Dyes and Pigments 7 (1986) 237–247

Phenylazo Derivatives of 1,8-Naphthalimides and of 7*H*-Benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones: Dyes for Synthetic Polymer Fibres

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(Received: 30 August, 1985)

SUMMARY

4-Amino- and 3-amino-1,8-naphthalic anhydrides, diazotised and coupled to N-β-hydroxyethyl-N-β-cyanoethylaniline, afford 4- and 3-[*4-*(*N-β-hydroxyethyl-N-β-cyanoethyl*)*aminophenylazo*]*-1,8-naphthalic anhydrides. These intermediates, and their O-acetyl derivatives, were condensed with amines and o-diamines to give orange to bluish-red dyes of excellent fastness to sublimation on polyester. Dyes derived from 4-amino-1,8-naphthalic anhydrides absorb at 50–60 nm longer wavelengths than related 3-amino based isomers and have better light fastness. The dyes are also suitable for the colouration of cellulose secondary acetate, cellulose tri-acetate and polyamide.*

1. INTRODUCTION

Amino-1,8-naphthalic anhydrides are useful intermediates for the synthesis of disperse dyes, giving bright yellow to orange dyes on condensation with amines and *o*-phenylenediamines. We have recently[1] described a range of imides and imidazoles derived from cyclic *tert*-amino-1,8-naphthalic anhydrides, the light fastness of which on polyester varied from poor to excellent depending on the nature of the amino residue.

Phenylazo derivatives of 1,8-naphthalimides giving scarlet to bluish-red hues on synthetic polymer fibres can be obtained[2–5] by coupling

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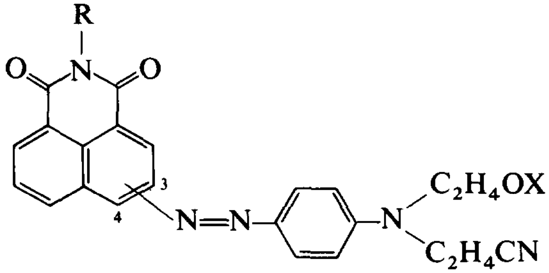
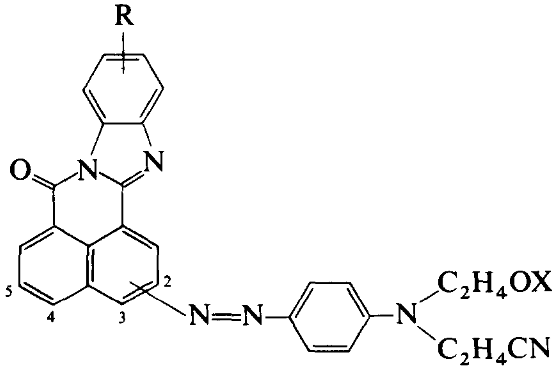
4-hydroxy-1,8-naphthalimides with diazotised arylamines. Diazotisation of 4-amino-1,8-naphthalimides, optionally substituted in the 3-position by nitro or halogeno groups, and coupling to arylamines gives red to blue disperse dyes[6,7] and similar coupling to 2,6-dihydroxy-3-cyano-4-methylpyridine affords yellow pigments.[8]

Continuing earlier investigations into substituent effects in azo disperse dyes derived from the use of *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline and its derivatives as coupling components,[9-13] we report here the synthesis and properties of a series of phenylazo derivatives of 1,8-naphthalimides (I–IV) and of 7*H*-benzimidazo (2,1-a)benz(*d*,*e*)-isoquinolin-7-ones (V–VIII).



