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Intermediates and Dyes for Synthetic-Polymer Fibres. Benzo[*b*]naphtho[3,2-*d*]thiophene-6,7-dicarboxylic Acid Imides and Benzimidazo Dibenzothiopheno[4,3,2-*d*,*e*]-isoquinolin-10-ones

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SUMMARY

Benzo[b]naphtho[2,3-d]thiophene-6,7-dicarboxylic anhydride (**I**) *is obtained by Pschorr intramolecular cyclisation of 2-(2-aminophenylthio)-1,8-naphthalic anhydride. Condensation with alkylamines and arylamines gives the corresponding imides, which colour synthetic-polymer fibres in greenish-yellow hues, and reaction with o-phenylenediamines affords the isomer mixtures of derivatives of benzimidazo[1,2-b]-dibenzothiopheno-[4,3,2-d,e]isoquinolin-10-one and of benzimidazo-[2,1-a]dibenzothiopheno-[4,3,2-d,e]isoquinolin-10-one, which dye polyester fibres bright reddish-orange. Both series of dyes have excellent fastness to light and sublimation. The colour of the dyes is discussed in relation to the isomeric compounds derived from benzo[k,l]thioxanthene-3,4-dicarboxylic anhydride* (**III**) *and from benzo[d]naphtho[1,2-b]thiophene-9,10-dicarboxylic anhydride* (**II**). *The synthesis of the individual isomers resulting from reaction of* **I** *with o-phenylenediamine is reported and their absorption maxima related to polar factors operative within each isomer.*

1. INTRODUCTION

We have previously described the synthesis and evaluation of dyes derived from a series of 1,8-naphthalic anhydrides substituted by fused sulphur

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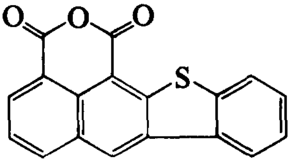
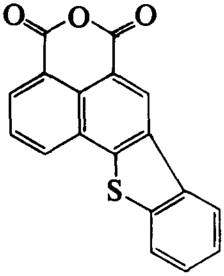
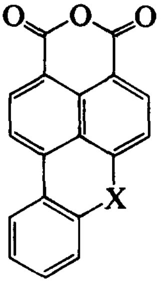
containing heterocyclic systems, i.e. the imides and benzimidazoles of benzo[*k*,l]thioxanthene-3,4-dicarboxylic anhydride (**III**)[1-4] and its 7,7-dioxo derivative (**IV**)[5,6] and of benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboxylic anhydride (**II**).[7] These compounds colour synthetic-polymer fibres in fluorescent greenish-yellow to orange hues of outstanding fastness to light and sublimation, the colour being influenced significantly by the nature and orientation of the hetero ring. We describe here the synthesis and properties of related dyes derived from benzo[*b*]naphtho-[3,2-*d*]thiophene-6,7-dicarboxylic anhydride (**I**) and a comparison of the colour of the dyes with respect to analogous derivatives of **II**–**IV**.



