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Synthesis of 4-Amino-3-benzoylnaphthalene-1,8-dicarboxylic Acid and its Derivatives

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SUMMARY

The synthesis of 4-amino-3-benzoyl-1,8-naphthalic acid and its derivatives by a novel route is described. Reaction of 4-nitro-1,8-naphthalic acid with benzyl cyanide in the presence of alkali gave the naphthisoxazole, which on reduction yielded 4-amino-3-benzoylnaphthalic acid. Reaction of this dicarboxylic acid derivative with arylamines and with o-phenylenediamine gave rise to a series of yellow to orange disperse dyes. Some other reactions of the aminobenzoyl derivative are also described.

1. INTRODUCTION

The importance of 4-amino-1,8-naphthalimide derivatives as disperse dyes and pigments is well known. It was anticipated that an electron-withdrawing acyl group *ortho*- to the amino function would improve the lightfastness and the other properties of these dyes.

We report in this paper a novel approach to the synthesis of such compounds and their properties. The synthetic approach involves the reaction of benzyl cyanide in alkaline medium on 4-nitronaphthalene-1,8-dicarboxylic acid (**1**); see Scheme 1. The anthranil derivative (**2**) obtained from this reaction may be reduced to yield the 4-amino-3-benzoylnaphthalene-1,8-dicarboxylic acid (**3**). The dicarboxylic acid is then reacted with different amines to give the respective imides (**4a–e**) and with

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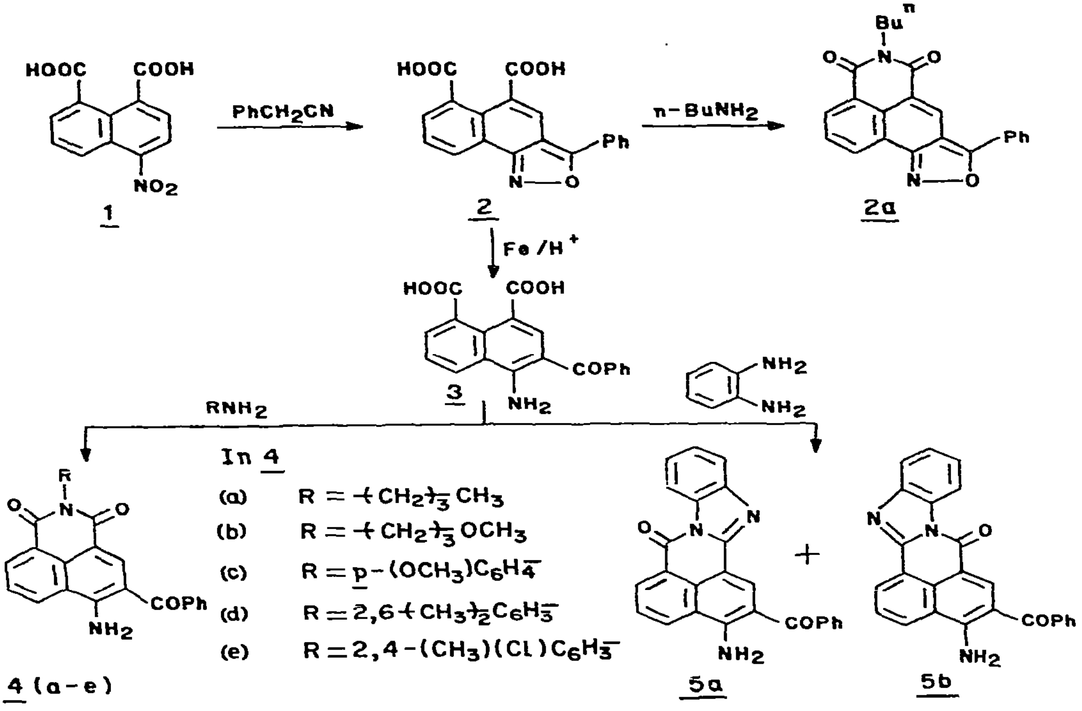
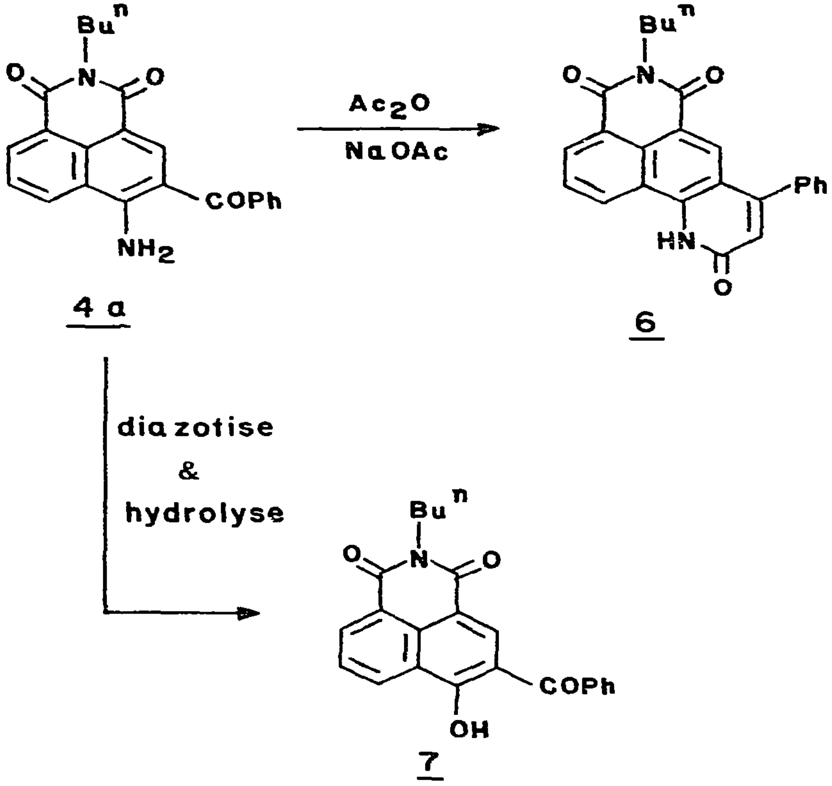