I $X = H$, azo at 4-position
II $X = Ac$, azo at 4-position
III $X = H$, azo at 3-position
IV $X = Ac$, azo at 3-position



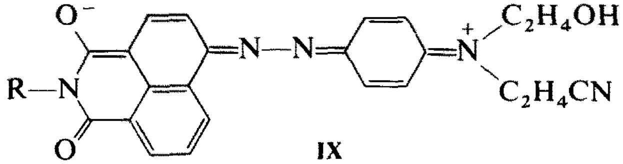
V $X = H$, azo at 3- and 4-positions
VI $X = Ac$, azo at 3- and 4-positions
VII $X = H$, azo at 2- and 5-positions
VIII $X = Ac$, azo at 2- and 5-positions

2. RESULTS AND DISCUSSION

Both 3-amino- and 4-amino-1,8-naphthalic anhydrides diazotised readily in nitrosylsulphuric acid and gave excellent yields of azo compounds on coupling with *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline. These, and their *O*-acetylated derivatives, condensed with alkylamines and arylamines to gives the dyes **I**–**IV**, some of which were also obtained by diazotisation of 4-amino-1,8-naphthalimides and coupling to *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline or its *O*-acetyl derivative. Similar condensation with *o*-phenylenediamines afforded the dyes **V**–**VIII**. For dyes **V** and **VI**, derived from *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline, condensation was preferably effected in 2-methoxyethanol followed by ring closure *in situ* of the resultant imide by addition of anhydrous zinc chloride. This obviated any acetylation of the β-hydroxy group, which tended to occur when the reaction was carried out in glacial acetic acid.

Introduction of the phenylazo chromophore into the 4-position of 1,8-naphthalimides results in a bathochromic shift in absorption maxima (**I**–**II**, Table 1) compared with the usual yellow colour of substituted 1,8-naphthalimides. Thus the 4-morpholino and 4-pyrrolidino derivatives absorb[1] in the 395 nm and 440 nm regions respectively; 3-nitro-4-*p*-anisidino derivatives have λ_{max} in the 400 nm and 450(sh) nm region[14] and imides of the ring-closed thioether, benzo(*k*,*l*)thioxanthene-3,4-dicarboxylic acid anhydride, around 460 nm.[15] The derivatives **I** and **II** absorb between 470 nm and 480 nm, the acetylated compounds **II** showing the hypsochromic shifts normally resultant[10] from addition or acylation reactions at the hydroxy group of *N*-β-hydroxyethylated coupling components. Replacement of the imide residue by a benzimidazole ring (dyes **V** and **VI**) results in further bathochromic shifts of 20–25 nm, a similar $\Delta\lambda$ to that observed[1] between the imide and benzimidazole derivatives of many substituted 1,8-naphthalic anhydrides.

The colour of the imides **I**–**II** is relatable to the typical electron delocalisations in conjugated donor–acceptor azo chromogens, e.g. **IX**.