I



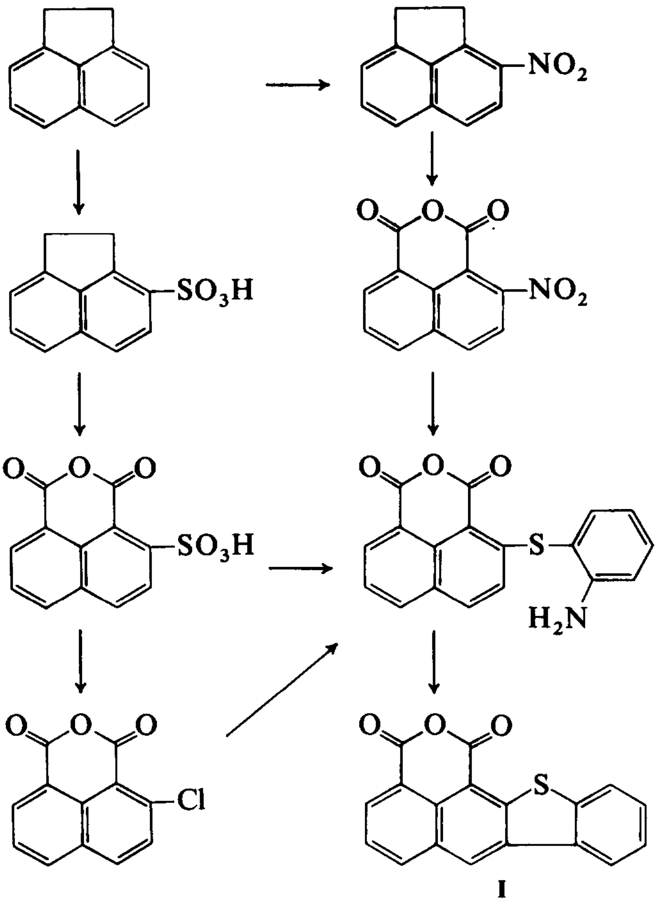
II



III; X = S
IV; X = SO_2

2. RESULTS AND DISCUSSION

Benzo[*b*]naphtho[2,3-*d*]thiophene-6,7-dicarboxylic anhydride (**I**) was synthesised by the route shown in the Scheme. 3-Nitroacenaphthene, and thence, 2-nitro-1, 8-naphthalic anhydride, were prepared by previously described methods.[8] Sulphonation of acenapthene at 100 °C afforded acenaphthene-3-sulphonic acid, oxidised by sodium dichromate to 1,8-naphthalic anhydride-2-sulphonic acid.[9] Conversion of the latter to 2-chloro-1,8-naphthalic anhydride was effected by reaction with sodium chlorate in hydrochloric acid, a method used extensively in the production of 1-chloro derivatives of anthraquinone and which has been utilised[10] for the conversion of 1,8-naphthalic anhydride-4-sulphonic acid to 4-chloro-1,8-naphthalic anhydride. This method was found to give a cleaner and simpler conversion than the alternative procedure[11] involving reaction of the sulphonic acid with phosphorus pentachloride.



I

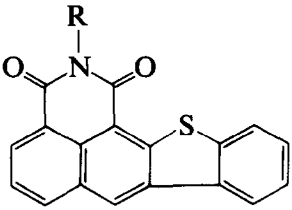
Scheme 1

Both the 2-sulpho and 2-chloro derivatives of 1,8-naphthalic anhydride condensed with 2-aminobenzenethiol to give 2-(2-aminophenylthio)-1,8-naphthalic anhydride. To avoid undue contamination with 2,2′-diaminodiphenyldisulphide, isolation of the product by filtration from a lower volume solvent reaction was found preferable to addition of the cooled reaction liquor to dilute hydrochloric acid and obviated the several recrystallisations necessary to remove the thiol oxidation product. Pschorr intramolecular cyclisation via reaction of the diazonium derivative of 2-(2-aminophenylthio)-1,8-naphthalic anhydride to boiling copper sulphate solution, the method described[12] for ring closure of 1-phenylthio-2-aminonaphthalene to benzo[*d*]naphtho[1,2-*b*]thiophene and of 3-amino-4-phenylthio-1,8-naphthalic anhydride to benzo[*d*]-naphtho[1,2-*b*]thiophene-9,10-dicarboxylic acid,[7] gave good yields of benzo[*b*]naphtho[3,2-*d*]thiophene-6,7-dicarboxylic acid (**I**). Attempted one-stage reaction of 2-nitro-1,8-naphthalic anhydride with 2-amino-benzenethiol in dimethylformamide, a procedure useful[13] for the conversion of 4-nitro-1,8-naphthalic anhydride into benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic anhydride (**III**), gave a complex mixture of condensation and reduction products containing, in addition to **I** (*m*/*e* 304), 2-(2-phenylthio)-1,8-naphthalic anhydride (*m*/*e* 306), 2,2′-diaminodiphenyl-disulphide (*m*/*e* 248), 9,10-dithiaphenanthrene (*m*/*e* 216), 2-amino-1,8-naphthalic anhydride (*m*/*e* 213) and unidentified higher molecular weight compounds (*m*/*e* 517 and *m*/*e* 622). Amounts of by-product were considerably higher than in the analogous reaction from 4-nitro-1,8-naphthalic anhydride and separation of the mixture (as described in ref. 13) afforded 24·3 % of **I**.

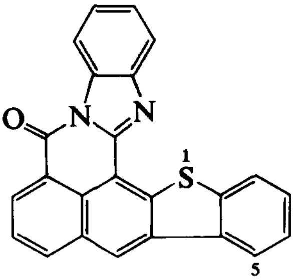
The modification of this synthesis, involving[13] stirring 2-(2-aminophenylthio)-1,8-naphthalic anhydride in dimethylformamide at room temperature, with addition of either sodium nitrite or amyl nitrite, gave a mixture of **I** and 2-(2-phenylthio)-1,8-naphthalic anhydride, from which **I** was separated in around 50 % yield. As in the analogous synthesis of **III** by this method,[7] the yield of product isolable by filtration of the reaction liquor was dependent on the solvent volume used and **I** was obtained in lower yield than **III**, even with lower solvent volume, by a direct filtration technique.

Condensation of **I** with alkylamines and arylamines gave the imides **V** and with *o*-phenylenediamines mixtures of the isomers benzimidazo-[1,2-*b*]dibenzothiopheno[4,3,2-*d*,*e*]isoquinolin-10-one (**VIa**) and benzimidazo[2,1-*a*]dibenzothiopheno[4,3,2-*d*,*e*]isoquinolin-10-one (**VIb**).

