy-1,8-naphthalic anhydride (Scheme 1, compound V), off-white prisms, m.p. 346–348°C (lit. 8, 350–351°C).

Compound V was also prepared from 4-chloro-1,8-naphthalic anhydride (Scheme 1), which was nitrated [10] to 4-chloro-3-nitro-1,8-naphthalic anhydride. This (27.75



Scheme 1

g, 0.1 mol) was stirred in 20% aq. sodium hydroxide (200 ml) for 8 h at 80–85°C. The dark red solution was cooled, stirred into ice-cold 10% aq. hydrochloric acid (500 ml) and the pale yellow residue filtered, washed neutral and recrystallised from glacial acetic acid to give pale yellow needles, m.p. 291–293°C, (17.6 g, 68%) of 4-hydroxy-3-nitro-1,8-naphthalic anhydride (VI) (P^+ at *m/e* 259) ($C_{12}H_5NO_6$ requires: C 55.6, H 1.9, N 5.4; found: C 55.2, H 1.7, N 5.2%).

A mixture of compound VI (15 g), tin(II) chloride (50 g) and conc. hydrochloric acid (80 ml) was stirred for 2 h at 80°C. The suspension was cooled and filtered; the residue was washed with 5% hydrochloric acid, then with water, dried and recrystallised from pyridine in orange-yellow needles (11 g, 83%) of 3-amino-4-hydroxy-1,8-naphthalic anhydride (VII), m.p. >340°C. (P^+ at *m/e* 229) ($C_{12}H_7NO_4$ requires: C 62.9, H 3.1, N 6.1; found: C 62.6, H 2.9, N 5.8%).

Compound VII (2.29 g, 0.01 mol) was stirred into conc. hydrochloric acid (10 ml) at 30–35°C and the suspension diluted with ice-water (20 ml) with vigorous stirring. A solution of sodium nitrite (0.7 g) in water (10 ml) was run in and after 1.5 h at 0–5°C hypophosphorous acid (5 ml) was added over 30 min (in 5 × 1 ml portions). Stirring was continued a further 2 h at room temperature and the yellow suspension filtered. The residue was recrystallised from 2-methoxyethanol (Norit) in buff-coloured prisms (1.56 g, 73%) of 4-hydroxy-1,8-naphthalic anhydride, m.p. 334–336°C. The deamination was also effected by adding amyl nitrite (5 × 1 ml, over 20 min) to a stirred solution of compound VII (5 g) in DMF (40 ml). After 30 min hypophosphous acid (6 × 1 ml, over 30 min) was added, the solution stirred for 30 min at room temperature and then at 45°C for 30 min. The cooled liquor was added to ice-water and the pale yellow residue collected and recrystallised from 2-methoxyethanol to give 68% of compound V. This was converted into the imides IV following standard procedures and afforded products identical to those obtained in method A.

3- (and 4-)-hydroxy-7*H*-benzimidazo(2,1-*a*)benz-(*d*,*e*)isoquinolin-7-ones

Compound V (2.14 g, 0.01 mol) was stirred under reflux in glacial acetic acid (25 ml) with *o*-phenylenediamine (2.16 g, 0.02 mol) for 2.5 h. The liquor was cooled, filtered and the dark yellow residue (2.63 g, 92%) recrystallised from glacial acetic acid in deep yellow needles of the isomer mixture of 3-and 4-hydroxy-7*H*-benzimidazo(2,1*a*)benz-(*d*,*e*)isoquinolin-7-ones, m.p. 309–312°C.

In a similar manner were prepared the analogous isomeric mixtures from 3,4-diaminotoluene, m.p. 279–282°C, and 4-chloro-*o*-phenylenediamine, m.p. 300–302°C.

