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# Amino Derivatives of 1,8-Naphthalic Anhydride and Derived Dyes for Synthetic-Polymer Fibres

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*SUMMARY*

*Condensation of 4-halogeno-1,8-naphthalic anhydride with the appropriate cyclic secondary amines gives the 4-morpholino-, 4-piperidino-, 4-pyrrolidino- and 4-piperazino- derivatives. These intermediates afford yellow to orange dyes for synthetic-polymer fibres when condensed with alkylamines, arylamines and o-phenylenediamines. Also described are 4-imidazolo- and pyrido[5,6-c]-1,8-naphthalic anhydrides; imides of these are colourless, but derived 7H-benzimidazo[2,1-a]benz[d,e]isoquinolin-7-ones are yellow dyes. Coloration and fastness properties of many of these derivatives on polyester are good. The effect of an additional nitro group ortho to the amino substituents is also investigated.*

## 1. INTRODUCTION

Aminonaphthalimides are known to act as yellow dyes for synthetic-polymer fibres. The earliest industrial use of such compounds was Celliton Brilliant Yellow FFA CF (C.I. Disperse Yellow 11, C.I. 56200), viz. *N*-2,4-dimethylphenyl-4-amino-1,8-naphthalimide. Deficiencies in fastness properties, especially on polyester, of dyes of this type led to the development of more satisfactory dyes, e.g. derivatives of 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one,[1] naphthalene-1,4,5,8-tetracarboxylic acid,[2] and benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic acid.[3]



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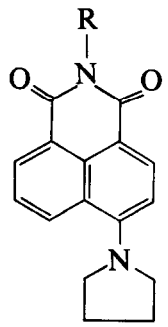
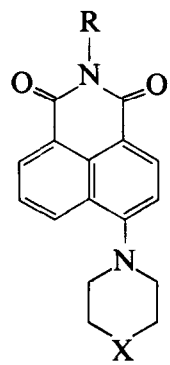
The presence of an amino group in the naphthyl ring of dyes of this type has not been extensively described, but the condensation products of 4-bromo-1,8-naphthalic anhydride and substituted *o*-phenylenediamines are stated[4] to give brilliant yellow to scarlet dyes of good fastness properties when the bromine is replaced by reaction with alkylamines, cycloalkylamines, arylamines or dialkylamines.

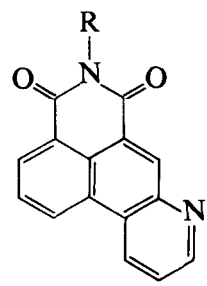
We report here the synthesis and properties of a series of *tert*-amino derivatives of 1,8-naphthalic anhydride, particularly those in which the *tert*-amino group is a member of a saturated or aromatic ring, viz. the 1,8-naphthalimides (**I–VI** and **XIV**) and the 7*H*-benzimidazo-[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**VII–XIII** and **XV**). In the latter, the specific formulae shown are representative of one component of the isomer mixture formed during the condensation of substituted 1,8-naphthalic anhydrides with substituted *o*-phenylenediamines.



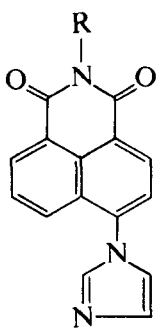
**I**



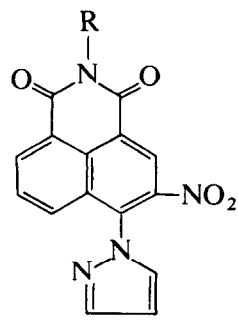
**II** X = $CH_2$
**III** X = O
**IV** X = NH



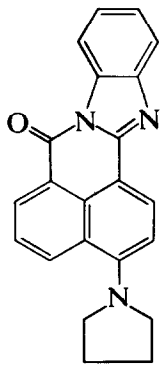
**V**



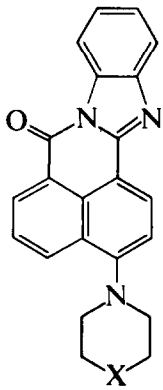
**VI**



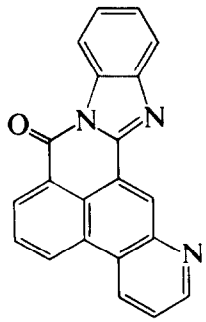
**XIV**



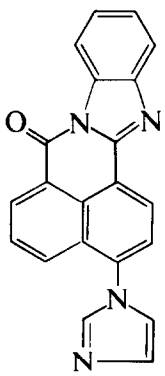
**VII**



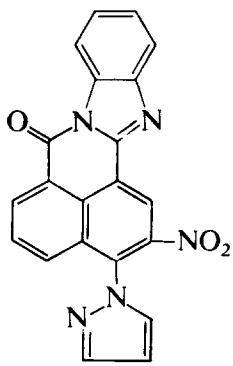
**VIII** X = $CH_2$
**IX** X = O
**X** X = NH
**XI** X = N·$COCH_3$



**XII**



**XIII**



**XV**

Additionally described are some nitro derivatives of the above, in which the nitro group is *ortho* to the *tert*-amino residue in the naphthyl ring. These derivatives will be referred to in the text with the suffix **N**, e.g. 3-nitro-4-pyrrolidino-1,8-naphthalimides **I.N**, etc. (except for the pyrazole derivatives **XIII** and **XIV** for which no unnitrated dyes were prepared).

## 2. RESULTS AND DISCUSSION

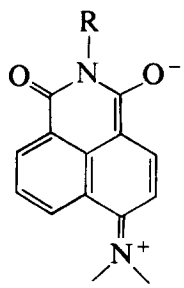
### 2.1. Synthesis and colour of unnitrated derivatives

4-Chloro-1,8-naphthalic anhydride condensed readily with the cyclic secondary amines used in this investigation. Using 2-methoxyethanol as

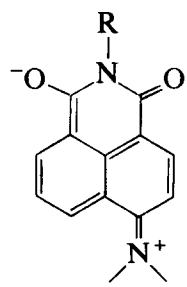
reaction solvent, reactions with morpholine and pyrrolidine required a larger excess of amine and more prolonged reaction times than in diethyleneglycol dimethyl ether, in which solvent quantitative conversion was rapidly obtained. The more reactive piperidine and piperazine gave satisfactory reaction in 2-methoxyethanol, although the resultant 4-piperazino-1,8-naphthalic anhydride was very soluble in the reaction medium, and in any aqueous medium the reaction liquor was drowned out into, making isolation of the reaction product more difficult than with the other amines. Imidazole did not react well with 4-chloro-1,8-naphthalic anhydride in 2-methoxyethanol and the use of the higher boiling diglyme was necessary for any satisfactory degree of condensation to occur. No significant reaction could be obtained between 4-chloro-1,8-naphthalic anhydride and pyrazole, even in reaction times up to 180 h.

Pyrido[5,6-*c*]-1,8-naphthalic anhydride was obtained by Skraup synthesis on 3-amino-1,8-naphthalic anhydride. Similar reaction from 4-amino-1,8-naphthalic anhydride gave pyrido[2,3-*c*]-1,8-naphthalic anhydride, previously obtained[5] by oxidation of pyrido[2,3-*c*]acenaphthene. Attempts to synthesise a dipyrido-1,8-naphthalic anhydride from 4,5-diamino-1,8-naphthalic anhydride gave a resinous, infusible black material from which no product could be isolated.

