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Intermediates and Dyes for Synthetic-Polymer Fibres. Derivatives of Benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboxylic Anhydride

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SUMMARY

The synthesis of the new heterocycle benzo[d]*naphtho*[*1,2-*b]*thiophene-9,10-dicarboxylic anhydride is described. Yellow dyes for synthetic-polymer fibres result from the condensation of this intermediate with alkylamines, arylamines and o-diamines. The colour, dyeing and fastness properties of these compounds are described, and compared with those of the isomeric derivatives from benzo*[k,l]*thioxanthene-3,4-dicarboxylic anhydride.*

1. INTRODUCTION

Benzo[*k,l*]thioxanthene-3,4-dicarboxylic anhydride (**I**) gives yellow dyes having excellent fastness to light and to sublimation on condensation with amines[1–4] and orange to red dyes on reaction with *o*-phenylenediamines.[5,6] We report here the synthesis and use as a dye intermediate of an isomer of **I**, viz. benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboxylic anhydride (**II**). The parent acenaphtheno[5,4-*b*]benzo[*d*]thiophene had been described,[7] and the related benzo[*d*]naphtho[1,2-*b*]thiophene has been prepared[8] by Pschorr intramolecular cyclisation of 2-amino-1-phenylthionaphthalene. The synthesis of **II** has not been previously reported.

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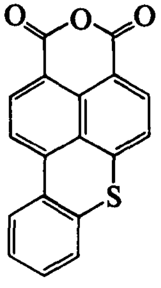
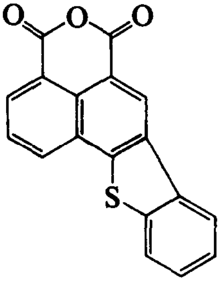


I

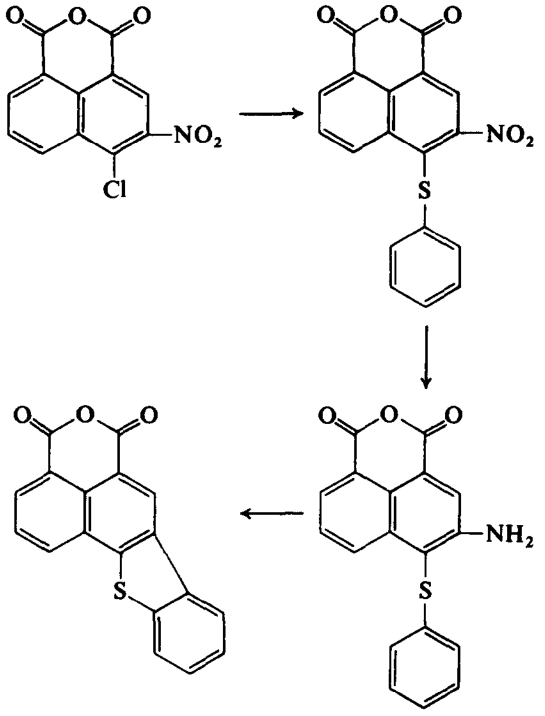


II

2. RESULTS AND DISCUSSION

Compound **II** was obtained by the reaction sequence shown in Scheme 1. Condensation of 4-chloro-3-nitro-1,8-naphthalic anhydride with thiophenol, and subsequent reduction of the product to 4-phenylthio-3-amino-1,8-naphthalic anhydride (**III**) were effected by standard procedures. Attempted cyclisation of **III** by the one-stage procedure useful[9] for the cyclisation of 4-(2-aminophenylthio)-1,8-naphthalic anhydride did not proceed cleanly. Thus, reaction of **III** with amyl nitrite or with sodium nitrite in *N*,*N*-dimethylformamide gave a mixture containing **II** and 4-phenylthio-1,8-naphthalic anhydride, together with small amounts of their methyl imides. The latter presumably arise through the decomposition of DMF and subsequent formation of methylated derivatives, as has been previously observed[10,11] with other reactions in the solvent. Compound **II** was isolated by chromatographic separation of the reaction mixture in 56% yield. Application of the Pschorr intramolecular cyclisation reaction,[12] involving addition of diazotised **III** to boiling copper sulphate solution, resulted in the minimal amount of reaction by-products and excellent yields of **II**. The mass spectrum of **II** showed similar features to that of the isomeric **I**, but, unlike **I**, the parent ion, *m/e* 304, was the base peak of the spectrum. Progressive loss of CO_2 (*m/e* 260, 43·9%, m* 222·4) and CO (*m/e* 232, 39%, m* 207·0) was typical of aromatic *ortho*-dicarboxylic anhydrides. The ions at *m/e* 187 (15·9%) and *m/e* 200 (2·4%), arising from similar pathways to those described for **I**,[13] are, as with all fragment ions of **II**, less abundant than those of **I**, indicating the greater stability of the molecular ion of the isomer **II**.