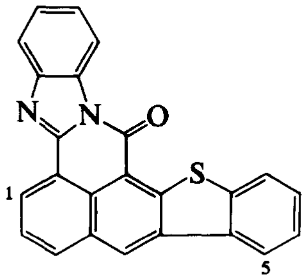
The isomers **VIa** and **VIb** were unambiguously synthesised from 1-nitro- and 6-nitro-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-ones, the preparation of which has been previously described.[14] Reaction of



V

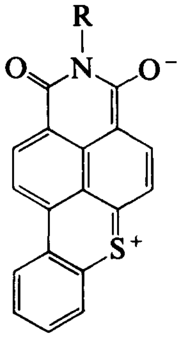


VIa

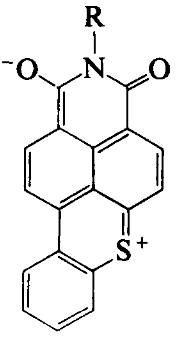


VIb

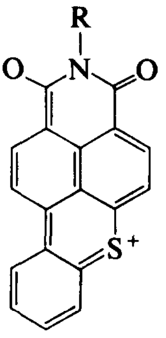
these nitro compounds with 2-aminobenzenethiol gave the corresponding 1- and 6-(2-aminophenyl)thio derivatives, with formation of the 1- and 6-amino derivatives as major by-products, and thence by Pschorr intramolecular cyclisation or by reaction with sodium nitrite or amyl nitrite in dimethylformamide, **VIa** and **VIb**. In comparing the colour of dyes obtained from the sulphur heterocycles **I**–**IV**, the imides of benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic anhydride **III** have absorption maxima at the longest wavelength, i.e. 460–480 nm, commensurate with the donor–acceptor interactions involving the sulphur atom and the carbonyl groups (**VIIa**–**VIIc**).[1] The imides of the uncyclised 4-phenylthio-1,8-naphthalic anhydride have λ_{max} in the 390 nm region[15] and in these



VIIa



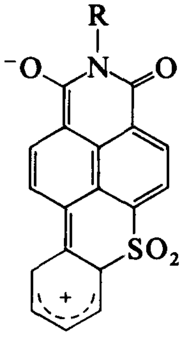
VIIb



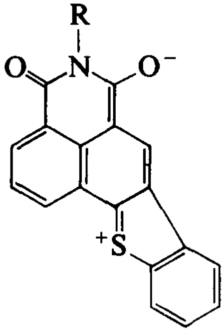
VIIc

compounds structures analogous to **VIIa** and **VIIb** only will be operative and not **VIIc** with the enhanced longitudinal conjugation.

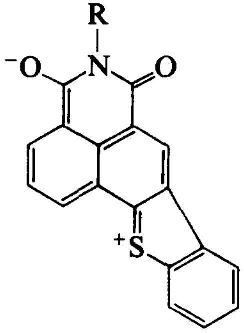
Oxidation of the hetero atom in **III** to the dioxo derivative **IV** gives derived imides which have λ_{max} at 380 nm and 400 nm,[5] the hypsochromic shifts being due to replacement of the donor thiol residue by the acceptor sulphone group and hence the absence of any delocalisation structures corresponding to **VIIa**–**VIIc**. Surprisingly, the sulphone-based imides, and related benzimidazole derivatives, absorb at longer wavelength than the donor substituted 4-phenylthio analogues and this has been related[6] to the possible contribution of an enhanced longitudinal interaction involving the diaryl moiety, i.e. **VIII**.



VIII



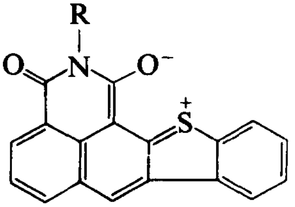
IXa



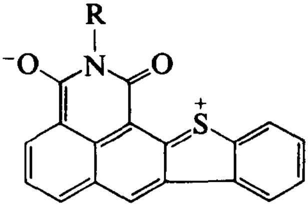
IXb

The five-membered isomeric imides derived from benzo[*d*]naphtho-[1,2-*b*]thiophene-9,10-dicarboxylic anhydride (**II**) have absorption maxima in the 380 nm region.[7] In these compounds, the delocalisation structures possible (**IXa** and **IXb**) are those analogous to **VIIa** and **VIIb** above, and no extended delocalisation through the phenyl ring, as in **VIIc**, or involving a diaryl moiety, as in **VIII**, is possible. Their colour can thus be expected to be of similar order to that of the imides of 4-phenylthionaphthalic anhydride, but is in fact hypsochromic with respect to them by 10 nm, indicating some loss of electron delocalisation resulting from ring closure due to steric factors (see later).