The development of colour in 1,8-naphthalimides is dependent on the presence of a strongly electron donating substituent conjugated with the carbonyl groups, giving the delocalisation structures **XVI** and **XVII**.



**XVI**



**XVII**

Whilst the strongly donating thioether group gives absorption maxima in the 370–390 nm range in the 1,8-naphthalic anhydride 4-thioethers,[6] the presence of amino groups is normally necessary to obtain shifts of absorption maxima into the visible.

The 1,8-naphthalimides synthesised in this current work were all yellow and were bathochromic in the order

pyrrolidino > piperidino > morpholino >
piperazino > imidazolo > pyridino

The relative electron donating properties of the pyrrolidine and piperidine rings can be explained in terms of steric factors. On the basis of the conformation of cyclopentane,[7-11] the pyrrolidine ring may be considered in terms of a pentagon somewhat distorted from planarity to reduce the torsional strain on the eclipsed protons. This can result in an 'envelope conformation',[9] in which a single atom is out of the plane containing the other four, and a 'half chair conformation'[9,12,13] in which three adjacent atoms are in one plane, with the other two twisted, one above the plane, the other below. As the molecule passes through the possible forms, departures from planarity are averaged around the ring by pseudo rotation,[7] giving bond angles in the order of 108·5° and thus allowing the nitrogen atom to be in an $sp^3$ arrangement with negligible ring strain.

Studies on the relative degree of $C_{AR}$–N interaction in *N,N*-dialkylanilines and related *N*-alicyclic analogues confirm the similarity of electron donor ability of the pyrrolidino ring to *N,N*-dialkyl substitution, but the decreased resonance interaction from the piperidino ring. Thus, both base strength and the exaltation of molar refraction ($\Delta R_D$), i.e. the difference between calculated and experimental values, have been used as a qualitative measurement of resonance energy. Inhibition of resonance lowers the stability of an aromatic amine relative to its conjugate acid, resulting in an increase in base strength and the $\Delta R_D$ values of a series of aromatic amines have been shown[11] to increase with increasing interaction between the amino nitrogen atom and the attached phenyl ring. Values for $\Delta R_D$ of 0·96 for *N*-phenylpiperidine, 1·49 for *N,N*-dimethylaniline and 1·64 for *N*-phenylpyrrolidine, and for $pK_a$ of 5·22, 4·39 and 3·45 respectively,[14] indicate the decreased resonance delocalisation in *N*-phenylpiperidine. Similarly, the $pK_a$ values for 4-aminobenzoic acids, in which the amino substituents are dimethylamino (6·01), diethylamino (6·19), pyrrolidino (6·07) and piperidino (5·75) confirm the close relationship of the electron donor capacity of the pyrrolidino and *N,N*-dialkylamino groups, but the decreased overlap due to twisting of the amine plane from the ring plane indicates decreased $C_{AR}$–N interaction from the piperidino substituents.[15]

Rotation about the $C_{AR}$–N bond to reduce steric crowding removes the nitrogen atom from optimum position of overlap with the aromatic $\pi$-electron cloud to a position of reduced overlap. The angle of twist $\theta$ (0° in the position of optimum overlap) has been estimated[16] as 45° in *N*-phenylpiperidine and 33° in 4-nitro-*N*-phenylpiperidine. Nuclear magnetic resonance spectroscopy also indicates the decreased $C_{AR}$–N mesomerism resulting from steric inhibition of resonance; the greater the electron donation by the amino nitrogen atom, the less is the deshielding of the 2,6-protons. Values of chemical shifts for 2,6-protons (in ppm in acetone-$d_6$) have been reported[16] for 4-nitro-*N*,*N*-dimethylaniline (6·72), *N*,*N*-diethylaniline (6·74), *N*-phenylpiperidine (6·92) and *N*-phenylpyrrolidine (6·57), i.e. a 0·2–0·3 ppm downfield shift for the 2,6-proton signals in *N*-phenylpiperidine, commensurate with decreased electron donation from this system. Similar studies[17] of the $^{13}$C-NMR spectra confirm, for *ortho*- and *para*- chemical shifts, these results. The chair configuration of the piperidine ring, with resultant steric inhibition of resonance, thus results in hypsochromic shifts in the absorption maxima for the dyes containing the *N*-piperidino substituent relative to those of the *N*-pyrrolidino analogues.

The further hypsochromic shifts resultant in the morpholino and piperazino derivatives are relatable to the $-I$ effect of the additional hetero atom in the $\gamma$-position, and the degree of shift increases with the increased strength of the inductive effect.

A similar order of bathochromicity of the amino substituents is apparent in the 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones, viz. pyrrolidino > morpholino > piperazino, although absorption maxima are generally shifted to longer wavelengths compared to the analogous imides, in accord[5] with the additional resonance interactions resultant from the introduction of the benzimidazole ring system. Whilst differences in the morpholino, piperidino and piperazino derivatives are of similar order (20 nm) to those observed between the imides and benzimidazoles derived from benzo[*d*]naphtho[3,4-*b*]thiophene-9,10-dicarboxylic acid,[18] the imides (**I**) and benzimidazoles (**VII**) from 4-pyrrolidino-1,8-naphthalic anhydride have similar absorption maxima. Significant differences in the colour of these when dyed on to polyester is however apparent, **I** being yellow and **VII** orange. Differences can be even more marked, e.g. in the order of 50 nm between benzo[*k*,*l*]thioxanthene-3,4-dicarboximides[19] and related benzimidazoles.[20]

Comparison of the absorption maxima of derivatives of 7*H*-

benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one can however only be general, since this is a composite absorption of the two isomers formed in the condensation of substituted 1,8-naphthalic anhydrides and *o*-phenylenediamine or of the four isomers resultant from the use of substituted *o*-phenylenediamine. The more activated amino group tends to react preferentially in the imide formation prior to ring closure,[21,22] the course of which will be influenced by substituent effects in both the phenyl and naphthyl ring.[5,22-24] Similar isomer mixtures result in the vat dyes obtained from naphthalene-1,4,5,8-tetracarboxylic acid dianhydride and *o*-phenylenediamine, the products being utilised as either the isomer mixture (C. I. Vat Red 14, C.I. 71110), or the separated *cis* (C.I. Vat Red 15, C.I. 71100) and *trans* (C.I. Vat Orange 7, C.I. 71105) isomers.

Whilst separation and/or unambiguous synthesis has been described, e.g. for isomers containing nitro,[5,23,24] methyl,[25] methoxy[21] and acetyl substituents,[26] few data have been recorded for isomers in which the naphthyl ring is substituted by an electron donor group. Differences in the order of 20 nm have however been noted[27] between the two isomeric benzimidazothioxanthenoisoquinolinones.

The hypsochromic shifts in the cycloalkyamino 1,8-naphthalimides resultant from the increased $-I$ effect of the $\gamma$-substituent in the ring system are further apparent when the cyclic amino residue contains additional electron attracting nitrogen atoms. Thus, the 4-imidazolo-1,8-naphthalimides (**VI**, Table 5) are colourless. Pyrido[5,6-*c*]-1,8-naphthalic anhydride and its imides (**V**, Table 5) have similar absorption to that of pyrido[2,3-*c*]-1,8-naphthalic anhydride.[5] Condensation of these anhydrides with *o*-phenylenediamines gives the isomeric pyrido-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**XII**, Table 5) which are coloured. The lack of any significant contribution of electron withdrawing substituents in the naphthyl ring to the colour of 7*H*-benzimidazo-[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones is illustrated by the similar absorption maxima of the unsubstituted compound,[5] its nitro[5] and sulphone[6] derivatives, and the pyridino derivatives reported here.