Synthesis of dyes I–III

Mono- and di-substituted arylamines (0.01 mol) were diazotised with sodium nitrite in aq. hydrochloric acid [11] and the trisubstituted anilines and heterocyclic amines with nitrosyl sulphuric acid [12] following standard procedures. The diazo liquor was added over 30 min to a stirred solution of the appropriate 4-hydroxy-1,8-naphthalimide or hydroxy-7*H*-benzimidazo(2,1-*a*)ben(*d*,*e*)isoquinolin-7-one (0.01 mol) in water (30 ml) containing potassium hydroxide (0.3 g) and potassium carbonate (0.3 g) at 0–5°C. The pH was maintained above 7.5 by addition of aq. potassium carbonate where appropriate. After coupling for 2 h the pH was adjusted to 5 by addition of dil. hydrochloric acid and the dyes filtered. The dyes were purified either by recrystallisation from 20% aq. 2-methoxyethanol (Norit) or by column chromatography on Silica Gel 60 (Merck), applying from solution in chlorobenzene and developing with toluene–ethyl acetate (up to 20% ethyl acetate as appropriate). Relevant characterisation data is shown in Tables 1 and 2.

General

Electronic spectra were recorded in chlorobenzene (see Tables 1 and 2) and, for some dyes, in absolute alcohol, glacial acetic acid and 0.1 mol/l potassium hydroxide in absolute ethanol (see Discussion) on a Pye Unicam PU 8800 spectrophotometer. Dyeings on polyester and fastness assessment were effected as previously described [13].

Amines used as diazo components were commercial samples except for the following. 2-amino-5-methylthio (m.p. 183–184°C, lit. 176–178°C [14]) and 5-ethylthio-1,3,4-thiadiazole (m.p. 139–140°C, lit. 136–137°C [14])

TABLE 1

Characterisation and fastness data for dyes I

	R	X	M.p. (°C)	λ_{max} in chlorobenzene (nm) (log ε)				Colour	Dyeing on polyester: Light 0.15	Light 0.55	Light 2.55	Subl.[a] (°C)
I.1	C_3H_6OMe	H	199–200	482* (3.92)	508 (4.05)	534*	(3.96)	Orange-red	5	5	5	180
I.2	C_3H_6OMe	4-Cl	196–197	481* (4.16)	511 (4.24)	538*	(4.15)	Orange-red	5	5–6	5–6	190
I.3	C_3H_6OMe	4-OPh	116–117	460 (4.04)	519 (4.13)	547	(4.08)	Red	5	5	5	190
I.4	C_3H_6OMe	2-NO_2	258–259		513 (4.43)	538*	(4.32)	Red	5	5	5–6	180
I.5	C_3H_6OMe	4-NO_2	235–236	492* (4.30)	514 (4.37)	539*	(4.26)	Bluish-red	5–6	5–6	6	190
I.6	C_3H_6OMe	2,4-$(NO_2)_2$	257–258	492* (4.42)	514 (4.49)			Bluish-red	5–6	5–6	5–6	200
I.7	C_3H_6OMe	2-Cl-4-NO_2	254–255	487* (4.31)	515 (4.40)	542*	(4.25)	Bluish-red	5	5–6	5–6	190
I.8	C_3H_6OMe	2-CN-4-NO_2	255–256	487* (4.39)	510 (4.42)			Bluish-red	5–6	5–6	6	190
I.9	C_3H_6OMe	2-OMe-4-NO_2	273–274	488* (4.30)	528 (4.49)	555*	(4.43)	Bluish-red	5	5–6	5–6	190
I.10	C_3H_6OMe	4-OMe-2-NO_2	235–233	502* (4.25)	532 (4.42)	564	(4.38)	Violet-red	5	5	5	190
I.11	C_3H_6OMe	2-Cl-4,6-$(NO_2)_2$	244–245	488* (4.27)	510 (4.30)	538*	(4.09)	Bluish-red	5	5	5–6	200
I.12	C_3H_6OMe	2-CF_3-4-Br	210–211	480 (4.13)	502* (4.10)	537*	(3.89)	Red-orange	5	5	5–6	180
I.13	C_3H_6OMe	2,6-Br_2-4-NO_2	219–220	492* (4.06)	505 (4.08)			Red	5–6	5–6	5–6	200
I.14	H	4-NO_2	282–283	488* (4.16)	514 (4.25)	539*	(4.12)	Bluish-red	5–6	6	6	200
I.15	Me	4-NO_2	275–277	488* (4.21)	514 (4.29)	538*	(4.16)	Bluish-red	5	5–6	5–6	190
I.16	Pr	4-NO_2	243–244	489* (4.23)	513 (4.31)	537*	(4.19)	Bluish-red	5	5	5–6	190
I.17	C_3H_6OH	4-NO_2	247–248	490* (4.28)	514 (4.35)	538*	(4.24)	Bluish-red	5	5	5–6	190
I.18	CH_2Ph	4-NO_2	258–259	491* (4.37)	515 (4.45)	538*	(4.34)	Bluish-red	5–6	5–6	5–6	200
I.19	Ph	4-NO_2	265–266	488* (4.25)	513 (4.31)	538*	(4.16)	Bluish-red	5–6	5–6	6	200
I.20	C_3H_6OMe	4-N=NPh	252–253	493* (4.32)	532 (4.48)	565	(4.43)	Dark-red	6	6	6	210
I.21	C_3H_6OMe	Note (b)	218–219		560 (4.42)			Purple-red	5–6	5–6	6	210
I.22	C_3H_6OMe	Note (c)	227–228		566 (4.48)			Purple-red	5–6	6	6	210

