

## Note

### Synthesis of benzimidazoxanthenoisoquinolinones, new intermediates and dyes for synthetic-polymer fibres

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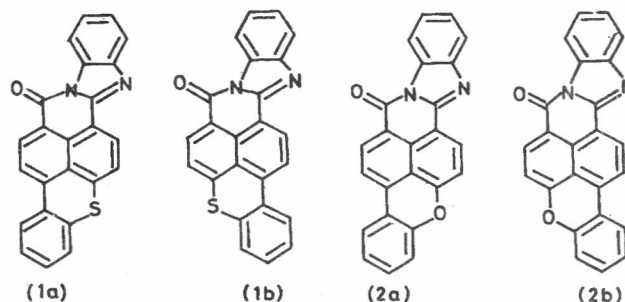
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The reaction of 4-chloronaphthalene-1, 8-dicarboxylic anhydride **3** with 2-nitrophenol in hot DMF and in the presence of copper powder as a catalyst gives **4** which is reduced to **5** with iron powder and glacial acetic acid. Compound **5** is cyclized to **6**. Condensation of benzo[*k,l*]xanthene-3, 4-dicarboxylic anhydride **6** with *o*-phenylenediamine affords isomeric derivatives of the new heterocyclic benzimidazo[1,2-*b*]xantheno[2,1,9-*d,e,f*]isoquinolin-7-one **2a** and benzimidazo[2,1-*a*]xantheno[2,1,9-*d,e,f*]isoquinolin-8-one **2b**. These are excellent new dyes for polyester fibers, giving fluorescent orange to red dyeings of outstanding fastness to light and sublimation.

Benzo[*k,l*]thioxanthene-3, 4-dicarboximides have been described in patent specifications<sup>1</sup> as yellow to red dyestuffs for synthetic fibers. These dyes have been prepared by different routes including Pschorr cyclization of 4-(2-aminophenylthio)-1, 8-naphthalimides and also by condensation of alkylamines with benzo[*k,l*]thioxanthene-3, 4-dicarboxylic anhydride<sup>2</sup>. Whilst condensation of substituted benzo[*k,l*]thioxanthene-3, 4-dicarboxylic anhydride with *o*-phenylenediamine affords the isomeric mixtures of benzimidazo[1,2-*b*]thioxanthene[2,1,9-*d,e,f*]isoquinoline-7-one **1a** and benzimidazo[2,1-*a*]thioxantheno[2,1,9-*d,e,f*]isoquinolin-8-one **1b**, many of which are excellent dyestuffs for synthetic fibers<sup>3,4</sup>, analogous derivatives of benzimidazo[1,2-*b*]xantheno[2,1,9-*d,e,f*]isoquinolin-7-one **2a** and benzimidazo[2,1-*a*]xantheno[2,1,9-*d,e,f*]isoquinolin-8-one **2b** have not been described.



Herein we wish to report the synthesis and dyeing properties of the new heterocycles **2a** and **2b**.

