

Heterocyclic Derivatives of Naphthalene-1,8-dicarboxylic Anhydride. Part II.
Colour and Dyeing Properties on Synthetic Fibres of Some Substituted
7*H*-Benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-ones.

P. H. Grayshan and Arnold T. Peters

Dyestuff Research Laboratories, School of Colour Chemistry and Colour Technology,
The University Bradford, Yorkshire, U.K.

Received March 16, 1973

The effect on colour resulting from substitution in the phenyl and naphthyl rings of 7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (I) is discussed; dyeing and fastness properties of these dyes on synthetic fibres are described and the synthesis of some new 1,8-naphthalimides and derivatives of I recorded.

Naphthalene-1,8-dicarboxylic anhydride and its derivatives have been extensively cited in the patent literature as intermediates for disperse, basic, acid and vat dyes, and as fluorescent brightening agents.

As dyes for synthetic fibres, substituted 1,8-naphthalimides tend to be deficient in fastness properties, more satisfactory dyestuffs being derived from 7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (I) (*e.g.* 1-3), naphthalene-1,4,5,8-tetracarboxylic dianhydride (*e.g.*, 4,5) and benzo[*k,l*]thioxanthene-3,4-dicarboxylic anhydride (*e.g.*, 6,7).

We report here the properties of a series of substituted derivatives of I. The synthesis of the six isomeric mononitro derivatives of I in which the nitro group is in the naphthalene ring has been described (Part I, previous paper); condensation of substituted naphthalene-1,8-dicarboxylic anhydrides with *o*-phenylenediamines afforded the other substituted I listed in Table I.

The electronic spectra data in Table I is from solution in glacial acetic acid for most compounds, solubility in ethanol or hexane being very low. Relatively large blue shifts in the long wavelength absorption band on changing from a non-polar (*e.g.*, hexane) to a polar (*e.g.*, ethanol) media are observed with many dyestuffs, *e.g.*, 2-methyl-4-amino- β,β -dicyanostyrenes, 17-42 nm (8), nitrodiphenylamines 11-31 nm (9), 4-nitroaminobenzenes, *ca.* 35 nm (10), and 1-methylaminoanthraquinone, 10 nm (10). Much smaller shifts (5 nm) occur with 2-anilino-*N*-phenyl-1,8-naphthalimide and in 2-*p*-anisidino-*N*-*p*-anisyl-1,8-naphthalimide, although these contain conjugated electron donor and acceptor substituents. 1-Amino-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one shows even smaller shifts, *viz.*, λ max 440 and 456 nm in ethanol; 407s, 428, 446s and 455 nm in hexane. Similar small shifts occur in the λ max of I in acetic acid and ethanol (Table I).

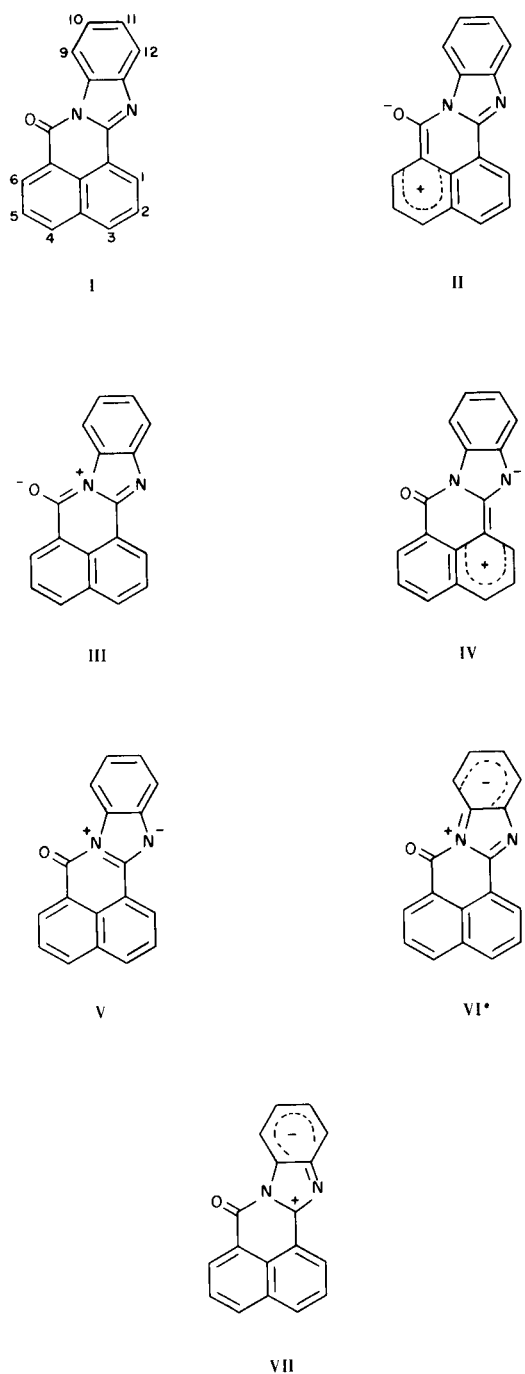
Previously reported data of some nitro derivatives of I in chloroform (11) indicate a hypsochromic shift from chloroform to acetic acid; in hexane, the apparent bathochromic shifts (Table I, footnote), are probably related to the vibrational structure showing more clearly in this solvent. The small blue shifts with change in solvent polarity, associated (12) with $n-\pi^*$ transitions, and the lack of deep colour generally in these dyes, confirms the limited contribution of extensive intramolecular charge transfer structures which have been described in other disperse dye classes, *e.g.*, 4-aminoazobenzenes (13,14). Localised charge transfer structures will also contribute to the observed electronic spectra, and in I, these involve structures with a limited degree of conjugation between donor and acceptor centers (Scheme I). Similar mesomeric limiting states have been described for other five membered heterocycles containing two nitrogen atoms, *e.g.*, for 1,3-diphenyl- Δ^2 -pyrazolines in terms of charge delocalisation into the phenyl rings (15,16) or within the heterocyclic system (17), and for imidazole (18,19).