IX

Whilst the nature of the imide residue R is not very significant in the

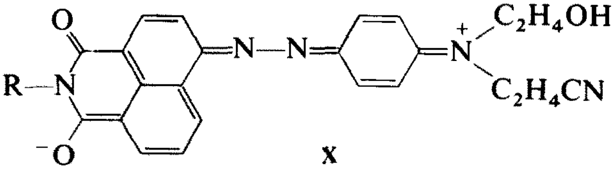
TABLE 1

Characterisation and Fastness Data for Imide Derivatives I–IV

Dye	*R*	*X*	*M.p.* (°*C*)	*Absorption in chlorobenzene*		*Fastness on polyester*			
				λ_{max} (*nm*)	*log ε*	*Light fastness*			*Sublimation* (*2·5% dye*) (°*C*)
						0·1%	*0·5%*	*2·5%*	
I.1	H	H	256–257	480	4·44	6	6	6	220
I.2	C_3H_6OH	H	223–224	482	4·48	4–5	4–5	5	220
I.3	C_3H_6OMe	H	172–173	476	4·46	5	5	5	210
I.4	C_3H_6OBu	H	113–114	476	4·48	5	5	5	220
I.5	CH_2Ph	H	207–208	479	4·46	5	5	5	210
I.6	Ph	H	243–244	478	4·47	5	5	5	220
II.1	H	Ac	177–178	472	4·56	6	6	6	220
II.2	C_3H_6OH	Ac	146–147	474	4·52	6	6	6	210
II.3	C_3H_6OMe	Ac	142–143	469	4·49	6	6–7	6–7	210
II.4	C_3H_6OBu	Ac	115–116	469	4·53	6	6–7	6–7	210
II.5	C_3H_6OAc	Ac	142–143	470	4·54	6	6–7	6–7	220
II.6	CH_2Ph	Ac	153–154	471	4·50	6	6	6–7	210
II.7	Ph	Ac	180–181	472	4·51	6	6–7	6–7	220
III.1	C_3H_6OH	H	186–187	424	4·32	3–4	3–4	4	220
III.2	C_3H_6OMe	H	142–143	423	4·36	4	4	4	210
III.3	Ph	H	224–225	425	4·34	4	4–5	4–5	210
IV.1	C_3H_6OH	Ac	229–230	422	4·34	4	4–5	4–5	220
IV.2	C_3H_6OAc	Ac	124–125	420	4·36	5	5	5	210
IV.3	C_3H_6OMe	Ac	176–177	420	4·31	4–5	4–5	5	210
IV.4	Ph	Ac	217–218	421	4·30	4–5	5	5	210

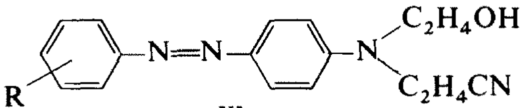
context of colour change, the colour of the dyes is influenced by the introduction of additional donor groups into the coupling residue and/or acceptor groups *ortho* to the azo link in the naphthalene residue.[7,8,16] Similar colour changes occur in related dyes in which the naphthalimide moiety is utilised as coupling component, for example in 3-arylazo-4-hydroxy-1,8-naphthalimides. The absorption maxima of such dyes, whilst relatively constant in dyes with the same arylazo residue but different imide substituents, vary significantly in dyes with the same imide substituent but different arylazo residues.[2,16] The imides **I** and **II** are hypsochromic with respect to the simplest of the 3-arylazo-4-hydroxy analogues (for example, 3-phenylazo-4-hydroxy-1,8-naphthalimide has λ_{max} 495 nm[2]), but replacement of the *N*-β-cyanoethyl-*N*-β-hydroxyethylaniline coupling residue in **I** by more donor moieties results in additional colour development.[16]

In **I** and **II**, the influence of the naphthyl residue in the diazo component and of the two carbonyl substituents, which, in addition to **IX**, can result in the delocalisation structure **X**, is shown by the absorption maxima in the 475 nm region.



X

Analogously substituted 4-aminoazobenzenes, e.g. **XI** (R = 4′-COOEt and R = 4′-CONH$_2$), have λ_{max} at 422 nm and 417 nm respectively[11] and



XI

even with an additional powerful acceptor, e.g. **XI** (R = 2′-NO$_2$-4′-COOEt), λ_{max} at 425 nm[12] is still 20 nm hypsochromic with respect to dyes **I**. The imidazole residue in **V** and **VII**, giving dyes of λ_{max} around 500 nm, is relatable in its colour development to the use of 2′-cyano-4′-nitro- (λ_{max} 505 nm) and 2′-methylsulphonyl-4′-nitro- (λ_{max} 500) substitution in **XI**.

In dyes **III**–**IV**, the lack of conjugation between the acceptor carbonyl groups and donor amino group of the coupling residue precludes the formulation of structures **IX** and **X** and this leads to marked hypsochromic shifts of *ca* 50 nm and decrease in absorbance relative to the dyes **I** and **II**. The effect of the naphthyl residue is, however, apparent and **III** are bathochromic with respect to analogous aminoazobenzenes **XI**, for example, **XI** (R = 3′-COOEt), λ_{max} 409 nm; **XI** (R = 3′-$CONH_2$), λ_{max} 406 nm. Using as comparison carboxamido substituted aminoazobenzenes **XI** and imides **I** and **III** where R = C_3H_6OMe, $\Delta\lambda$ values between dyes based on phenyl and naphthylimide diazo components are 17 nm for the *meta*-substituted dyes **III.2** and **XI**, and 59 nm for the *para*-substituted dyes **I.3** and **XI**. In dyes **XI**, $\Delta\lambda$ between the 3′- and 4′-$CONH_2$ derivatives is 11 nm, but in the imide derivatives, $\Delta\lambda$ between **III.3** and **I.3** is 53 nm, further indicating the bathochromic effect of the naphthylimide residue in azo dyes.