### Results and Discussion

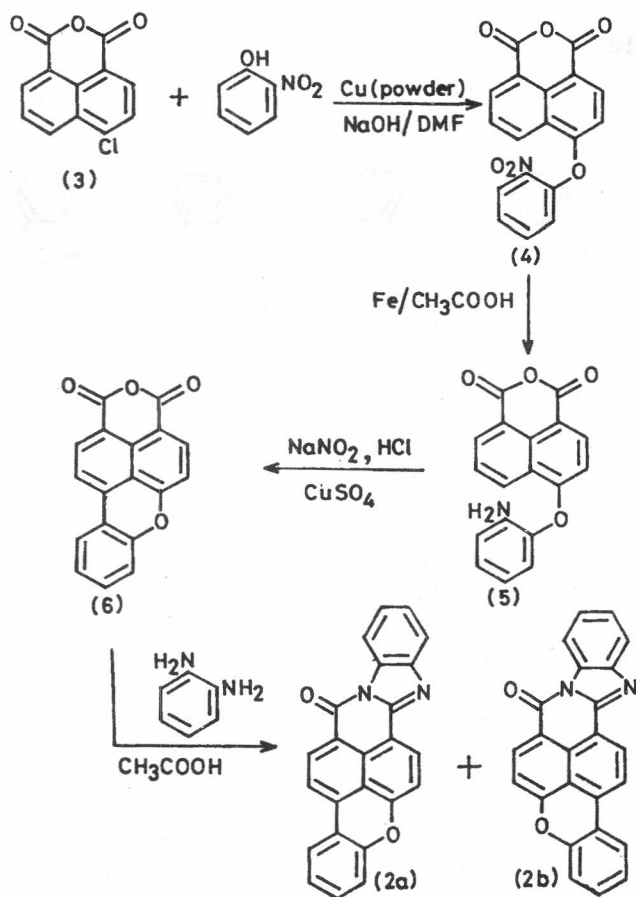
The reaction of 4-chloronaphthalene-1, 8-dicarboxylic anhydride **3** with 2-nitrophenol was unsatisfactory and gave **4** without any byproduct formation. However, in hot DMF solution and in the presence of copper powder and sodium hydroxide as catalysts the reaction took place smoothly with satisfactory yield (82%) of **4**. Use of copper salt in nucleophilic substitution reaction is common<sup>6,7</sup>.

Compound **4** was reduced to 4-(2-aminophenoxy)naphthalene-1, 8-dicarboxylic anhydride **5** with iron powder in glacial acetic acid. Compound **5** underwent cyclization by the Pschorr reaction<sup>8</sup> giving **6** in an excellent yield.

The preferred reaction conditions include relatively prolonged diazotiazation period (above 5 hr) and slow addition of the diazonium liquor to copper sulphate solution. Rapid addition in the latter stage resulted in **6** highly contaminated with 4-(2-hydroxyphenoxy)naphthalene-1, 8-dicarboxylic anhydride.

The electronic spectrum of **6** when compared with that of **5** showed a bathochromic shift of 67 nm.

Condensation of **6** with *o*-phenylenediamine afforded an isomeric mixture of the new heterocyclic system benzimidazo[1,2-*b*]xantheno[[2,1,9-*d,e,f*]isoquinolin-7-one **2a** and benzimidazo[2,1-*a*]xantheno[2,1,9-*d,e,f*]isoquinolin-8-one **2b**. However, no attempt was made to separate the



Scheme I

individual components. The reaction sequence is shown in Scheme I.

The excellent dyeing and fastness properties of the anhydride **6** was noted. It gave a deep yellow colour with good fastness to washing despite the presence of the alkali-soluble anhydride group.

The dye was not removed on boiling the dyeings in 15% aqueous sodium carbonate or 5% aqueous sodium hydroxide solution.

The isomeric mixture of **2a** and **2b**, prepared in the present work, is also an excellent new dye for polyester fibers giving fluorescent orange to red dyeings. However, coloration of secondary cellulose acetate and cellulose triacetate was generally unsatisfactory.

Light fastness of this isomeric mixture at all depths was excellent and all dyeings had a very fastness to sublimation as assessed on the basis<sup>9</sup> of the temperature of initial visible mark-off on to adjacent undyed polyester.

In conclusion the new heterocycles benzimidazo-xanthenoisoquinolinones form the basis of a novel range of fluorescent orange to red dyes of excellent fastness to light and sublimation for polyester substrates.

### Experimental Section

**General.** All melting points are uncorrected. IR spectra were recorded on a Unicam 8700 series. UV spectra were obtained on a Philips UV/vis spectrometer and mass spectra scanned on a Varian mat 34 instrument at 70 eV.