The main visible absorption in the electronic spectra of the imides (**IV**) of **II** (Table 1) is in the 380 nm region, showing a considerably



II **III**

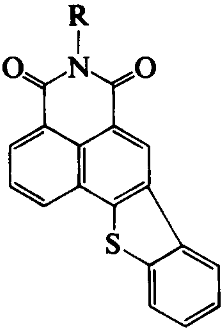
Scheme 1.

hypsochromic shift compared to the corresponding imides of **I**, which, in addition to an absorption at 380 nm, have a principal absorption band in the 460–480 nm region.[4] The imides **IV** also exhibit a very low intensity absorption in the 450–470 nm region (log ϵ 2·8–2·9) with not very well defined maximum. The colour of **II** is thus a more neutral yellow than that of **I**, indicative of the decreased electron delocalisation resulting from the presence of the five-membered hetero ring system. Delocalisation through the phenyl ring of the hetero residue, possible in **I**,[4] is not feasible in **II**, the principal electron delocalisation giving rise to structure **IVa**, viz. analogous to that which can be formulated for the non-cyclised analogues from 4-phenylthio-1,8-naphthalic anhydride.

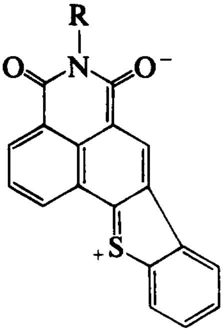
The principal absorption maximum at 380 nm in **II** is hypsochromic by 10 nm compared to that of 4-phenylthio-1,8-naphthalic anhydride, a similar difference being observed[14] between the imides **IV** and the imides of 4-phenylthio-1,8-naphthalic anhydride. These differences indicate the

TABLE 1
Colour and Fastness Properties of Dyes **IV** and **V**

Dye	*R*	*Yield* (%)	*m.p.* (°C)	λ_{max}(log ε) *in monochlorobenzene*		*Dyeings on polyester*			
						Lightfastness			*Sublimation fastness* (°C) (*2–5% dyeing*)
						0·1%	*0·5%*	*2·5%*	
IV.1	H	97	206–207	380 (4·02)		6–7	6–7	6–7	190
IV.2	Me	92	273–274	381 (4·01)		7	7	7	190
IV.3	n-C_3H_7	82	225–226	379 (4·03)		7	7	7	190
IV.4	$—CH_2CH_2CH_2OH$	88	199–200	382 (4·04)		7	7	7	210
IV.5	$—CH_2CH_2CH_2OAc$	—	163–164	378 (4·03)		7	7	7	210
IV.6	$—CH_2CH_2CH_2OMe$	76	136–137	380 (4·02)		6–7	6–7	7	200
IV.7	$—C_7H_{11}$	79	275–276	379 (4·01)		7	7	7	210
IV.8	$—CH_2Ph$	81	274–275	380 (4·04)		6–7	6–7	7	210
IV.9	—Ph	77	304–305	381 (4·01)		6–7	7	7	210
IV.10	$—C_6H_4 \cdot OMe$-p	72	297–298	380 (4·02)		6–7	7	7	210
IV.11	$—C_6H_4C_2H_4OH$-p	74	284–285	382 (4·01)		7	7	7	210
V.1	H	96	233–234	403 (4·08)	424 (3·95)	7+	7+	7+	190
V.2	Me	94	239–240	390 (4·08)	424 (3·87)	7+	7+	7+	200
V.3	OMe	91	244–245	392 (4·09)	425 (3·92)	7+	7+	7+	200
V.4	Cl	96	247–248	396 (4·07)	425 (3·94)	7+	7+	7+	200
V.5	CF_3	92	252–253	397 (4·05)	420 (3·91)	7+	7+	7+	190