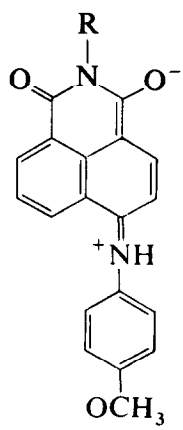
### 2.2 Synthesis and colour of nitrated derivatives

Replacement of the 4-chloro in naphthalic anhydrides is facilitated by the additional electron attracting nitro group and 4-chloro-3-nitro-1,8-naphthalic anhydride reacted readily in ethanol with morpholine, piperidine, pyrrolidine and piperazine. With piperazine, a very viscous

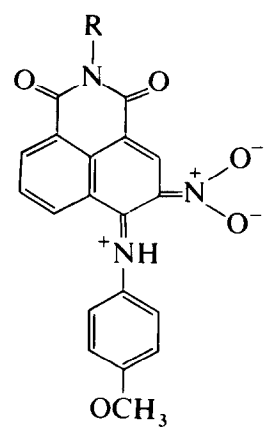
almost unstirrable mass was formed in the initial stages of the condensation, gradually yielding a more filterable suspension on prolonged heating. Imidazole did not react well in ethanol, but in 2-methoxyethanol satisfactory condensation proceeded. Pyrazole had even more limited reactivity (cf. its lack of reactivity with 4-chloro-1,8-naphthalic anhydride) and the use of boiling diethylene glycol diethyl ether was necessary to effect satisfactory reaction.

Introduction of a nitro group *ortho* to the cyclic amino group generally resulted in a bathochromic shift in absorption maxima compared to the unnitrated analogues. Thus, in the anhydrides, the presence of the nitro group results in shifts of *ca.* 20 nm for the morpholino and piperidino derivatives and of *ca.* 30 nm for the piperazino derivative. The pyrrolidino anhydride is shifted hypsochromically in the order of 30 nm for the principal absorption band, with an inflexion in a similar region to the principal absorption of the unnitrated analogue. Shifts in the corresponding imides are of a similar order, the nitropyrrolidino imides again being hypsochromic.

The principal absorption bands (400 nm and 450s nm) of 4-(4-methoxy)anilino-3-nitro-1,8-naphthalimides have been related[28] to the delocalisation structures **XVIII** and **XIX** and analogy drawn to their relationship with nitrodiphenylamine derivatives, in which structures of type **XIX** may be stabilised by hydrogen bonding. A similar absorption pattern appears, with either incomplete resolution or a conjoint absorption band, in the 3-nitro-4-cycloalkylamino-1,8-naphthalimides (Table 6). It may be reasonable to associate the lower wavelength




**XVIII**




**XIX**

absorption in the 400 nm region to the amino–carbonyl interaction, i.e. in the same region to that observed in the imides of the unnitrated derivatives (Tables 1–4), and the longer wavelength absorption to nitro–amino interaction, occurring at lower wavelength than in the 3-nitro-4-arylamino-1,8-naphthalimides because of loss of additional conjugation from the phenyl ring. 4-(3-Hydroxypropylamino)-*N*-(3-hydroxypropyl)-1,8-naphthalimide and similar open chain alkyl derivatives[24] and also 3-nitro-4-(*N*,*N*-bis-*β*-hydroxyethylamino)-*N*-(3-methoxypropyl)-1,8-naphthalimide,[6] all absorb in the 396–397 nm region, i.e. a similar region to that of the lower wavelength absorption for the 3-nitro-4-cycloalkylamino-1,8-naphthalimides reported here.

However, it is of interest to note that the absorption maxima of the unnitrated compounds 4-(3-methoxypropyl)amino-*N*-(3-methoxypropyl)-1,8-naphthalimide and 4-(4-methoxy)anilino-*N*-(4-methoxy)phenyl-1,8-naphthalimide are at 428 and 440 nm respectively.[6] A similar substitution pattern, but in a less conjugated orientation, gives,[5] with 2-arylamino-*N*-aryl-1,8-naphthalimides, absorption in the 430–435 nm region. Thus, introduction of a nitro group into the 3-position of straight chain 4-alkylamino-1,8-naphthalimides is hypsochromic, despite the additional resonance interaction **XIX**. Similar shifts to lower wavelength are apparent in analogous 4-arylamino derivatives, and with the cycloalkylamino derivatives in this present investigation, introduction of a nitro group can result in bathochromic or hypsochromic shifts depending on the nature of the cycloalkyl moiety. A similar tendency is apparent[6] in the 4-thioethers and 3-nitro-4-thioethers of 1,8-naphthalic anhydride and their imides.

The nitrated 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**VIII.N**–**IX.N**) are bathochromic (Table 7) compared to the unnitrated derivatives **VIII**–**IX** (Tables 2–4) by a similar order to that observed with the imides, but the pyrrolidino derivative (**VII.N**), although bathochromic with respect to the 3-nitro-4-pyrrolidino-1,8-naphthalimides (**I.N**) (Table 6), are hypsochromic relative to the unnitrated pyrrolidino-7*H*-benz[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**VII**, Table 1).

4-Imidazolo-1,8-naphthalic anhydride and its imides (**VI**, Table 5) are, as anticipated from the presence of the electron attracting nitrogen atom in the hetero ring, colourless, and introduction of an additional electron acceptor into the 3-position gives no further colour development. 3-Nitro-4-imidazolo- and 3-nitro-4-pyrazolo-1,8-naphthalic anhydride and their imides (**XII.N**; **XIV**, Table 6) do not absorb in the visible.

Imides of 4-pyrazolo-1,8-naphthalic anhydride have been described[29] as satisfactory fluorescent whitening agents. Shifts of absorption maxima into the visible result in the imidazolo- (**XIII**, Table 5), nitro-imidazolo- (**XIII.N**, Table 7) and nitro-pyrazolo-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**XV**, Table 7). The imidazoles derived from *o*-phenylenediamine and substituted 4-pyrazolo-1,8-naphthalic anhydride are reported[30] to be yellow to orange dyes of good fastness on synthetic-polymer fibres.

### 2.3 Dyeing and fastness properties of unnitrated dyes.

The 4-morpholino-(**III**), 4-piperidino-(**II**) and 4-pyrrolidino-1,8-naphthalimides (**I**) all coloured polyester fibres in bright fluorescent greenish-yellow hues, showing excellent build-up to deep shades. With the 4-piperazino-1,8-naphthalimides (**IV**), the conventional grinding of the dyes to fine dispersion for dyeing produced a solution and resultant dyeings were unsatisfactory, only slight coloration of polyester being obtained. The 7*H*-benzimido[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one derivatives of the above (**VII–IX**) gave fluorescent deep orange dyeings of similar brightness to the imides, but the piperazino derivatives (**X**) again had very limited build-up. The undesirable hydrophilic character resulting from the NH group in the piperazine residue was less evident in the *N*-acetylpiperazino derivatives (**XI**) which gave fluorescent deep orange dyeings.