The isomeric benzo[*b*]naphtho[3,2-*d*]thiophene-6,7-dicarboxylic acid (**I**) gives imides which absorb (see Table 1) at wavelengths in the order of 20 nm and 40 nm longer than imides of **II**. Delocalisation structures (**Xa**, **Xb**) will be relatable to **VIIa** and **VIIb**, but with less extended conjugation

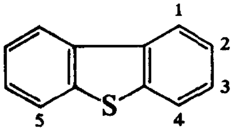


Xa



Xb

between the donor and acceptor centres than in derivatives of **II**. Whilst comparison of the imides of **I** and **II** might indicate, on the basis of the more extended conjugation in the latter, that structures **IXa–IXb** would result in greater colour development than in **Xa–Xb**, it is the latter that absorb at the longer wavelengths. The basic heterocyclic system in both **I** and **II** is dibenzothiophene (**XI**), bond length and bond angle data of



XI

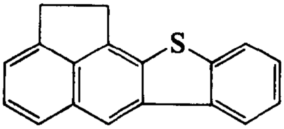
which[16] indicate that the individual five- and six-membered rings are planar, but that the molecule as a whole has a small but significant deviation from planarity which imparts a slightly folded configuration. Electron release from the hetero atom gives delocalisation structures with increased electron availability at the 2- and 4-positions, electrophilic substitution being more favoured at the 2-position.

Studies of the absorption spectra of the phenyl derivatives of **XI**[17] show the principal absorption band of the 2- and 3-phenyl derivatives to be shifted bathochromically, indicative of enhanced conjugation in these systems. The spectra of the 1- and 4-phenyl derivatives, however, show a degeneration to that of the parent heterocycle, indicating absence of coplanarity in these two isomers. Steric crowding due to the overlap of the 9-H atom of **XI** with the hydrogen atom of the phenyl ring in the 1-position, and similar overlap between the 4-phenyl substituent and the adjacent sulphur atom are most probably obviated by rotation of the phenyl groups out of the molecular plane of the parent heterocycle, with consequent absence of bathochromic shifts in the absorption maxima.

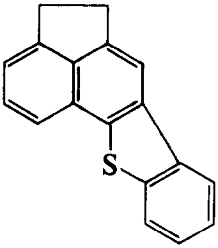
In **II**, a similar steric crowding effect can be envisaged, due to the fused phenyl ring in the 3,4-position of the dibenzothiophene ring, whereas in **I**, the ring fusion is across the 2,3-positions, i.e. in a non-sterically hindered position. On this basis, the greater bathochromicity of the derivatives of **I** can be rationalised.

Further, in the isomers **I** and **II**, the carbonyl function in the anhydride residue can be considered as involving substitution into dibenzothiophene at the 4- and 2-positions respectively. Whilst the preferred substitution of **XI** by electrophiles at the 2-position indicates a greater electron availability in this position, it could be concluded that substitution in **XI** of electron-acceptor residues, by virtue of a more extended donor–acceptor conjugation, would be more bathochromic in the 2-position. However, data for 2-nitrodibenzothiophene[18,19] and for 4-nitrodibenzothiophene[20–22] show that the latter is the more bathochromic. The electronic spectra of the 2-acetyl (λ_{max} 315 nm) and 4-acetyl derivatives (λ_{max} 353 nm) of **XI** also show that substitution by carbonyl functions results in absorption maxima being at longer wavelengths for 4-substitution (as in **I**) relative to 2-substitution (as in **II**). Both electronic and steric factors are thus relatable to the increase in absorption maxima of derivatives of **I** relative to those of **II**, and the hypsochromic shifts of derivatives of **II** relative to those of 4-phenylthio-1,8-naphthalic anhydride is similarly explained on the basis of steric crowding factors.

Absorption maxima[23] of benzo[*b*]naphtho[3,2-*d*]thiophene (λ_{max} 357 nm (3·48) and 370 nm (3·53)) and of benzo[*d*]naphtho[1,2-*b*]-thiophene (λ_{max} 333 nm (3·33) and 349 nm (3·23)) confirm the above observations, and similar differences are apparent in the acenaphtheno derivatives, acenaphtheno[4,3-*d*]benzo[*b*]thiophene (**XII**) absorbing[23] at longer wavelength than acenaphtheno[4,5-*d*]benzo[*d*]thiophene (**XIII**).



XII



XIII

Analogues of **XII** and **XIII** in which the phenyl ring is replaced by a cyclohexyl residue additionally show[24] the compounds related to **I** to be more bathochromic than those of **II**. In addition, extinction coefficients of the above analogues of **II** are lower than those of **I**, further indicative of steric crowding factors in the former. The imides **V** (Table 1), in addition to being more bathochromic than the imides **IX**,[7] also have the higher extinction coefficients.