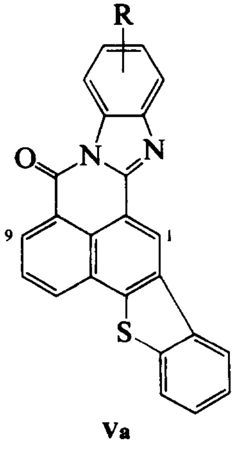
IV



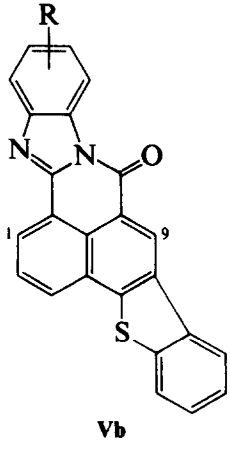
IVa

decreased electron delocalisation in **II** and its derivatives compared to those of the uncyclised phenylthio compound, presumably due to some loss of planarity resulting from ring closure. The absorption maximum of **II** and its derivatives are of a similar order to those of the sulphone analogues of **I**, viz. 7,7-dioxobenzo[*k*,*l*]thioxanthene-3,4-dicarboximides.[15]

Condensation of **II** with substituted *o*-phenylenediamines gave an isomer mixture, derivatives of benzimidazo[1,2-*b*]dibenzthiopheno-[2,3,4-*d*,*e*]isoquinolin-10-one (**Va**) and benzimidazo[2,1-*a*]dibenzthiopheno[2,3,4-*d*,*e*]isoquinolin-10-one (**Vb**). These imidazole derivatives are bathochromic by about 40 nm compared to the imides **IV**, commensurate with the increased delocalisation resulting from the presence of the imidazole ring,[16] and also exhibit significant hypsochromic shifts (in the



Va



Vb

region of 100 nm) in absorption maxima with respect to the corresponding imidazole derivatives of benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic anhydride.[5]

The imides **IV** all coloured polyester fibres fluorescent greenish-yellow. Whilst build-up of the alkyl imides was very good, the cyclohexyl (**IV.7**), benzyl (**IV.8**) and aryl derivatives (**IV.9–11**) had more limited build-up. The imidazole isomer mixtures (**V**) gave orange–yellow dyeings of very good build-up. Fastness to both light and sublimation was of a very high order and both **IV** and **V** can thus be considered excellent new dyes for polyester fibres. Selected dyes were assessed on other fibres. The 3-methoxypropylimide (**IV.6**) coloured both secondary acetate and triacetate in very greenish yellow hues of excellent build-up; on polyamide, a considerable reddening of hue was apparent. Lightfastness on the acetate fibres was good (6–7) but poor (2) on polyamide. The unsubstituted imidazole derivative **V** had limited build-up on acetate fibres (lightfastness 7) and on polyamide (lightfastness 3) and could not be regarded as a satisfactory dye for these substrates.

3. EXPERIMENTAL

3.1. 3-Nitro-4-phenylthio-1,8-naphthalic anhydride

4-Chloro-3-nitro-1,8-naphthalic anhydride (35 g) was stirred under reflux in ethanol (300 ml) with thiophenol (7·2 g) for 3 h. The liquor was reduced in volume to 150 ml and filtered, giving 25·2 g (56·5 %) of 3-nitro-4-phenylthio-1,8-naphthalic anhydride, m.p. 178–179 °C (2-methoxyethanol) (Found: C, 61·5; H, 2·45; N, 3·7; S, 9·0. $C_{18}H_9NO_5S$ requires: C, 61·5; H, 2·6; N, 4·0; S, 9·1 %). Addition of the filtrate to water yielded an additional 37 % of crude product, the mass spectrum of which showed it to contain diphenyldisulphide (*m*/*e* 218). Two recrystallisations from ethanol removed this thiophenol oxidation product.

3.2. 3-Amino-4-phenylthio-1,8-naphthalic anhydride (III)

The above nitro compound (10 g) was stirred into a mixture of stannous chloride (30 g) and conc. hydrochloric acid (30 ml). After warming to 40 °C, the temperature rose spontaneously to 80 °C and was maintained at 80 °C for 30 min (colour change from orange to olive-green). The suspension was cooled and filtered to give 9·8 g of a yellow solid (10·7 % yield, contamination with stannous chloride). Recrystallisation from pyridine gave dark greenish-yellow needles, m.p. 224–225 °C, of 3-amino-4-phenylthio-1,8-naphthalic anhydride (Found: C, 67·2; H, 3·3; N, 4·2; S, 9·8. $C_{18}H_{11}NO_3S$ requires: C, 67·3; H, 3·4; N, 4·4; S, 10·0 %.)