The *N*-3-methoxypropylimides (**I.4–III.4**) and the unsubstituted 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones (**VII.1–IX.1**) were also assessed on other substrates. In each case the hue and build-up on cellulose tri-acetate was similar to that observed on polyester, whilst on polyamides, dyeings were somewhat redder and duller in hue. On cellulose secondary acetate, the imides gave excellent dyeings of good build-up but the imidazoles were poor, in accord with the previous observation[31] that simply substituted derivatives of 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one have low substantivity on secondary acetate.

Imides of 4-imidazolo-(**VI**) and pyrido[5,6-*c*]-1,8-naphthalic anhydride (**V**) did not absorb in the visible, but on polyester imparted a strong fluorescence. The benzimidazole derivatives (**XII.1–XII.3**) of 4-imidazolo-1,8-naphthalic anhydride gave bright yellow dyeings of good strength, and similar good build-up to fluorescent greenish yellow and yellow hues of good clarity resulted from the derivatives (**XII.1–X11.6**) of

the pyrido intermediate. The quaternary salts derived from the pyrido-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinoline-7-ones dyed 'Courtelle' in somewhat duller and browner hues, with decreased fluorescence. Lightfastness properties of the dyeings varied considerably. In general, fastness was good with the 4-morpholino derivatives, moderate to good with the 4-piperidino derivatives and moderate to poor with the 4-pyrrolidino dyes. The 4-piperazino derivatives dyed so poorly that the lightfastness was of little significance, but the pale dyeings obtained had moderate fastness.

Acetylation of the NH group (**XI**, Table 4) resulted in considerable improvement in both coloration and lightfastness properties. The general order of lightfastness is in accord with previous observations in 4-amino-azobenzene disperse dyes[32,33] in which the lightfastness is concluded to improve with increase in the $-I$ effect of the terminal ring hetero atom. Thus the pyrrolidino and piperidino derivatives, with no $-I$ influence, tend to be somewhat fugitive, especially the former, but the morpholino derivatives have an acceptably good fastness, as have the *N*-acetyl piperazino derivatives. Introduction of the more highly electron deficient pyridino ring system results in dyes of outstanding lightfastness (**XII.1–XII.5**); the nitro-*o*-phenylenediamine derivative **XII.6** has lower fastness and a similar effect is observed[20] in the nitro substituted benzimidazothioxanthenoisoquinolinones. The lightfastness of the pyridino quaternary salts on 'Courtelle' was also of an acceptably high order, with the exception of the nitro derivative (Table 8).

Sublimation fastness of the majority of the dyes was good, tending to be higher with the increased mass and polarity of the 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinoline-7-ones. Taking an overall assessment of the dyeing properties, light and sublimation fastness, the derivatives of 4-morpholino-, 4-*N*-acetylpiperazino- and pyrido[5,6-*c*]-1,8-naphthalic anhydride can be considered good dyes for synthetic polymer fibres, with the 4-piperidino and 4-imidazolo derivatives yielding generally satisfactory products.

### 2.4 Dyeing and fastness properties of nitrated derivatives

The nitrated analogues of all the above dyes coloured polyester deep yellow (imides) to orange (benzimidazoles). Build-up was generally good and in many cases better than that of the unnitrated dyes. Nitro-piperazino derivatives were more water soluble and coloration properties

were poor. None of the dyeings had the clarity of hue and fluorescence of the unnitrated compounds and were markedly duller.

Whilst sublimation fastness was of a generally high order, lightfastness was considerably decreased compared to the unnitrated analogues and none of these dyes had satisfactory lightfastness. The lightfastness of derivatives of 3-nitro-4-amino-1,8-naphthalic anhydrides appears to be closely related to the nature of the substituted amino residue. 3-Nitro-4-arylamino-1,8-naphthalimides[28] have an acceptably good fastness. Whilst this may be associated with the stabilisation of these nitro-diarylamine-type compounds by intramolecular hydrogen bonding, the corresponding 4-alkylamino analogues, in which hydrogen bonding factors are still operative, have very poor lightfastness,[28] similar to the fastness of the *tert*-amino derivatives reported here, and in which no hydrogen bonding is possible. The improved fastness resulting from 3-nitro-4-arylamino-1,8-naphthalic anhydride is more probably associated with basicity of the amino group; in these dyes, the arylamino residue is readily replaced by more basic alkylamines[28] during *N*-alkylimide formation. We have observed[6] improved fastness in other more weakly basic amino derivatives such as 3-nitro-4-(2-benzothiazolylamino)-1,8-naphthalimides and a similar relationship between fastness and amine basicity is apparent in other dye series, e.g. 1-arylaminoanthraquinones (6–7) and 1-alkylaminoanthraquinones (5–6). The nitro group is also an additional potential site for photodegradation and in derivatives of 1,8-naphthalic anhydrides containing thioether or sulphone substituents in the 4-position, introduction of a nitro group into the 3-position results[6] in a marked decrease in lightfastness.

## 3. EXPERIMENTAL

### 3.1 4-Pyrrolidino-1,8-naphthalic anhydride

4-Chloro-1,8-naphthalic anhydride (23·2 g) and pyrrolidine (9·2 g) were refluxed for 2 h in diethylene glycol dimethyl ether (100 ml). The liquor on cooling deposited orange needles (17·1 g, 55·2%) of 4-pyrrolidino-1,8-naphthalic anhydride, m.p. 279–281 °C. The mother liquor on adding to water gave a further 35% of product, m.p. 279 °C. Recrystallisation from ethanol gave orange needles, m.p. 280–281 °C; $\lambda_{max}$ ($\log\varepsilon$) in chlorobenzene, 438 nm (4·12) ($C_{16}H_{13}NO_3$ requires: C, 71·9, H, 4·9, N, 5·2%; Found: C, 72·1, H, 4·8, N, 5·3%).

### 3.2. 4-Morpholino-1,8-naphthalic anhydride

Replacing pyrrolidine in the above by morpholine (13 g) gave, as first crop, 25 g (78%) of 4-morpholino-1,8-naphthalic anhydride, recrystallised from 2-methoxyethanol in deep yellow needles, m.p. 232–233 °C; $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 396 nm (4·05) ($C_{16}H_{13}NO_4$ requires: C, 67·8, H, 4·6, N, 4·9%; Found: C, 67·6, H, 4·5, N, 5·1%).

### 3.3. 4-Piperidino-1,8-naphthalic anhydride

4-Chloro-1,8-naphthalic anhydride (23·2 g) and piperidine (10 g) were refluxed for 2 h in 2-methoxyethanol (200 ml). On cooling, 13 g (41%) of 4-piperidino-1,8-naphthalic anhydride was deposited, m.p. 175 °C. The mother liquor on addition to 5% aq. hydrochloric acid gave a further 43%, m.p. 158–160 °C. Recrystallisation from ethanol gave orange needles, m.p. 175–176 °C; $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 409 nm (4·08) ($C_{17}H_{15}NO_3$ requires: C, 72·6, H, 5·4, N, 6·0%; Found: C, 72·8, H, 5·2, N, 5·0%).