Scheme 1

o-phenylenediamine to yield the benzimidazolone (**5a,b**) (mixture of isomeric structures). The *N*-butylimide (**4a**) can be prepared by two alternative routes: (a) by reaction of the isoxazole (**2**) with butylamine, to yield **2a**, followed by reduction to **4a**; and (b) by reaction of the aminobenzoyl derivative (**3**) with butylamine. The products obtained by the two routes have been found to be identical by m.p., TLC and superimposable IR spectrum.

The compounds thus synthesised have been studied for their absorption and emission characteristics and also applied on polyester fibre as disperse dyes. The results are set out in the Table. The dyeings were generally unsatisfactory with the exception of the imidazolone (**5a,b**), which gave bright orange yellow dyeings having good tinctorial power with light- and sublimation fastness of rating 4.

An interesting structural variant has been synthesised (Scheme 2). This consisted of the quinolone derivative (**6**) obtained by the reaction of the



Scheme 2

o-aminoketone (**4a**) with sodium acetate and acetic anhydride. This dye showed very poor tinctorial power.

In view of the importance of 4-hydroxy-1,8-naphthalimides as optical brighteners, the *o*-aminobenzoyl derivative (**4a**) was converted to the corresponding *o*-hydroxybenzoyl derivative (**7**) by diazotisation and hydrolysis. The product was characterised by its elemental analysis and characteristic ferric chloride coloration. However, the compound exhibited only feeble greenish yellow fluorescence in solution.

2. EXPERIMENTAL PROCEDURE

All melting points are uncorrected. 4-Nitronaphthalene-1,8-dicarboxylic acid (**1**) was prepared by a known method.[1]

TABLE 1
Physical Data of Various Fused Naphthalene Heterocycles

Compound	*Molecular formula*[a]	*m.p. (°C)*	*Yield (%)*	*Absorption in DMF*		*Emission λ_{max} (nm)*	*IR max./nujol (cm^{-1})*
				λ_{max} (nm)	*log E*		
2	$C_{19}H_{11}NO_5$	234–236 (aq. DMF)	79	—	—	—	—
2a	$C_{23}H_{16}N_2O_3$	187 (PhCl)	81	—	—	—	—
3	$C_{19}H_{13}NO_5$	285 (DMF)	67	—	—	—	3 320, 3 420 (—NH_2) 1 715, 1 770 ($>$C=O)
5	$C_{24}H_{15}N_3O_2$	216–218 (PhCl)	81	410	4·53	495	—
4a	$C_{23}H_{20}N_2O_3$	256 (PhCl)	80	380	4·43	485	3 360 (—NH_2) 1 645, 1 685 (imide)
4b	$C_{23}H_{20}N_2O_4$	237–238 (PhCl)	77	385	4·32	485	3 390 (—NH_2) 1 650, 1 695 (imide)
4c	$C_{26}H_{18}N_2O_4$	257–259 (ODCB)	71	380	4·40	—	3 460 (—NH_2) 1 660, 1 700 (imide)
4d	$C_{27}H_{20}N_2O_3$	285 (ODCB)	79	380	4·32	—	3 380 (—NH_2) 1 680, 1 720 (imide)
4e	$C_{26}H_{17}ClN_2O_3$	285 (ODCB)	77	380	4·51	—	—
6	$C_{25}H_{20}N_2O_3$	285 (aq. DMF)	50	380	4·34	—	—
7	$C_{23}H_{19}NO_4$	193–194 (DMF)	35	—	—	—	—

[a] Satisfactory elemental analyses obtained: C ± 0·3; H ± 0·23; N ± 0·3%.