The imidazole derivatives **VI** absorb at only slightly higher wavelength than the imides **V**, differences being lower than those between the imides and imidazoles of **II**[7] and of **III**.[1,4] The additional electron delocalisations due to the presence of the imidazole ring usually result in bathochromic shifts in the absorption maxima compared with the imides,

TABLE 1
Characterisation and Fastness Data for Imides V and Imidazoles VI

Dye	*R*	*Yield (%)*	*M.p. (°C)*	*Spectra in monochlorobenzene*		*Light fastness (0·1%, 0·5%, 2·5%)*				*Sublimation fastness (°C) (2·5% dyeing)*
				λ_{max} (log ε) (nm)	*λ_{max} (log ε) (nm)*	*Secondary acetate*	*Triacetate*	*Nylon*	*Polyester*	
V.1	H	86	252–253	403 (4·21)	423[a] (4·15)				6–7 7 7	180
V.2	$CH_2CH_2CH_3$	68	220–221	403[a] (4·19)	423 (4·22)				6–7 7 7	180
V.3	$CH_2CH_2CH_2OH$	61	227–228	407[a] (4·17)	427 (4·24)				6–7 6–7 7	190
V.4	$CH_2CH_2CH_2OCH_3$	64	185–186	404[a] (4·22)	424 (4·24)	6–7 6–7 6–7	5–6 6 6	1–2 2 2	6–7 6–7 6–7	180
V.5	$\overline{CH(CH_2)_4}CH_2$	74	251–252	403 (4·22)	421[a] (4·20)				6 6–7 6–7	180
V.6	CH_2Ph	71	200–201	404 (4·20)	423 (4·20)	6 6–7 6–7	5–6 5–6 6	1–2 2 2	6 6–7 6–7	190
V.7	C_6H_5	73	327–328	405 (4·19)	427 (4·20)	6 6–7 6–7	5–6 5–6 6	2 2 2	6 6–7 6–7	190
V.8	$C_6H_4 \cdot OCH_3$-*p*	76	330–332	405[a] (4·20)	424 (4·22)				6–7 6–7 7	190
VI.1	H	96	233–234	392 (4·24)	431 (4·26)	5–6 6 6	5 5–6 5–6	2 2 2	7 7 7	190
VI.2	CH_3	94	229–231	394 (4·25)	428 (4·27)				7 7 7	190
VI.3	OCH_3	93	244–245	404 (4·26)	425 (4·26)				7 7 7	200
VI.4	Cl	98	247–248	395 (4·24)	426 (4·25)				7 7 7	190
VI.5	Br	92	261–263	394 (4·23)	427 (4·24)				7 7 7	200

[a] Shoulder or incompletely resolved band.

but whilst **V** and **VI** have similar absorption maxima, the expected bathochromic shift is evident in the much redder hue of the dyeings of **VI** on polyester. Similar slight differences in absorption maxima, but significant in the colour of dyeings on synthetic-polymer fibres, have been observed with the imides and imidazoles derived from 4-pyrrolidino-1,8-naphthalic anhydride;[25] such apparent anomalies are related to the spectra of the imidazole derivatives being a broad composite absorption of the four isomers formed during the condensation between substituted 1,8-naphthalic anhydrides and substituted *o*-phenylenediamines.

The absorption maxima of the isomers **VIa** (λ_{max} 390 and 426 nm) and **VIb** (λ_{max} 395 and 442 nm) are in accord with the greater interaction between the hetero sulphur atom and the more polar carbonyl group in **VIb** relative to the pyridino nitrogen atom in **VIa**. Hückel Molecular Orbital calculations[26] of 7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one indicate a lower π-electron density at the 6-position than at the 1-position, i.e. the carbonyl group is the more highly deactivating residue in the imidazole ring; introduction of electron-donor groups into the 6-position would thus be expected to produce a higher electron interaction, and hence bathochromic shifts in absorption maxima, relative to substitution at the 1-position. Such an order is however not observed in the isomeric benzimidazo-thioxantheno-isoquinolinones derived from condensation of benzo[*k,l*]thioxanthene-3,4-dicarboxylic anhydride with *o*-phenylenediamine,[3] a factor which has been explained in terms of the enhancement of lateral conjugation through the phenyl ring of the thioxanthene residue, as in **VIIc**, a resonance interaction not possible in simpler substituted derivatives. Where such lateral conjugation is not possible, substitution into the carbonyl-containing ring of the naphthyl residue gives the more bathochromic shift. Thus, 6-*p*-toluenesulphonamido-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one absorbs at longer wavelength than the 1-*p*-toluenesulphonamido derivative,[27] and spectral curves of 3- and 4-amino-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one show[28] the latter to be the more bathochromic. The visible spectra of **VIa** and **VIb** are in accord with these observations and confirm the greater colour development resulting from the presence of simple donor functions in the carbonyl-containing ring.