### 3.4. 4-Piperazino-1,8-naphthalic anhydride

4-Chloro-1,8-naphthalic anhydride (23·2 g) and piperazine (11·5 g) were refluxed for 6 h in 2-methoxyethanol (200 ml). The liquor was reduced in volume to 50 ml and the thick yellow suspension filtered to give 19·7 g (61%) of a yellow solid. Traces of 4-chloro-1,8-naphthalic anhydride were removed by slurrying the product in hot 2-methoxyethanol and filtering, insoluble material being pure 4-piperazino-1,8-naphthalic anhydride, m.p. > 330 °C; $\lambda_{max}$ (log $\varepsilon$) in water, 389 (3·93) ($C_{16}H_{14}N_2O_3$ requires: C, 68·1, H, 5·0, N, 9·9%; Found: C, 68·0, H, 5·1, N, 10·0%).

### 3.5. 4-*N*-Acetylpiperazino-1,8-naphthalic anhydride

The product from section 3.4 (3 g) was suspended in a mixture of glacial acetic acid (10 ml) and acetic anhydride (10 ml) and the mixture stirred under reflux for 1 h, during which time a clear yellow solution formed. No solid deposited on cooling and addition to water gave a clear yellow solution. The liquor was concentrated to dryness to give 4-*N*-acetylpiperazino-1,8-naphthalic anhydride, m.p. 218–220 °C (glacial acetic acid) ($C_{18}H_{16}N_2O_4$ requires: C, 67·1, H, 4·35, N, 8·7%; Found: C, 66·9, H, 4·2, N, 8·6%).

### 3.6. 4-Imidazolo-1,8-naphthalic anhydride

4-Chloro-1,8-naphthalic anhydride (10 g), imidazole (4·4 g) and anhydrous potassium carbonate (2 g) were refluxed with stirring for 2 h in diethyleneglycol dimethyl ether. The suspension was cooled and filtered to give a brown solid (12·9 g, 86%). Recrystallisation from ethanol gave pale greyish-yellow needles of 4-imidazolo-1,8-naphthalic anhydride, m.p. 234–235 °C, $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 342 nm (4·07) ($C_{15}H_8N_2O_3$ requires: C, 68·1, H, 3·0, N, 10·6%; Found: C, 67·6, H, 2·8, N, 10·4%).

### 3.7. Pyrido[5,6-*c*]-1,8-naphthalic anhydride

A mixture of 3-amino-1,8-naphthalic anhydride (2 g), conc. sulphuric acid (4 g), glycerol (4 g) and nitrobenzene (1·5 g) was stirred at room temperature. The temperature rose spontaneously to 50–60 °C and, after allowing to subside, was raised to 140 °C and maintained for 3 h. The liquor was cooled and extracted twice with boiling water (100 ml). The aqueous extracts were neutralised with 10% aq. NaOH and a brown solid collected. This was extracted with 6 × 100 ml boiling acetone and the acetone extract evaporated to dryness. Recrystallisation of the residue from pyridine gave off-white needles, 1·4 g (42%) of pyrido[5,6-*c*]-1,8-naphthalic anhydride, m.p. 306 °C; $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 332 nm (4·11) ($C_{15}H_7NO_3$ requires: C, 72·3, H, 2·8, N, 5·6%; Found: C, 71·9, H, 2·7, N, 5·3%).

### 3.8. General synthesis of imides

4-Morpholino-1,8-naphthalic anhydride (1·4 g) was refluxed in ethanol (50 ml) with 3-methoxypropylamine (0·6 g) for 1 h. The volume was reduced to 30 ml, cooled and filtered to give 1·2 g (68%) of N-3-methoxypropyl-4-morpholino-1,8-naphthalic anhydride (**III.4**), m.p. 145–147 °C. Recrystallisation from ethanol gave bright greenish-yellow needles, m.p. 151–152 °C. ($C_{20}H_{22}N_2O_4$ requires: C, 67·8, H, 6·2, N, 7·9%; Found; C, 67·6, H, 6·0, N, 7·5%).

Using 25% molar excess of amine, and reacting for 1 h in ethanol as solvent for condensations with alkylamines, and 2-methoxyethanol as solvent with arylamines, other imides were similarly prepared from 4-pyrrolidino-(**I.1–I.6**, Table 1), 4-piperidino-(**II.1–II.8**, Table 2), 4-morpholino-(**III.1–III.8**, Table 3), 4-piperazino (**IV.1–IV.6**, Table 4), 4-

imidazo-(**VII.1**, Table 5) and pyrido[5,6-*c*]-1,8-naphthalic anhydrides (**V.1–V.2**, Table 5). All yields recorded in the Tables are those isolated by direct filtration of the reaction liquor as above; in all cases, addition of the mother liquor to 5% aq. hydrochloric acid brought the yield up to 95–100%. All melting points quoted here are after recrystallisation from ethanol or, in the case of the piperazino derivatives, 30% aq. ethanol.

### 3.9. General synthesis of 7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones

4-Piperidino-1,8-naphthalic anhydride (1·4 g) and 4-chloro-*o*-phenylenediamine (0·9 g) were refluxed for 1·5 h in glacial acetic acid (100 ml). The volume was reduced to 30 ml, the liquor cooled and filtered to give 1·6 g (83%) of orange needles of the isomer mixture of 3-(and 4-)piperidino-10-(and 11-)chloro-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one (**VIII.4**), m.p. 208–210°C (acetic acid).

In a similar manner were prepared analogous derivatives from 4-pyrrolidino-(**VII.1–VII.3**, Table 1), 4-piperidino-(**VIII.1–VIII.5**, Table 2), 4-morpholino-(**IX.1–IX.5**, Table 3), 4-piperazino-(**X.1–X.3**, Table 4), 4-N-acetylpiperazino-(**XI.1–XI.3**, Table 4), 4-imidazolo-(**XIII.1–XIII.3**, Table 5) and pyrido[5,6-*c*]1,8-naphthalic anhydrides (**XII.1–XII.6**, Table 5). All yields reported in the Tables are as obtained by filtration of the reaction liquor as above; all melting points are after recrystallisation from glacial acetic acid, or, for pyrazino derivatives, 30% aqueous acetic acid.

### 3.10. 3-Nitro-4-morpholino-1,8-naphthalic anhydride

To a refluxing solution of 3-nitro-4-chloro-1,8-naphthalic anhydride (20 g) in ethanol (100 ml) was added morpholine (7·5 g) dropwise over 30 min. The solution was refluxed for 1 h, cooled and filtered to give 18·4 g (71%) of 3-nitro-4-morpholino-1,8-naphthalic anhydride, yellow needles, m.p. 258°C (ethanol); $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 419 nm (4·03) ($C_{16}H_{12}N_2O_6$ requires: C, 58·4, H, 3·7, N, 8·5%; Found: C, 5·86, H, 3·9, N, 8·7%). A further 24% of product was recovered from the reaction mother liquor on addition to 5% aq. hydrochloric acid.