(a) Sublimation fastness (2.5%)
(b) 4-N=$NC_6H_4N(Et)(C_2H_4OH)$-*p*
(c) 4-N=$NC_6H_4N(C_2H_4OH)_2$-*p*

TABLE 2

Characterisation and fastness data for dyes II and III

	X(II) or R(III)	M.p. (°C)	λ_{max} in chlorobenzene (nm) (log ε)				Colour	Dyeing on polyester: Light 0.15	Light 0.55	Light 2.55	Subl.[a] (°C)
II.1	2-Thiazolyl	230–231		485 (4.16)	550*	(3.70)	Bluish-red	5	5	5	180
II.2	2-Benzothiazolyl (BT)	227–228	491* (4.28)	515 (4.32)	551*	(4.08)	Dark bluish-red	6–7	6–7	6–7	210
II.3	2-(6-SO_2Me-BT)	255–256		510 (4.32)			Bluish-red	6–7	6–7	6–7	220
II.4	2-(6-NO_2-BT)	275–275		512 (4.36)			Bluish-red	6	6	6	200
II.5	2-(6-Cl-BT)	217–218		516 (4.33)	552*	(4.09)	Bluish-red	6–7	6–7	6–7	210
II.6	2-(6-OMe-BT)	194–195	490* (4.32)	523 (4.37)	580*	(3.93)	Ruby-red	6–7	6–7	6–7	210
II.7	2-(5-SMe-1,3,4-thiadiazolyl)	218–219	411 (3.98)	490 (4.22)			Red	5	5–6	5–6	190
II.8	2-(5-SEt-1,3,4-thiadiazolyl)	192–193	423 (4.00)	490 (4.24)			Red	5	5–6	5–6	190
III.1	H	305–308		549 (4.20)			Ruby-red	7	7	7	210
III.2	Me	294–297		553 (4.24)			Ruby-red	7	7	7	210
III.3	Cl	317–320		547 (4.26)			Bluish-red	7	7	7	210

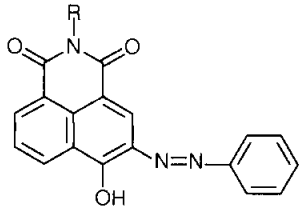
were prepared by condensation of thiosemicarbazide with carbon disulphide [15] and alkylation of the resultant 2-amino-5-mercapto-1,3,4-thiadiazole [14]. 4'-Nitro-4-*N*-ethyl-*N*-β-hydroxyethylaminoazobenzene and 4'-nitro-4-*N*,*N*-bis-β-hydroxyethylaminoazobenzene [11] were reduced with sodium sulphide in ethanol to give corresponding 4'-amino derivatives, m.p. 143–144°C and 149–150°C respectively.

RESULTS AND DISCUSSION

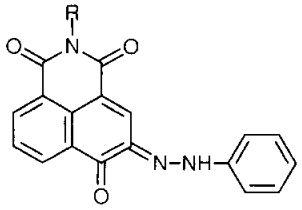
4-Hydroxy-1,8-naphthalimides (IV) were obtained by two routes, in which either the imide or the hydroxy substituents were introduced at the final stage of the synthesis (Scheme 1). Sulphonation of acenaphthene and oxidation of the resultant 5-sulphonic acid with dichromate afforded 1,8-naphthalic anhydride-sodium-4-sulphonate [7,8]. Conversion of this to 4-hydroxy-1,8-naphthalic anhydride by reaction with alkali was not successful due to ring opening and decarboxylation, with formation of 5-hydroxy-1-naphthoic acid as the major reaction product. Replacement of the sulphonic acid group was therefore effected after imide formation, the reaction of 1,8-naphthalimide sodium-4-sulphonates with aq. potassium hydroxide [16] giving good yields of compound IV.