**4-(2-Nitrophenoxy)-1, 8-naphthalic anhydride 4.** A mixture of 4-chloronaphthalic anhydride (2.04 g, 8.8 mmoles), *o*-nitrophenol (0.68 g, 17 mmoles), sodium hydroxide (0.05 g) and copper powder (0.08 g) was refluxed in DMF (45 mL) for 1 hr. To this solution hydrochloric acid (150 mL, 20%) was added the precipitated solid, filtered off and recrystallized from AcOH to afford the title compound in 82% yield, m.p. 266-68°C; FTR(KBr): 1763, 1728, 1525, 1344 and 1253 cm<sup>-1</sup>; UV (DMF): 352.4 nm; MS: *m/z* 335.6 (M<sup>+</sup>, 18%), 216.4 (14), 185.3 (38), 141.2 (62), 122.2 (100), 113.2 (52), 94.1 (22).

**4-(2-Aminophenoxy)-1, 8-naphthalic anhydride 5.** A mixture of compound **4** (1 g, 3.2 mmoles) and iron powder (0.48 g) was refluxed in glacial acetic acid (30 mL) for 1 hr. To this brown solution, water (60 mL) was added. The precipitated yellow solid was filtered off and washed several time with water to afford the title compound in 94% yield, m.p. 171-72°C; FTIR(KBr): 3466, 3375, 1768, 1730 cm<sup>-1</sup>; UV(DMF): 357.2 nm; MS: *m/z* 305.

**Benzo[*k*, *l*]xanthene-3, 4-dicarboxylic anhydride 6.** A solution of compound **5** (0.5 g, 1.7 mmoles) in glacial acetic acid (12 mL) was treated with hydrochloric acid (1 mL) and sodium nitrite (1.14 g in 4 mL water) at 0°C. After 60 min a solution of copper sulphate (1.12 g) in water (20 mL) was added. The reaction mixture was refluxed further for 1/2 hr. This solution was cooled in an ice-bath and the precipitated solid filtered off, washed with water and crystallized from DMF to afford the title compound, yield 93.2%, m.p. 155-160°C (dec.); FTIR(KBr): 1772, 1728, 1160 cm<sup>-1</sup>; UV(DMF): 425.1 nm; MS: *m/z* 288.5 (M<sup>+</sup>, 45%),

2465 (18) 216.4 (22), 187.4 (58), 170.1 (20), 122.2 (41), 60.1 (100).

**Benzimidazo[1, 2-*b*]xantheno[2, 1, 9-*d, e, f*]-isoquinolin-7-one 2a and benzimidazo[2, 1-*a*]xantheno[2, 1, 9-*d, e, f*]isoquinolin-8-one 2b.** Compound **6** (0.02 g, 0.07 mmole), prepared as above, was refluxed with *o*-phenylenediamine (0.02 g, 0.2 mmole) in glacial acetic acid (5 mL). The liquor was cooled and filtered to give an orange-reddish solid which was recrystallized from DMF to afford the title compounds, yield 85%, m.p. 279-281°C; FTIR(KBr): 1699, 1579, 1232  $\text{cm}^{-1}$ ; UV(DMF): 447.5 nm.

## References

- 1 Farbwerk Hcechst A G, *British Pat*, 1,095,784 and 1,112,726; *French Patent* 1,489,487; *Chem. Abstr*,
- 2 Grayshan P H, Kadhim A M & Peters A T, *J Heterocyclic Chem*, 11, 1974, 33.
- 3 Kadhim A M & Peters A T, *Tetrahedron*, 30, 1974, 2245.
- 4 Grayshan P H, Mak K H R & Peters A T, *J Appl Chem Biotechnol*, 24, 1974, 121-130.
- 5 Grayshan P H & Peters A T, *J Heterocyclic Chem*, 10, 1973, 699.
- 6 Paine A J, *J Am Chem Soc*, 109, 1987, 1496.
- 7 Lendley J, *Tetrahedron*, 40, 1984, 1433.
- 8 Pschorr R, *Ber*, 29, 1896, 496.
- 9 Al-kassim & Peters A T, *JSDC*, 89, 1973, 359.