### 3.11. 3-Nitro-4-piperidino-1,8-naphthalic anhydride

Replacing morpholine in the above by piperidine (8 g) gave 68% of yellow needles of 3-nitro-4-piperidino-1,8-naphthalic anhydride, m.p. 247°C

**TABLE 1**
Characterisation and Fastness Data for Pyrrolidino Derivatives I and VII

| *Dye* | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in chlorobenzene* | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | *log ε* | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **I.1** | H | 97 | 298–299 | 439 | 4·13 | 1 | 2 | 2–3 | 160 |
| **I.2** | $CH_2CH_2CH_3$ | 62 | 156–157 | 439 | 4·14 | 1 | 2 | 2–3 | 150 |
| **I.3** | $CH_2CH_2CH_2OH$ | 54 | 161–162 | 443 | 4·17 | 1–2 | 2 | 2–3 | 160 |
| **I.4** | $CH_2CH_2CH_2OCH_3$ | 69 | 94–95 | 440 | 4·15 | 1 | 2–3 | 2–3 | 160 |
| **I.5** | Ph | 72 | 263–264 | 440 | 4·21 | 1–2 | 2 | 2–3 | 170 |
| **I.6** | $C_6H_4 \cdot OCH_3$-*p* | 77 | 214–215 | 440 | 4·22 | 1–2 | 2 | 2–3 | 170 |
| **VII.1** | H | 72 | 267–269 | 443 | 4·36 | 2 | 2 | 3 | 180 |
| **VII.2** | $OCH_3$ | 70 | 280–282 | 443 | 4·32 | 2 | 2 | 3 | 180 |
| **VII.3** | Cl | 68 | 279–281 | 440 | 4·21 | 2 | 2–3 | 3 | 180 |

**TABLE 2**
Characterisation and Fastness Data for Piperidino Derivatives II and VIII

| *Dye* | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in chlorobenzene* | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | *log ε* | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **II.1** | H | 96 | 262–263 | 406 | 4·08 | 3–4 | 4 | 4 | 150 |
| **II.2** | $CH_2CH_2CH_3$ | 82 | 174–175 | 406 | 4·03 | 3–4 | 4 | 4–5 | 140 |
| **II.3** | $CH_2CH_2CH_2OH$ | 63 | 162–164 | 410 | 4·06 | 4 | 4 | 4 | 150 |
| **II.4** | $CH_2CH_2CH_2OCH_3$ | 71 | 92–93 | 405 | 4·05 | 3–4 | 4 | 4 | 150 |
| **II.5** | $CH_2(CH_2)_4CH_2$ | 79 | 206–207 | 404 | 4·05 | 4 | 4–5 | 4–5 | 160 |
| **II.6** | $CH_2Ph$ | 76 | 154–155 | 407 | 4·06 | 4 | 4–5 | 4–5 | 160 |
| **II.7** | Ph | 66 | 252–253 | 407 | 4·05 | 4 | 4–5 | 4–5 | 170 |
| **II.8** | $C_6H_4 \cdot OCH_3$-*p* | 77 | 287–288 | 406 | 4·06 | 4 | 4 | 4–5 | 170 |
| **VIII.1** | H | 87 | 172–173 | 426 | 4·26 | 4 | 4 | 4 | 170 |
| **VIII.2** | $CH_3$ | 72 | 173–174 | 430 | 4·21 | 4 | 4 | 4 | 170 |
| **VIII.3** | $OCH_3$ | 80 | 289–290 | 436 | 4·27 | 4 | 4 | 4 | 170 |
| **VIII.4** | Cl | 83 | 208–210 | 432 | 4·26 | 4 | 4 | 4–5 | 180 |
| **VIII.5** | Br | 84 | 199–200 | 433 | 4·33 | 4 | 4 | 4–5 | 180 |

**TABLE 3**
Characterisation and Fastness Data for Morpholino Derivatives **III** and **IX**

| *Dye* | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in chlorobenzene* | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | *log ε* | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **III.1** | H | 98 | 278–279 | 394 | 4·06 | 4–5 | 5 | 5–6 | 170 |
| **III.2** | $CH_2CH_2CH_3$ | 54 | 175–176 | 392 | 4·03 | 5–6 | 6 | 6 | 160 |
| **III.3** | $CH_2CH_2CH_2OH$ | 47 | 197–198 | 398 | 4·09 | 6 | 6 | 6 | 170 |
| **III.4** | $CH_2CH_2CH_2OCH_3$ | 64 | 151–152 | 394 | 4·09 | 5–6 | 5–6 | 5–6 | 160 |
| **III.5** | $\overline{CH_2(CH_2)_4CH_2}$ | 64 | 230–231 | 392 | 4·02 | 5 | 5–6 | 5–6 | 160 |
| **III.6** | $CH_2Ph$ | 72 | 181–182 | 393 | 4·03 | 5–6 | 5–6 | 5–6 | 160 |
| **III.7** | Ph | 75 | 230–231 | 396 | 4·04 | 5 | 5 | 5–6 | 170 |
| **III.8** | $C_6H_4 \cdot OCH_3$-*p* | 62 | 275–276 | 397 | 4·04 | 5 | 5 | 5–6 | 170 |
| **IX.1** | H | 78 | 292–293 | 415 | 4·21 | 5–6 | 5–6 | 5–6 | 170 |
| **IX.2** | $CH_3$ | 70 | 253–254 | 421 | 4·15 | 5–6 | 5–6 | 6 | 180 |
| **IX.3** | $OCH_3$ | 71 | 300–302 | 430 | 4·16 | 5–6 | 5–6 | 6 | 180 |
| **IX.4** | Cl | 64 | 236–237 | 419 | 4·16 | 6 | 6 | 6–7 | 180 |
| **IX.5** | Br | 67 | 283–284 | 419 | 4·14 | 6 | 6 | 6–7 | 180 |

**TABLE 4**
Characterisation and Fastness Data for Piperazino and *N*-Acetylpiperazino Derivatives **IV, X** and **XI**

| *Dye* | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in water* | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | log ε | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **IV.1** | H | 70 | 310–311 | 390 | 3·98 | | | | |
| **IV.2** | $CH_2CH_2CH_3$ | 43 | 328–330 | 390 | 3·96 | | | | |
| **IV.3** | $CH_2CH_2CH_2OH$ | 40 | 330–332 | 392 | 3·95 | | | | |
| **IV.4** | $CH_2CH_2CH_2OCH_3$ | 52 | 266–267 | 390 | 3·97 | 1 | 1 | 1 | 190 |
| **IV.5** | Ph | 34 | 334–335 | 392 | 3·94 | 1–2 | 1–2 | 1–2 | 190 |
| **IV.6** | $C_6H_4 \cdot OCH_3$-*p* | 38 | 335–336 | 393 | 3·95 | | | | |
| **X.1** | H | 28 | 329–330 | 414 | 4·03 | 3–4 | 3–4 | 4 | 190 |
| **X.2** | OMe | 46 | 341–342 | 424 | 4·01 | 3 | 3–4 | 4 | 200 |
| **X.3** | Cl | 22 | 337–338 | 420 | 3·98 | 3–4 | 4 | 4–5 | 200 |
| **XI.1** | H | 74 | 259–260 | 413 | 4·09[a] | 5 | 5 | 5–6 | 190 |
| **XI.2** | OMe | 81 | 269–270 | 418 | 4·08[a] | 5 | 5–6 | 5–6 | 190 |
| **XI.3** | Cl | 79 | 244–246 | 410 | 4·09[a] | 5–6 | 6 | 6 | 190 |

[a] Absorption in chlorobenzene.