2.1. Preparation of 3-phenylnaphth[1,2-*c*]isoxazole-5,6-dicarboxylic acid (2)

To a well-stirred cooled mixture of KOH (18 g, 0·32 mole) in methanol (70 ml) at 0–5 °C, benzyl cyanide (2·4 g, 0·021 mole) was added. After 15 min, **1** (5·2 g, 0·02 mole) was added and the mixture stirred for 30 min at 0–5 °C and then at room temperature for 6 h. The reaction mixture was poured into ice water (200 ml), carefully acidified (pH 6), filtered, washed and dried. The isoxazole (**2**) was crystallised from aqueous DMF in 79 % yield, m.p. 234–236 °C. Found, N 4·0 %; $C_{19}H_{11}NO_5$ requires N 4·2 %.

2.2. Synthesis of 4-amino-3-benzoylnaphthalene-1,8-dicarboxylic acid (3)

To a refluxing mixture of DMF (30 ml) and glacial acetic acid (20 ml) containing **2** (8·7 g, 0·02 mole), iron filings (4·5 g, 0·08 mole) were added in portions with stirring during 3 h. After refluxing for a further hour the reaction mixture was filtered hot. The filtrate was diluted with water (100 ml) and filtered. The crude **3** was purified by dissolving in dilute alkali (2%) and reprecipitating with acid (pH 6). Crystallisation from DMF gave **3** in 67% yield as yellow needles, m.p. 285 °C. Found: N 4·0%; $C_{19}H_{13}NO_5$ requires N 4·2%.

2.3. General method for the synthesis of substituted imides (2a and 4)

To *o*-dichlorobenzene (7 ml), **2** or **3** (0·003 mole) and an appropriate amine [RNH_2—see Scheme 1 (0·015 mole)] were added and the mixture refluxed in the presence of boric acid (10–15 mg) for 10–12 h. The reaction mixture was cooled, solvent removed by steam distillation and the product (**2a** or **4a–e** respectively) filtered, washed and dried. Relevant data are given in Table 1.

2.4. Synthesis of 4-amino-3-benzoyl-1,8-naphthalene-1′,2′-benzimidazole (5a,b)

To *o*-dichlorobenzene (7 ml) **3** (1 g, 0·003 mole) and *o*-phenylenediamine (0·36 g, 0·0033 mole) were added and refluxed. The product (**5**) was isolated according to procedure 2.4 and was crystallised from chlorobenzene as pale brownish orange granules in 81% yield, m.p. 215 °C. Found: N 11·2%; $C_{25}H_{15}N_3O_2$ requires N 10·8%.

2.5. Synthesis of 4-amino-3-benzoylnaphthalene-1,8-dicarboxy-*N*-butylimide (4a) from (2a)

To a hot refluxing solution of **2a** (0·75 g, 0·002 mole) in DMF (6 ml) and acetic acid (5 ml), iron filings (0·50 g, 0·008 mole) were added. The procedure 2.2 was followed to obtain the product (**4a**), which was purified by crystallisation from *o*-dichlorobenzene in 71% yield, m.p. 256 °C.

2.6. Synthesis of 4-phenylnaphtho[1,2-*e*]-1*H*-pyridin-2-one-6,7-dicarboxy-*N*-butylimide (6)

A mixture of **4a** (0·74 g, 0·002 mole); sodium acetate (0·25 g, 0·003 mole) and acetic anhydride (1·2 g, 0·012 mole) was refluxed for 6 h. After cooling, the mixture was diluted with water, the product filtered, washed with benzene (5 ml) and dried. The product (**6**) was crystallised from a mixture of DMF and alcohol in 50% yield, m.p. 285 °C. Found: N 6·8%; $C_{25}H_{20}N_2O_3$ requires N 7·0%.

2.7. Synthesis of 4-hydroxy-3-benzoylnaphthalene-1,8-dicarboxy-N-butylimide (7)

A mixture of **4a** (0·74 g, 0·002 mole) and $NaNO_2$ (0·16 g, 0·0023 mole) was added in portions to conc. H_2SO_4 (5 ml) at 0–5 °C over 15 min. The mixture was stirred for 30 min, excess of nitrite destroyed and the solution added dropwise to boiling H_2SO_4 (80%, 10 ml). The mixture was refluxed for 2 h, cooled, carefully diluted with water, filtered, washed and dried. The product (7) was crystallised from DMF in 35% yield, m.p. 193–194 °C. Found: N 3·5%; $C_{23}H_{19}NO_4$ requires N 3·8%.

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REFERENCE

1. Mitsuo Okazaki, Yasuo Suhona and Masayuki Fujiyama, *Yuki Gosei Kagaku Kyokai Shi*, **14**, 394 (1956); *Chem. Abstr.*, **51**, 8051 (1956).