The imides **I** and **II** dyed polyester in bright scarlet hues of generally good build-up, the 3-alkoxy- and 3-acyloxy-propyl imides **I.3**, **I.4** and **II.3–II.5** giving the deepest colourations; the *O*-acyl derivatives **II** generally showed better build-up than **I**. Light fastness of all dyeings was good, particularly that of the *O*-acyl derivatives **II**, which showed a 0·5–1 point improvement relative to **I**. Sublimation fastness was of an equally high order, being significantly better than that of 4-*N*-β-cyanoethyl-*N*-β-hydroxyethylaminobenzenes of similar hue.[11,12]

The imides **III** and **IV** gave similarly deep dyeings, but of an orange hue, with little difference in build-up between the acylated and hydroxy derivatives **IV** and **III**, the alkoxypropyl and related imides **III.2** and **IV.2–3** showing better build-up than other derivatives. Whilst sublimation fastness was high, light fastness was lower than for analogous *para*-substituted dyes, although that of the *O*-acetyl derivatives **IV** was generally good. The lower fastness of **III** and **IV** relative to **I** and **II** is not in agreement with the association of lower light fastness with increased electron mobility.[17] Factors influencing the light fastness of azo disperse dyes are complex and have been discussed in relation to the wide variation in fastness observed in 2′,4′,6′-trisubstituted-4-*N*-β-hydroxyethyl-4-*N*-β-cyanoethylaminoazobenzenes.[13] In comparing dyes **I** and **III**, the decreased electron delocalisation in **III**, where delocalisation structures such as **IX** and **X** cannot be formulated, presumably results in a greater electron density in the dyes, relative to **I**, on either or both of the azo and amino nitrogen atoms, thus facilitating photodegradation at these sites.

Dyeings of some imides (**I.3**, **II.1**, **II.5** and **IV.3**) were carried out on other substrates, namely cellulose secondary and triacetates, and polyamide. The dyes built up to similar depths of shade on these fibres to those on polyester and in similar hues, except on polyamide, which gave dyeings bluer, but not significantly duller, than on the acetate fibres. Light fastness was of a similar order to the values reported in Table 1 for polyester, with a tendency to be 0·5 point greater on cellulose secondary acetate and 0·5 point lower on polyamide.

The imidazole derivatives **V–VI** and **VII–VIII** gave deep bluish-red and orange-red hues respectively on polyester, the *O*-acetyl derivatives **VI** and **VIII** having the better build-up. Sublimation and light fastness were similar to those of the imide derivatives, the *meta*-substituted dyes **VI** and **VIII** again having lowest fastness. Colouration of other fibres by selected dyes (i.e. **V.1**, **VI.1**, **VII.1** and **VIII.1**) was also good, and light fastness varied ±0·5 points as with the imide derivatives. Dyeings on polyamide were much bluer than on other substrates; dye **V.1**, for example, gave a purple colouration of polyamide compared with bluish-red on other substrates.