**TABLE 5**
Characterisation and Fastness Data for Pyridino (V and XII) and Imidazolo (VI and XIII) Derivatives

| *Dye* | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in chlorobenzene* | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | *log* ε | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **V.1** | H | 98 | >300 | 333 | 4·13 | | | | |
| **V.2** | $CH_2CH_2CH_2OCH_3$ | 54 | 181–182 | 333 | 4·11 | | | | |
| **XII.1** | H | 65 | 293–294 | 384 | 4·12 | 6–7 | 6–7 | 7 | 180 |
| **XII.2** | $CH_3$ | 60 | 253–254 | 393 | 4·14 | 7 | 7 | 7 | 180 |
| **XII.3** | $OCH_3$ | 58 | 285–286 | 395 | 4·15 | 7 | 7 | 7 | 180 |
| **XII.4** | Cl | 47 | 293–294 | 387 | 4·19 | 6–7 | 7 | 7 | 180 |
| **XII.5** | Br | 56 | 286–287 | 387 | 4·18 | 6–7 | 7 | 7 | 180 |
| **XII.6** | $NO_2$ | 42 | 315–316 | 366 | 4·13 | 4–5 | 5 | 5 | 190 |
| **VI.1** | $CH_2CH_2CH_2OCH_3$ | 84 | 167–168 | 345 | 4·03 | | | | |
| **XIII.1** | H | 62 | 272–273 | 397 | 4·07 | 4–5 | 4–5 | 5 | 180 |
| **XIII.2** | $OCH_3$ | 74 | 288–289 | 408 | 4·08 | 4–5 | 4–5 | 5 | 180 |
| **XIII.3** | Cl | 69 | 264–265 | 402 | 4·04 | 5 | 5 | 5 | 180 |

(ethanol); $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 431 nm (4·06) ($C_{17}H_{14}N_2O_5$ requires: C, 62·6, H, 4·3, N, 5·6%; Found: C, 63·0, H, 4·4, N, 8·6%).

### 3.12. 3-Nitro-4-pyrrolidino-1,8-naphthalic anhydride

Similar reaction with pyrrolidine (7·5 g) gave 75% of 3-nitro-4-pyrrolidino-1,8-naphthalic anhydride, yellow needles, m.p. 240–241 °C (ethanol); $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 403 nm (4·25) and 436 s nm (4·02) ($C_{16}H_{12}N_2O_5$ requires: C, 61·5, H, 3·9, N, 9·0%; Found: C, 61·5, H, 4·0, N, 9·3%).

### 3.13. 3-Nitro-4-piperazino-1,8-naphthalic anhydride

Similar reaction with piperazine (7 g) gave a very viscous yellow mass, which gradually dispersed on prolonged stirring (24 h). The cooled suspension was filtered, washed with a little ethanol, reslurried in boiling 2-methoxyethanol (100 ml) and filtered to give yellow needles (24 g, 93%) of 3-nitro-4-piperazino-1,8-naphthalic anhydride, m.p. > 330 °C; $\lambda_{max}$ (log $\varepsilon$) in water, 395 s (3·76) and 433 nm (4·02) ($C_{16}H_{13}N_3O_5$ requires: C, 58·7, H, 4·0, N, 12·8%; Found: C, 58·8, H, 3·9, N, 12·6%).

### 3.14. 3-Nitro-4-imidazolo-1,8-naphthalic anhydride

A solution of imidazole (3·1 g) in 2-methoxyethanol (10 ml) was added, over 30 min, to a refluxing solution of 3-nitro-4-chloro-1,8-naphthalic anhydride (10 g) in 2-methoxyethanol (150 ml). After refluxing for 2 h the liquor was cooled and the yellow solid (6 g, 48%) collected; recrystallisation from ethanol gave yellow needles of 3-nitro-4-imidazolo-1,8-naphthalic anhydride, m.p. 265–266 °C; $\lambda_{max}$ (log $\varepsilon$) in chlorobenzene, 347 nm (4·08) ($C_{15}H_7N_3O_5$ requires: C, 58·3, H, 2·3, N, 13·6%; Found: C, 56·8, N, 2·6, N, 13·1%).

### 3.15. 3-Nitro-4-pyrazolo-1,8-naphthalic anhydride

3-Nitro-4-chloro-1,8-naphthalic anhydride (10 g) and pyrazole (3·1 g) were refluxed for 20 h in diethyleneglycol dimethyl ether (100 ml). The solution was cooled and filtered to give a yellow-brown material (7·4 g, 59%), recrystallised from ethanol in brownish-yellow needles of 3-nitro-4-pyrazolo-1,8-naphthalic anhydride, m.p. 245–246 °C; $\lambda_{max}$ (log $\varepsilon$) in

chlorobenzene, 347 nm (4·11) ($C_{15}H_7N_3O_5$ requires: C, 58·3, H, 2·3, N, 13·6%; Found: C, 57·2, H, 2·5, N, 13·2%).

### 3.16. Imides and benzimidazoles from 3-nitro-4-amino-1,8-naphthalic anhydrides

3-Nitro-4-piperidino-1,8-naphthalic anhydride (1·6 g) was refluxed with aniline (0·6 g) in ethanol (50 ml). The liquor deposited, on cooling, deep orange-yellow needles (1·33 g, 68%) of 3-nitro-4-piperidino-*N*-phenyl-1,8-naphthalimide (**II.N.3**, Table 6), m.p. 274–275 °C (ethanol). ($C_{23}H_{19}N_3O_4$ requires: C, 68·4, H, 4·8, N, 10·5%; Found: C, 68·8, H, 4·7, N, 10·4%).

In a similar manner were prepared the 3-nitro-4-pyrrolidino-(**I.N.1–I.N.4**), 3-nitro-4-piperidino-(**II.N.1–II.N.4**), 3-nitro-4-morpholino-(**III.N.1–III.N.4**), 3-nitro-4-piperazino-(**IV.N.1–IV.N.4**), 3-nitro-4-imidazolo-(**VI.N.1**) and 3-nitro-4-pyrazolo-1,8-naphthalimides (**XIV.1**) described in Table 6.

The benzimidazo derivatives were prepared as described in section 3.9. Table 7 lists the dyes thus obtained from 3-nitro-4-pyrrolidino-(**VII.N.1–VII.N.3**), 3-nitro-4-piperidino-(**VIII.N.1–VIII.N.3**),3-nitro-4-morpholino-(**IX.N.1–IX.N.3**), 3-nitro-4-piperazino (**X.N.1–X.N.3**), 3-nitro-4-imidazolo-(**XIII.N.1**) and 3-nitro-4-pyrazolo-1,8-naphthalic anhydrides (**XV.1**).

### 3.17. Quaternary salts of pyrido[2,3-*c*]-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*] isoquinolin-7-ones

The benzimidazole (**XII.3**, Table 5) derived from pyrido[5,6-*c*]-1,8-naphthalic anhydride and 4-methoxy-*o*-phenylenediamine (1 g) was refluxed in monochlorobenzene (100 ml) and dimethyl sulphate (1 g) added. Refluxing was continued (1 h) until the initially clear solution gradually deposited an orange solid. This was filtered from the cooled liquor, washed with chlorobenzene and dried (1·29 g, 88%). Other quaternary salts similarly prepared are listed in Table 8.

### 3.18. Electronic spectra, dyeing and fastness

These tests were carried out as previously described.[20] The purity of all dyes and intermediates was confirmed by TLC, mass spectrometry and elemental analysis.