On polyester, the imides **V** and imidazoles **VI** gave bright yellow and bright clear orange colorations respectively, of excellent build-up and of redder hue than shown by the analogous imides and imidazoles of **II**. Whilst coloration of cellulose secondary and triacetates by the imidazoles was only moderate, the imides gave deep greenish-yellow dyeings of good fastness on both fibres; on polyamide, dyeings were much redder and duller in hue and lightfastness on this substrate was poor. Fastness of the dyeings of both **V** and **VI** to light and sublimation was of a high order, similar to those observed for derivatives of **II**, **III** and **IV**; this further illustrates the general utility of 1,8-naphthalic anhydrides containing fused sulphur-containing heterocyclic rings as a source of fluorescent greenish-yellow to scarlet dyes of good clarity of hue and excellent fastness properties.

Dyeings of **V** and **VI** were fluorescent, a property typical also of related derivatives of **II**, **III** and **IV**. The fluorescence and phosphorescence of dibenzothiophene (**XI**) and its sulphones is well established and the fluorescence quantum efficiency of **XI** is of a similar order to that of thiophene, but less than that of fluorene and carbazole.[29,30] The lifetime of luminescence of **XI** has been visually estimated[31] at 2 s, and the phosphorescence yield is high relative to fluorene,[32] probably due to the hetero atom reducing the energy difference between the singlet and triplet states of the biphenyl moiety present in both compounds.

3. EXPERIMENTAL

3.1. 2-Nitro-1,8-naphthalic anhydride

3-Nitroacenaphthene was obtained by nitration of acenaphthene with nitric acid in acetic anhydride, and oxidised with chromium trioxide in glacial acetic acid, by previously described methods, to give 2-nitro-1,8-naphthalic anhydride.[8]

3.2. 1,8-Naphthalic anhydride-2-sulphonic acid[9]

Acenaphthene (110 g) and conc. sulphuric acid (80 g) were stirred at 100 °C for 12 h and the black coloured viscous liquor cooled and added to water (500 ml). Insoluble material (10·5 g) containing acenaphthene and 3,3′-diacenaphthylsulphone, m.p. 247 °C (lit.[33] m.p. 230–232 °C), was filtered and the aqueous filtrate neutralised with 20 % aq. sodium hydroxide. The basified liquor was heated to 95–100 °C and salted with sodium chloride to give 190 g (104 %) of a grey material. Sodium chloride was removed by dissolving the crude reaction product (10 g) in the minimum amount of boiling water (Norit), filtering and diluting with ethanol (10 ml) to give off-white platelets of acenaphthene-3-sodium sulphonate.

A mixture of the above product (10 g), sodium dichromate (30 g) and glacial acetic acid (100 ml) was heated gradually to 65 °C. The heat source was removed and the reaction proceeded spontaneously, rising to reflux for 15 min, during which time the colour changed from deep orange to dark green. After refluxing a further 30 min, the liquor was cooled and diluted with glacial acetic acid (50 ml) to facilitate filtration, which yielded a pale yellow solid (7·6 g, 70 %), used without future purification.

3.3. 2-Chloro-1,8-naphthalic anhydride

A solution of 1,8-naphthalic anhydride-2-sodium sulphonate (10 g) in conc. hydrochloric acid (40 ml) and water (100 ml) was stirred under reflux and a solution of sodium chlorate (5 g) in water (30 ml) added dropwise over 1 h. After refluxing a further 2 h, the liquor was filtered hot and the residue washed with hot water to give 5·61 g (72·4 %) of a cream solid which was recrystallised from glacial acetic acid in off-white needles of 2-chloro-1,8-naphthalic anhydride, m.p. 244–245 °C (lit.[11] m.p. 246–247 °C).

Alternatively, a mixture of 1,8-naphthalic anhydride-2-sodium sulphonate (5 g) and phosphorus pentachloride (50 g) was heated with stirring until the mass became liquid at 140 °C; on further heating to 180 °C the mass remained fluid and then solidified. It was then heated rapidly to 250 °C for 2 min, cooled and diluted with ice. After the residual phosphorus pentachloride was hydrolysed, the aqueous liquor was heated to 95 °C and filtered. Insoluble residue was extracted with boiling 100 ml glacial acetic acid to give off-white needles (2·01 g, 51·9 %), m.p. 242–244 °C.

3.4. 2-(2-Aminophenylthio)-1,8-naphthalic anhydride

2-Nitro-1,8-naphthalic anhydride (5 g) and 2-aminobenzenethiol (3 g) were refluxed for 1 h in ethanol (75 ml). The liquor was cooled and filtered to give 2-(2-aminophenylthio)-1,8-naphthalic anhydride (4·3 g, 62·4 %), yellow needles, m.p. 207–208 °C (ethanol) ($C_{18}H_{11}NO_3S$ requires: C, 67·3; H, 3·4; N, 4·4; S, 10·0. Found: C, 66·9; H, 3·1; N, 4·1; S, 9·8 %). The reaction mother liquors contained 2-(2-aminophenylthio)-1,8-naphthalic anhydride and 2,2′-diaminodiphenyldisulphide (cf. ref. 1) and extraction with warm 3% aqueous sodium hydroxide, filtration and acidification of the filtrate yielded a further 12·2% of the required reaction product.