3.3 Benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboxylic anhydride (II)

Glacial acetic acid (2 ml) was added to nitrosyl sulphuric acid prepared from sodium nitrite (10·7 g) and conc. sulphuric acid (10 ml). The mixture was cooled to 10 °C and to it was added, portionwise over 1 h, **III** (3·2 g). After stirring for 2 h, the dark red viscous liquor was added over 90 min to a boiling solution of cupric sulphate (90 g) in water (1 litre) and glacial acetic acid (125 ml). The resultant suspension was then filtered to give 2·6 g (85 %) of an orange solid, m.p. 288 °C. Thin layer chromatography and mass spectra indicated the product **II** (*m*/*e* 304) to be contaminated with a small amount of 4-phenylthio-1,8-naphthalic anhydride (*m*/*e* 306). Recrystallisation from 2-methoxyethanol gave pure **II**, orange needles, m.p. 307–308 °C (Found: C, 70·8; H, 2·7; S, 10·7. $C_{18}H_8O_3S$ requires: C, 71·05; H, 2·6; S, 10·5 %.) (λ_{max} (log ε), in monochlorobenzene, 380 (4·04) and 455 (2·96) nm).

3.4. Benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboximides (IV)

Compound **II** (1·5 g) was refluxed for 1 h in ethanol (50 ml) with 3-methoxypropylamine (10·6 g). The liquor was cooled and filtered to give dull orange needles (yield, 76 %) of *N*-3-methoxypropylbenzo[*d*]naphtho-[1,2-*b*]thiophene-9,10-dicarboximide (**IV.6**), m.p. 136–137 °C. Similar reaction with other amines (25 % molar excess), using ethanol as solvent for alkylamines and 2-methoxyethanol as solvent for arylamines, gave the imides listed in Table 1. The yields recorded in the table are those resulting from direct filtration of the cooled reaction liquor; almost quantitative recovery was obtained by addition of the reaction liquor to dilute hydrochloric acid and filtration.

The *N*-3-acetoxypropyl imide (**IV.5**) was prepared from the *N*-3-hydroxypropyl derivative (**IV.4**) by the previously described[4] acylation procedure.

3.5. Benzimidazo[1,2-*b*]dibenzthiopheno[2,3,4-*d*,*e*]isoquinolin-10-ones (Va) and benzimidazo[2,1-*a*]dibenzthiopheno[2,3,4-*d*,*e*]-isoquinolin-10-ones (Vb)

Compound **II** (1·5 g) and 3,4-diaminotoluene (0·95 g) were refluxed for 1·5 h in glacial acetic acid (75 ml). The cooled reaction liquor, on addition to 5% hydrochloric acid (200 ml), gave the isomer mixture (**V.2**) of 13- and 14-methyl-benzimidazo[1,2-*b*]- and 13- and 14-methyl-benzimidazo[2,1-*a*]-dibenzthiopheno[2,3,4-*d*,*e*]isoquinolin-10-ones, m.p. 229–231 °C. Similar condensation with other *o*-diamines afforded the isomer mixtures **V** listed in Table 1.

3.6. Colour and fastness properties

Dye characterisation, electronic spectra data collection, dyeings and fastness tests were carried out as previously described.[6] Relevant data are shown in Table 1. The purity of all dyes was confirmed by elemental analysis, TLC and mass spectrometry.

4. CONCLUSIONS

Benzo[*d*]naphtho[1,2-*b*]thiophene-9,10-dicarboximides (**IV**) colour polyester, cellulose secondary acetate, triacetate and polyamide fibres in fluorescent greenish yellow hues of good build-up and fastness properties, with the exception of lightfastness on polyamide, which is poor. The related benzimidazo-benzo-thionaphtheno-isoquinolinones (**V**) give bright orange–yellow dyeings of excellent fastness on polyester, but are not suitable for the acetate fibres or polyamide. The colour of **IV** and **V** is hypsochromic with respect to the analogous dyes derived from benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic acid and is more relatable to that of the uncyclised derivatives of 4-phenylthio-1,8-naphthalic anhydride.

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