**TABLE 6**

Characterisation and Fastness Data for 3-Nitro-4-amino-1,8-naphthalimide Derivatives

| *Dye*[a] | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in chlorobenzene* | | | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | log ε | $\lambda_{max}$ (*nm*) | log ε | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **I.N.1** | $CH_2CH_2CH_2OH$ | 66 | 193–194 | 400 | 4·28 | 420s | 3·84 | 1 | 1 | 1–2 | 180 |
| **I.N.2** | $CH_2CH_2CH_2OCH_3$ | 75 | 110–111 | 398 | 4·24 | 418s | 3·81 | 1 | 1 | 1–2 | 170 |
| **I.N.3** | Ph | 80 | 265–266 | 407 | 4·08 | | | 2 | 2–3 | 3 | 170 |
| **I.N.4** | $C_6H_4 \cdot OCH_3$-*p* | 72 | 254–255 | 406 | 4·07 | | | 2 | 2–3 | 3 | 170 |
| **II.N.1** | $CH_2CH_2CH_2OH$ | 68 | 179–180 | 400 | 4·20 | 416s | 3·87 | 1 | 1 | 1–2 | 170 |
| **II.N.2** | $CH_2CH_2CH_2OCH_3$ | 62 | 109–110 | 397 | 4·22 | 417s | 3·84 | 1 | 1 | 1–2 | 180 |
| **II.N.3** | Ph | 68 | 274–275 | 426 | 3·89 | | | 1–2 | 1–2 | 2 | 180 |
| **II.N.4** | $C_6H_4 \cdot OCH_3$-*p* | 73 | 280–281 | 427 | 3·92 | | | 1–2 | 1–2 | 2 | 180 |
| **III.N.1** | $CH_2CH_2CH_2OH$ | 73 | 188–189 | 400 | 4·24 | 432s | 3·84 | 1 | 1–2 | 1–2 | 190 |
| **III.N.2** | $CH_2CH_2CH_2OCH_3$ | 78 | 112–113 | 397 | 4·21 | 430s | 3·87 | 1 | 1–2 | 2 | 190 |
| **III.N.3** | Ph | 80 | 269–270 | 393 | 4·11 | 433s | 3·81 | 2 | 2–3 | 3 | 190 |
| **III.N.4** | $C_6H_4 \cdot OCH_3$-*p* | 82 | 291–292 | 394 | 4·08 | 434s | 3·82 | 2 | 2–3 | 3 | 190 |
| **IV.N.1** | $CH_2CH_2CH_2OH$ | 18 | 303–304 | 417 | 3·67 | | | | | | |
| **IV.N.2** | $CH_2CH_2CH_2OCH_3$ | 33 | 230–231 | 415 | 3·59 | | | 1 | 1 | 1 | 210 |
| **IV.N.3** | Ph | 38 | 304–305 | 416 | 3·76 | | | | | | |
| **IV.N.4** | $C_6H_4 \cdot OCH_3$-*p* | 41 | 291–292 | 417 | 3·74 | | | | | | |
| **VI.N.1** | $CH_2CH_2CH_2OCH_3$ | 64 | 272–275 | 348 | 4·08 | | | | | | |
| **XIV.1** | $CH_2CH_2CH_2OCH_3$ | 59 | 97–98 | 347 | 4·23 | | | | | | |

[a] Dye references N signify nitrated analogue, e.g. **I.N.1** is nitro derivative of **I.1**.

**TABLE 7**
Characterisation and Fastness Data for 2-Nitro-3-amino-7*H*-benzimidazobenzisoquinolin-7-one Derivatives

| *Dye*[a] | *R* | *Yield* (%) | *M.p.* (°C) | *Absorption in chlorobenzene* | | *Fastness on polyester* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (*nm*) | *log ε* | *Lightfastness* 0·1% | 0·5% | 2·5% | *Sublimation* (°C) (2·5% *dyeing*) |
| **VII.N.1** | H | 64 | 209–210 | 424 | 4·26 | 2 | 2 | 2 | 180 |
| **VII.N.2** | $OCH_3$ | 74 | 203–204 | 426 | 4·29 | 2 | 2–3 | 2–3 | 190 |
| **VII.N.3** | Cl | 62 | 194–195 | 429 | 4·31 | 2 | 2 | 2 | 180 |
| **VIII.N.1** | H | 81 | 241–242 | 450 | 4·10 | 1 | 2 | 2 | 170 |
| **VIII.N.2** | $OCH_3$ | 73 | 221–222 | 449 | 4·08 | 1–2 | 2–3 | 2–3 | 180 |
| **VIII.N.3** | Cl | 78 | 212–213 | 452 | 4·16 | 1–2 | 2 | 2 | 180 |
| **IX.N.1** | H | 71 | 251–252 | 433 | 4·04 | 1–2 | 2 | 2–3 | 190 |
| **IX.N.2** | $OCH_3$ | 82 | 300–301 | 446 | 4·02 | 1–2 | 2 | 2–3 | 200 |
| **IX.N.3** | Cl | 66 | 297–298 | 442 | 4·10 | 1–2 | 2 | 2–3 | 200 |
| **X.N.1** | H | 52 | 312–313 | 437 | 3·91 | 1 | 2 | 2 | 220 |
| **X.N.2** | $OCH_3$ | 43 | 315(d) | 440 | 3·84 | | | | |
| **X.N.3** | Cl | 70 | 320(d) | 435 | 3·88 | | | | |
| **XIII.N.1** | H | 43 | 254–255 | 393 | 4·04 | 1–2 | 2 | 2 | 200 |
| **XV.1** | H | 58 | 230–231 | 406 | 4·04 | 1–2 | 2 | 2 | 190 |

[a] See footnote to Table 6.

**TABLE 8**
Absorption Spectra and Fastness Data for Quaternised Pyridino Derivatives

| *Dye*[a] | *R* | *Yield* (%) | *Absorption in water* | | *Lightfastness on 'Courtelle'* | | |
|---|---|---|---|---|---|---|---|
| | | | $\lambda_{max}$ (*nm*) | *log ε* | *0·1%* | *0·5%* | *2·5%* |
| **V.Q.1** | $CH_2CH_2CH_2OCH_3$ | 76 | 364 | 4·12 | | | |
| **XII.Q.1** | H | 83 | 400 | 3·97 | 5–6 | 5–6 | 6 |
| **XII.Q.2** | $CH_3$ | 91 | 402 | 3·94 | 5–6 | 6 | 6 |
| **XII.Q.3** | $OCH_3$ | 88 | 402 | 3·97 | 5–6 | 6 | 6 |
| **XII.Q.4** | Cl | 87 | 400 | 3·96 | 5–6 | 5–6 | 6 |
| **XII.Q.5** | Br | 89 | 401 | 3·95 | 5–6 | 5–6 | 6 |
| **XII.Q.6** | $NO_2$ | 80 | 398 | 3·94 | 3–4 | 3–4 | 3–4 |

[a] **V.Q.1** signifies quaternary salt of dye **V.1.**, etc.

## 4. CONCLUSIONS

Derivatives of 1,8-naphthalimide and of 7*H*-benzimidazo[2,1-*a*]benz-[*d*,*e*]isoquinolin-7-ones substituted by cyclic *tert*-amino substituents in the naphthyl ring are generally good dyes for synthetic-polymer fibres. The most satisfactory imides were those derived from 4-morpholino-1,8-naphthalic anhydride and, to a lesser extent, 4-piperidino-1,8-naphthalic anhydride. These two intermediates, together with 4-imidazolo-,4-*N*-acetylpiperazino- and pyrido[5,6-*c*]-1,8-naphthalic anhydrides, give excellent dyes on condensation with *o*-phenylenediamines. Introduction of a nitro group *ortho* to the amino group in all these dyes results in a large decrease in lightfastness.

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