Alternatively, 2-chloro-1,8-naphthalic anhydride (1·5 g) was refluxed for 2 h in 2-methoxyethanol (30 ml) with 2-aminobenzenethiol (1 g). The cooled liquor was added to 5% aqueous hydrochloric acid, filtered and the dark orange-brown residue extracted with 3% aqueous sodium hydroxide as above to give 1·24 g (74·6%) of yellow-orange needles (2-methoxyethanol), m.p. 206–207 °C, of 2-(2-aminophenylthio)-1,8-naphthalic anhydride.

3.5. Benzo[*b*]naphtho[3,2-*d*]thiophene-6,7-dicarboxylic acid (I)

2-(2-Aminophenylthio)-1,8-naphthalic anhydride (3·2 g) was added over 30 min at 10–12 °C to a mixture of glacial acetic acid (3 ml) and nitrosylsulphuric acid prepared from sodium nitrite (0·7 g) and conc. sulphuric acid (5 ml). Diazotisation was continued for 3 h and the diazo liquor then added to a boiling solution of cupric sulphate (70 g) in water (1 litre) and glacial acetic acid (125 ml). After boiling for 1 h, the suspension was cooled and filtered to give an orange solid (2·3 g, 75·9%), which recrystallised from 2-methoxyethanol in deep orange-yellow needles, m.p. 304–305 °C, of **I**. ($C_{18}H_8O_3S$ requires: C, 71·0; H, 2·7; S, 10·5. Found: C, 70·8; H, 2·6; S, 10·6%) λ_{max} (log ε) in monochlorobenzene, 404 nm (4·19) and 422 nm (4·19); mass spectra, P^+ *m/e* 304 (100%); loss of CO_2, *m/e* 260 (37·8%), *m** 222·4; further loss of CO, *m/e* 232 (46·7%), *m** 207·0; *m/e* 200 (4·5%); *m/e* 187 (17·8%) (cf. similar fragmentations for **II**,[7] **III**[2]).

Alternatively, a solution of 2-(2-aminophenylthio)-1,8-naphthalic anhydride (0·6 g) in dimethylformamide (5 ml) at room temperature was treated with amyl nitrite (0·8 ml). After stirring for 60 min, the liquor was filtered to give yellow-orange needles (0·14 g), m.p. 286–289 °C, containing mainly **I** and some 2-(2-phenylthio)-1,8-naphthalic anhydride. The mother liquor added to 3% aq. hydrochloric acid gave a yellow-brown solid (0·39 g, m.p. 260–266 °C) of a similar mixture but containing a higher proportion of deaminated material. Two recrystallisations from 2-methoxyethanol of the first-crop product gave 0·11 g of **I**. Preparative layer chromatography (as described in ref. 13) of the mother liquor product gave, from a lower R_F yellow zone, 0·19 g of **I** (total yield 52·1%). Replacing amyl nitrite in the above by sodium nitrite (0·3 g) gave (cf.

ref. 13) 17% **I** as first-crop material and a further 36% by PLC of the mother liquor material.

3.6. Benzo[*b*]naphtho[3,2-*d*]thiophene-6,7-dicarboximides (V)

Compound **I** (1·5 g) was refluxed for 1 h in 2-methoxyethanol (30 ml) with aniline (0·6 g). The cooled liquor was filtered to give brownish-yellow needles (1·15 g, 61·4%) of *N*-phenylbenzo[*b*]naphtho[3,2-*d*]thiophene-6,7-dicarboximide (**V.7**), m.p. 327–328 °C ($C_{24}H_{13}NO_2S$ requires: C, 76·0; H, 3·5; N, 3·7; S, 8·5%. Found: C, 75·8; H, 3·5; N, 3·4; S, 8·6%).

Other imides were similarly prepared, using 25% molar excess of alkylamine or arylamine. Relevant data are shown in Table 1. All melting points quoted are after recrystallisation of the products from 2-methoxyethanol; all yields quoted are those obtained by filtration of the reaction liquor as above. Alternatively, addition of the reaction liquor to 5% hydrochloric acid (150 ml) and filtering gave the crude reaction product in 92–98% yield.

3.7. Benzimidazo-dibenzothiopheno-isoquinolinones (VI)

Compound **I** (1·5 g) was refluxed for 1·5 h with 3,4-diaminotoluene (0·8 g) in glacial acetic acid (50 ml). The cooled liquor was added to 5% aq. hydrochloric acid (200 ml) and the orange-red solid (1·80 g, 94%) collected. Recrystallisation from glacial acetic acid afforded reddish-orange needles, m.p. 229–231 °C, of the isomer mixture (**VI.2**) of 13- and 14-methylbenzimidazo[1,2-*b*]dibenzothiopheno[4,3,2-*d*,*e*]isoquinolin-10-one and of 13- and 14-methylbenzimidazo[2,1-*a*]dibenzothiopheno-[4,3,2-*d*,*e*]isoquinolin-10-one. Other imidazole derivatives **VI** were similarly prepared and relevant details are shown in Table 1.