Compounds of structure IV were also obtained by reaction of 4-hydroxy-1,8-naphthalic anhydride (V) with the appropriate amine. Compound V was prepared by hydrolysis of diazotised 4-amino-1,8-naphthalic anhydride and also by deamination of 3-amino-4-hydroxy-1,8-naphthalic anhydride by the action of hypophosphorous acid on the diazonium compound. The imides IV derived from these products were identical to those obtained from 1,8-naphthalic anhydride-sodium-4-sulphonate, thus confirming that the alkaline hydrolysis of sodium-4-sulphonate derivatives proceeded without the intramolecular rearrangement reported to occur on alkali fusion of 4-halogeno derivatives (with formation of the 3-hydroxy compounds) [17]. Condensation of compound V with *o*-phenylenediamines gave the isomer mixtures of 3- and 4-hydroxy-7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones. The imides and imidazoles thus prepared coupled readily with diazotised arylamines, yielding the azo derivatives I–III.

Taking the phenylazo imides I as an example, the dyes can be represented in the hydroxy-azo (VIII) or keto-hydrazone configurations (IX). In former case polar interactions could occur between the donor hydroxy and acceptor carbonyl groups, but those would not contribute significantly to the colour of the dyes, 4-hydroxy-1,8-naphthalimides being colourless and of interest more as fluorescent brightening agents than as colorants. The typical u.v. absorption of 4-hydroxy-1,8-naphthalimides is also present in dyes I–III, all of which show intense absorption bands in the 350–380 nm region. The presence in the dyes of a basic structural unit that exhibits good FBA characteristics probably contributes to the very bright hues shown by many of the dyes. Additional interactions involving the 4-hydroxy group and conjugated acceptor substituents in the phenylazo residue would result in distinct bathochromic shifts, but these are not apparent in the λ_{max} values (Table 1).



VIII



IX

Factors governing azo–hydrazone tautomerism in phenylazonaphthols have been well documented [18]. Whilst in 1-phenylazo-4-naphthols the extent of the tautomerism is significantly influenced by both substituent and solvent effects, in the isomeric 2-phenylazo-1-naphthols and 1-phenylazo-2-naphthols the hydrazone form is stabilised by intramolecular hydrogen bonding, and these dyes are less sensitive to solvent effects. 2-Phenylazo-1-naphthol-4-sulphonic acids, which have similar structural features to dyes I, have also been shown [19] to exist predominantly as hydrazones in a variety of solvents; n.m.r. studies of various sulphonated *o*-hydroxyazonaphthalene-based acid dyes have shown that, in polar solvents, the hydrazone configuration is the more prevalent [20,21]. In such dyes, in which the hydrazone form predominates, the introduction of electron acceptor groups into the phenyl ring of the diazonium residue would increase the hydrazone contribution, and electron donor groups would increase the azo form. Changes in hydrazone–azo ratio in accord with this have been established for some 1-phenylazo-2-naphthols [22].

In the phenylazo derivatives I no significant differences in absorption characteristics were apparent between spectra recorded in ethanol and in acetic acid (e.g. I.1 λ_{max} 497 and 525(s) nm in ethanol, λ_{max} 500 and 530(s) nm in acetic acid; I.5 λ_{max} 508 and 534(s) nm in ethanol, λ_{max} 506 and 536(s) nm in acetic acid). Thus in these solvents the dyes do not show the resolution of the azo and hydrazone forms as observed in 1-phenylazo-4-naphthols [23].