3. EXPERIMENTAL

3.1. 3- and 4-[4-(*N*-β-Cyanoethyl-*N*-β-hydroxyethyl)amino phenylazo]-1,8-naphthalic anhydrides

4-Amino-1,8-naphthalic anhydride (21·3 g, 0·1 mol) was added over 30 min at 10 °C to nitrosylsulphuric acid prepared from sodium nitrite (7 g) and conc. sulphuric acid (20 ml), followed by dilution with glacial acetic acid (20 ml). Diazotisation was continued for a further 3 h at 10 °C and the diazo liquor added slowly to *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline (19 g, 0·1 mol) in ice-cold 30% aq. hydrochloric acid. After stirring for 2 h, the mixture was stirred into ice–water (1000 ml) and filtered, to give a dark red solid (36·3 g, 87·6%), which was recrystallised from ethanol in dark bluish-red needles of 4-[4-(*N*-β-cyanoethyl-*N*-β-hydroxyethyl)aminophenylazo]-1,8-naphthalic anhydride, m.p. 222–223 °C, λ_{max} (log ε) in chlorobenzene, 480 nm (4·43). $C_{23}H_{18}N_4O_4$ requires: C, 66·7; H, 4·35; N, 13·5. Found: C, 66·9; H, 4·5; N, 13·3%.

3-Amino-1,8-naphthalic anhydride similarly gave 3-[4-*N*-β-cyanoethyl-*N*-β-hydroxyethyl)aminophenylazo]-1,8-naphthalic anhydride, 79·2%, brownish-red needles, m.p. 149–150 °C, λ_{max} (log ε) in chlorobenzene, 425 nm (4·29). Found: C, 66·6; H, 4·2; N, 13.2%.

3.2. 3- and 4-[4-(*N*-β-Cyanoethyl-*N*-β-acetoxyethyl)aminophenylazo]-1,8-naphthalic anhydrides

The intermediates (10 g) prepared in Section 2.1 above were acetylated by refluxing for 30 min in acetic anhydride (50 ml) and acetic acid (50 ml). The resulting solution was reduced to 50 ml, cooled and filtered to give two anhydrides. (i) 4-[4-(*N*-β-Cyanoethyl-*N*-β-acetoxyethyl)aminophenylazo]-1,8-naphthalic anhydride, 89·2%, m.p. 181–182°C (ethanol), λ_{max} (log ε) in chlorobenzene, 481 nm (4·50). $C_{25}H_{20}N_4O_5$ requires: C, 65·8; H, 4·4; N, 12·3. Found: C, 65·7; H, 4·6; N, 12·3%. (ii) 3-[4-(*N*-β-Cyanoethyl-*N*-β-acetoxyethyl)aminophenylazo)-1,8-naphthalic anhydride, 92·4%, m.p. 175–176°C (ethanol), λ_{max} (log ε) in chlorobenzene, 424 nm (4·38). Found: C, 65·6; H, 4·3; N, 12·1%).

3.3. 3- and 4-Phenylazo-1,8-naphthalimides (I–IV)

4-[4-*N*-β-Cyanoethyl-*N*-β-acetoxyethyl)aminophenylazo]-1,8-naphthalic anhydride (4·14 g, 0·01 mol) was refluxed for 1 h with 3-methoxypropylamine (1·3 g, 0·015 mol) in ethanol (200 ml). Volume was reduced to 70 ml and the solution filtered to give dark red prisms (4·0 g, 80%) of 4-[4-(*N*-β-cyanoethyl-*N*-β-hydroxyethyl)aminophenylazo-*N*-(3-methoxypropyl)-1,8-naphthalimide (**I.3**), m.p. 172–173°C (ethanol). $C_{27}H_{27}N_5O_4$ requires: C, 66·8; H, 5·6; N, 14·4. Found: C, 66·5; H, 5·6; N, 14·0%. The product was identical to that obtained as in Section 3.1 above by diazotisation of 4-amino-1,8-(*N*-3-methoxypropyl)naphthalimide and coupling to *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline.

The above dye (1 g) was acetylated by refluxing for 30 min in acetic acid–acetic anhydride (50ml) and adding to ice–water to give 4-[4-(*N*-β-cyanoethyl-*N*-β-acetoxyethyl)aminophenylazo]-*N*-3-methoxypropyl-1,8-naphthalimide (**II.3**), dark red needles, m.p. 142–143°C (2-methoxyethanol). $C_{29}H_{29}N_5O_5$ requires: C, 66·0; H, 5·5; N, 13·3. Found: C, 65·6; H, 5·5; N, 13·0%. The same dye was also prepared in 87% yield by diazotising 4-amino-*N*-(3-methoxypropyl)-1,8-naphthalimide (2·84 g, 0·01 mol) and coupling to *N*-β-cyanoethyl-*N*-β-acetoxyethylaminoaniline (2·3 g) as in Section 3.1 above.