3.8. Benzimidazo[1,2-*b*]dibenzothiopheno[4,3,2-*d*,*e*]isoquinolin-10-one (VIa)

1-Nitro-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one (0·25 g) (the synthesis of which has been previously[14] described) and 2-aminobenzenethiol (0·12 g) were stirred for 2 h at 135–140 °C in dimethylformamide (6 ml). The cooled reaction liquor on addition to 10% aq. hydrochloric acid (50 ml) gave a brownish-yellow solid (0·30 g, 97%), m.p. 271–275 °C.

Preparative layer chromatography on silica gel, applying the product from solution in dimethylformamide and developing (multiple run) with toluene gave, from a higher R_F yellow zone, 1-(2-aminophenylthio)-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one (0·18 g, 61 %), m.p. 227–228 °C (2-methoxyethanol) ($C_{24}H_{15}N_3OS$ requires: C, 73·3; H, 3·9; N, 10·7; S, 8·2. Found: C, 73·0; H, 3·7; N, 10·4; S, 8·0 %). A lower pinkish-yellow zone yielded orange needles, m.p. 300–301 °C (0·07 g) of 1-amino-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one (*m*/*e* 285) (lit.[27] m.p. 296–297 °C).

1-(2-Aminophenylthio)-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one (0·4 g) was stirred into conc. sulphuric acid (8 ml) at 0–5 °C and diazotised by addition of nitrosylsulphuric acid prepared from sodium nitrite (0·075 g). Diazotisation was continued for 2 h and the diazo liquor carefully diluted with glacial acetic acid (20 ml) whilst maintaining a temperature of 0–5 °C. The resultant less viscous liquor was added gradually over 1 h to a boiling solution of hydrated copper sulphate (1·5 g) in water (30 ml) and after boiling a further 1 h, the liquor was cooled and the dark yellow-brown residue collected (0·33 g, 87 %), m.p. 220–226 °C. Preparative layer chromatography, as above, yielded, from a higher R_F yellow zone, orange-yellow needles of **VIa**, (0·2 g, 54 %), m.p. 254–255 °C (glacial acetic acid). λ_{max} in monochlorobenzene (log ε), 390 nm (4·21) and 426 nm (4·14). Other zones were not worked up; the lower of the principal yellow zones was the hydrolysis product, 1-(2-hydroxyphenylthio)-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one.

Alternatively, a solution of the 1-(2-aminophenylthio) derivative (0·4 g) in dimethylformamide (5 ml) was treated with sodium nitrite (0·4 g) and copper sulphate (0·3 g) and stirred at room temperature for 1 h and then warmed to 100 °C for 5 min before adding to 5 % aq. hydrochloric acid. The brownish-yellow product (0·17 g) gave, from a lower R_F zone, 0·07 g (36 %) of **VIa**. A higher R_F principal yellow zone was not worked up, but contained the deaminated 2-(2-phenylthio)-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]-isoquinolin-7-one.

3.9. Benzimidazo[2,1-*a*]dibenzothiopheno[4,3,2-*d*,*e*]isoquinolin-10-one (VIb)

6-Nitro-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one similarly gave 58 % of 6-(2-aminophenylthio)-7*H*-benzimidazo[2,1-*a*]benz[*d*,*e*]isoquinolin-7-one, yellow needles, m.p. 249–250 °C (2-methoxyethanol). (Found: C, 72·9; H, 3·7; N, 10·4; S, 7·9 %). Pschorr intramolecular cyclisation as above gave 34% of **VIb**, dark yellow needles, m.p. 272–273 °C (glacial acetic acid). λ_{max} in monochlorobenzene (log ε), 395 nm (4·25) and 442 nm (4·27).

3.10. Dye characterisation, electronic spectra data, dyeings and fastness tests

These were effected as previously described.[4] The purity of all dyes was confirmed by satisfactory elemental analysis, TLC and mass spectrometry.

4. CONCLUSIONS

Benzo[*d*]naphtho[3,2-*d*]thiophene-6,7-dicarboxylic anhydride is a useful source of fluorescent yellow and orange dyes, which result from its condensation with primary amines and with *o*-phenylenediamines respectively. The coloration properties on synthetic-polymer fibres are excellent, with the exception of the benzimidazole derivatives, which are only suitable for polyester. Both light and sublimation fastness are of a high order. The dyes absorb at longer wavelength than the corresponding isomers from benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboxylic acid, but are hypsochromic with respect to derivatives of benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic anhydride. The absorption maxima of these, and related compounds, are dependent on combination of electronic and steric factors pertinent to each intermediate.

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