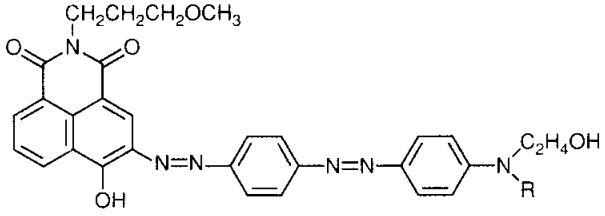
The use of ethanol as solvent for general comparison of structure–colour relationships in dyes I–III was not satisfactory, several dyes having limited solubility in this solvent. The dyes had more acceptable solubility in 2-methoxyethanol, but whilst in some cases λ_{max} in ethanol and in 2-methoxyethanol were of similar order (e.g. I.4 505 nm, 496 nm; I.5 508 nm, 504 nm; I.12 493 nm, 492 nm), in other dyes distinct hypsochromic shifts occurred (e.g. I.1 470(s), 494 and 520 nm in ethanol, 425 and 485 nm in 2-methoxyethanol; I.3 513 and 542(s) nm in ethanol, 430 and 478 nm in 2-methoxyethanol; I.20 524 and 548(s) nm in ethanol, 510 nm in 2-methoxyethanol). In many of the heterocyclic-based dyes II the yellowish-red coloured solutions at higher concentrations, on dilution to a strength suitable for λ_{max} assessment in these solvents (absorbance in the 0.6–1.4 range) underwent marked bathochromic shifts. Thus dye II.1 had λ_{max} at 565 and 594 nm, II.2 at 550(s), 584 and 626 nm, and II.7 at 566 and 614(s) nm, i.e. violet to blue colours. This is presumably due to solute–solvent interactions at the heterocyclic nitrogen atom; similar shifts have been noted in 2-amino derivatives of 1,4-dihydroxyanthraquinone [24].

In the absence of any significant solvent effects in dyes I (see above) between solvents that are either unstructured or capable of forming a two-dimensional structure, and favouring the azo configuration, e.g. ethanol, and solvents that are capable of forming a three-dimensional structure, and favouring the hydrazone configuration, e.g. acetic acid. [19], chlorobenzene was used for the data shown in Tables 1 and 2. The spectra of dyes I.1 and I.5 in chlorobenzene were very similar to those in both ethanol and glacial acetic acid (see above), both the principal absorption band and the longer wavelength inflexion being at 4–8 nm longer wavelength in chlorobenzene. The resolution of the azo–hydrazone forms in this solvent is thus not significantly different to that in ethanol and acetic acid. Chlorobenzene was also a suitable solvent for those dyes having limited solubility in ethanol, and showed no complications with the development of a blue colour with dyes II.

The effect of substituent changes in the phenyl residue of the diazo moiety is illustrated by the *N*-3-methoxypropyl-3-arylazo-4-hydroxy-1,8-naphthalimides (I.1–I.13.). The unsubstituted derivative I.1 shows a broad absorption centred at 508 nm, with a well defined longer wavelength inflexion at 534 nm and a less well defined lower wavelength inflexion at 482 nm. Introduction of electron acceptor substituents into the phenyl ring produces only limited colour shifts. The 4′-nitro derivative (I.5), for example, shows a bathochromic shift of 6 nm in chlorobenzene (in ethanol the shift is 10 nm, compared with the 25 nm shift in the isomeric 4-phenylazo-1-naphthols [23]). This small shift is not significantly changed in other acceptor-substituted derivatives (I.4–I.8, I.11) and is indicative of the limited contribution of the azo configuration to the dyes. Thus differences in λ_{max} between the aniline and 6-chloro-2,4-dinitroaniline derivatives (I.1 and I.11) are only 2 nm, compared with 104 nm in 4-aminoazobenzene derivatives derived from the same diazo components [25]. The largest bathochromic shifts are apparent in the dyes with electron donor substituents in the phenyl ring, i.e. 4′-phenoxy-, I.3, 11 nm; 2′-methoxy-4′-nitro-, I.9, 20 nm, and 4′-methoxy-2′-nitro-, I.10, 24 nm. Steric effects are also more limited, as illustrated by the 2′,6′-dibromo-4′-nitro derivative I.13, which shows a hypsochromic shift of 9 nm relative to the 4′-nitro dye (cf. hypsochromic shift of 38 nm in aminoazobenzene derivatives [25]), although quite a marked decrease in λ_{max} values are apparent.