Using the above methods, the imides **I–IV**, data for which are shown in Table 1, were prepared. 4-Amino-1,8-naphthalimides used in the syntheses were prepared as previously described.[18]

TABLE 2

Characterisation and Fastness Data for Imidazole Derivatives **V–VIII**

Dye	*R*	*X*	*M.p. (°C)*	*Absorption in chlorobenzene*		*Fastness on polyester*			
				λ_{max} *(nm)*	*log* ε	*Light fastness*			*Sublimation (2·5% dye) (°C)*
						0·1%	*0·5%*	*2·5%*	
V.1	H	H	220–222	498	4·43	5	5	5–6	220
V.2	OMe	H	199–201	496	4·45	5	5	5–6	220
V.3	Cl	H	256–258	491	4·40	5	5–6	5–6	220
VI.1	H	Ac	226–227	492	4·51	6	6	6	220
VI.2	OMe	Ac	109–112	496	4·44	6	6	6	220
VI.3	Cl	Ac	208–212	490	4·45	6	6	6	220
VII.1	H	H	208–210	434	4.31	4	4	4	220
VII.2	Cl	H	217–220	430	4.34	4	4	4	220
VIII.1	H	Ac	227–228	429	4·39	4–5	4–5	4–5	210
VIII.2	Cl	Ac	194–197	425	4·37	4–5	5	5	210

3.4. Phenylazo derivatives of 7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-ones (V–VIII)

4-[4-(*N*-β-Hydroxyethyl-*N*-β-cyanoethyl)aminophenylazo]-1,8-naphthalic anhydride (4 g) was refluxed for 1 h in 2-methoxyethanol (75 ml) with *o*-phenylenediamine (1·4 g). Anhydrous zinc chloride (4 g) was added, refluxing continued for 30 min, the solution cooled and added to ice-cold 5 % aq. hydrochloric acid (300 ml). Filtration yielded 4·5 g (92·6 %) of the isomer mixture of 3- and 4-[4-(*N*-β-hydroxyethyl-*N*-β-cyanoethyl)-aminophenylazo]-7*H*-benzimidazo(2,1-*a*)benz(*d*,*e*)isoquinolin-7-one (**V.1**), dark brownish-red needles, m.p. 220–222 °C (2-methoxyethanol).

Other **V–VIII**, data for which are shown in Table 2, were similarly prepared. The dyes **VI** and **VIII** were also obtained by standard[1] synthesis in glacial acetic acid, under which conditions the hydroxyethylated derivatives for **V** and **VII** tended to acetylate.

3.5. Electronic spectra, dyeing and fastness properties

Electronic spectra (in monochlorobenzene), and dyeings and fastness assessments were carried out as in previous investigations.[1,11–13]

4. CONCLUSIONS

Both the imide and imidazole derivatives are excellent dyes for synthetic polymer fibres giving yellow-orange to bluish-red hues, depending on the orientation of the phenylazo residue. Colouration of other synthetic polymer fibres by the dyes is good and fastness properties of the dyeings to light and sublimation, particularly of the 4-phenylazo substituted derivatives, is very good. Whilst the dyes reported in this present work utilise *N*-β-hydroxyethyl-*N*-β-cyanoethylaniline and its *O*-acetyl derivative as coupling component, further hue modification in these dyes can result from the use of other coupling residues,[16] and the dyes **I–VIII** are illustrative of a useful structural basis for the synthesis of dyes of good colouration and fastness properties on synthetic polymer fibres.

ACKNOWLEDGEMENT

We thank the S.E.R.C. for the award of a Research Studentship to M.J.B.

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