The introduction of a second azo moiety produces quite noticable bathochromic shifts, the 4′-azophenyl derivative I.20 absorbing at 24 nm longer wavelength than dye I.1 for the principal resolved absorption maxima, and showing a similar shift in the longer wavelength band also. The presence of conjugated donor substituents into such a structure (dyes I.21 and I.22) induces further large bathochromic shifts to 560 nm and 566 nm respectively in chlorobenzene. The λ_{max} values in acetic acid are of similar order (±1 nm), but marked hypsochromic shifts are apparent in ethanolic solvents (i.e. I.21 535 nm, 535 nm; I.2, 545 nm, 542 nm in absolute ethanol and in 2-methoxyethanol respectively).

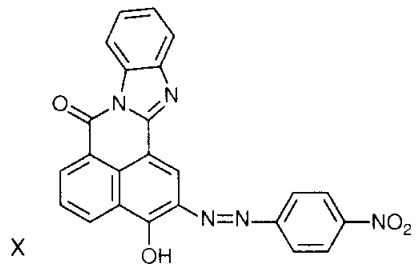
Replacement of the phenylazo residue in 4-aminoazobenzene dyes by thiazolylazo and benzothiazolylazo residues results in bathochromic shifts of 70 and 100 nm respectively [26], commensurate with enhanced donor–



I.21 R = Et
I.22 R = C_2H_4OH

acceptor interaction in an azo structure. In dyes II the thiazolyl derivative II.1 is hypsochromic with respect to the phenyl analogue I.1, and the benzothiazolyl derivative II.2 shows a small bathochromic shift of 7 nm. The presence of further electron acceptor substituents into the hetero residue (dyes II.3–II.5) gives hypsochromic shifts, and that of electron donor substituents (II.6) bathochromic shifts, i.e. the reverse of those observed in conjugated donor–acceptor azo configurations.The thiadiazole derivatives (II.7 and II.8) are also hypsochromic by 18 nm relative to derivative I.1 and, whilst showing similar λ_{max} to the thiazolyl dye II.1, they do not show the extended longer wavelength inflexion of that dye, and the colours of dyes II.1 and II.7 are not comparable.

Changes in the nature of the imide residue R in dyes I result in only slight colour shifts, as is observed generally in 1,8-naphthalimide derivatives. The 4′-nitrophenylazo derivatives I.5 and I.14–I.19 all have very similar λ_{max} values. Replacement of the imide residue by the imidiazole moiety (dyes III.1–III.3), however, results in significant bathochromic shifts. Thus the isomer mixture (III.1) of 2-(4′-nitrophenylazo)-3-hydroxy-7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-one (X) (and the 4-hydroxy-5-(4′-nitrophenylazo) isomer formed with it during the dye synthesis) absorbs at 549 nm, i.e. at 35 nm longer wavelength than the imide I.5. This shift is somewhat larger than usually observed (20–25 nm) in comparisons of analogously substituted imides and imidazole derivatives of substituted 1,8-naphthalic anhydrides (I). These dyes absorb in a similar area to the disazo dyes I.20–I.23, but do not show the longer wavelength inflexion apparent in the latter dyes.



X

Dyes I–III gave orange-red to bluish dyeings of excellent build-up on polyester. Hues were generally very bright, particularly with the phenylazo derivatives I.1–I.13. The thiadiazolyl dyes (II.7 and II.8) were also very bright, and the bright hue of the benzothiazolyl dyes tended to flatten as the absorption maxima shifted to longer wavelengths. Thus the 6-methoxy-2-aminobenzothiazole derivative II.6 gave very intense, but relatively dullish, ruby-red dyeings. A similar effect was apparent in the disazo derivatives (I.20–I.22) and the imidazoles (II.1–II.3).

Light fastness of the dyeings was generally good, being slightly better than those of 3- and 4-phenylazo-1,8-naphthalimides [1]. Particularly high fastness was shown by dyeings of the disazo derivatives (I.20–I.23), the imidazoles (III) and the monoazo dyes derived from 2-aminobenzothiazoles as diazo component (II.2–II.6). Sublimation fastness was also good, slight variations within the dyes being attributable to mass effects.

The use of imides and imidazole derivatives of 4-hydroxy-1,8-naphthalic anhydride as coupling components thus affords a range of red dyes of wide hue variation, and having good coloration and fastness properties.

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