The principal resonance forms involve electron transfer initiated either by the acceptor carbonyl group acting on the naphthalene ring (II) or the adjacent nitrogen atom (III), and by the electron acceptor pyridine nitrogen atom acting through the naphthalene ring (IV) or the conjugated nitrogen atom (V). A more minimal contribution involving VI and VII may also be considered.

Substitution in both the phenyl ring and the naphthalene ring can thus affect the colour of I by additional localised charge transfer interactions originating at the substituent, and by perturbation effects of the substituent on the general resonance structures in Scheme I.

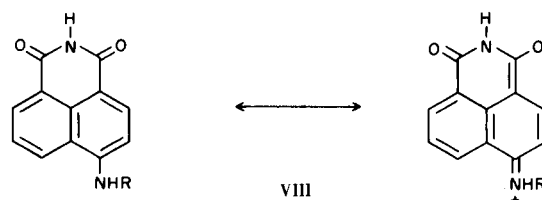
Scheme I related the colour of I to the presence of both the C=N and C=O groups. 1,8-Naphthalimide (no

SCHEME I



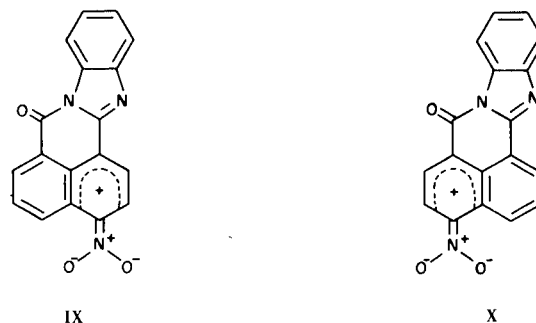
C=N groups) is colourless and requires introduction of electron donor groups into the molecule to produce significant bathochromic shifts. Thus, 4-amino-1,8-naphthalimide and 4-alkylamino derivatives (VIII) are yellow dyes (20), although 4-acetamido-1,8-naphthalimide is only slightly coloured (21,22), and like 4-alkoxy-*N*-alkyl-1,8-naphthalimides (23), can be used as fluorescent brightening

agents. Introduction of a strong donor conjugated to the carbonyl group is thus necessary for visible absorption; the polarisation effects in VIII have been related to shifts in carbonyl stretching frequencies in the ir spectrum (24,25). Reaction of I with lithium aluminum hydride (26), or photoreduction in 2-propanol (27) results in reduction of the carbonyl group with retention of the C=N group, giving colorless reduction products.



Compounds related to I, but containing only C=O or C=N groups have therefore little colour; the relative effect of introduction of a phenyl group in conjunction with both C=O and C=N groups is illustrated by the greater bathochromicity of I (*ca.* 40 nm) compared to *N*-phenyl-1,8-naphthalimide, which shows λ_{\max} 334, 342s and 349s nm in ethanol (10).

Introduction of nitro groups into I can thus be expected to produce only minimal shifts in λ_{\max} , with additional resonance forms IX and X.



Analogous substitution in the ring containing the C=O group is more bathochromic than in the ring containing the C=N group, confirming the increased polarity resulting from substitution in this ring (see Part 1), *viz.*, λ_{\max} 1-NO₂ > 6-NO₂; 2-NO₂ > 5-NO₂; 4-NO₂ > 3-NO₂. Substitution in each ring is bathochromic in the order *p* > *o* > *m* to the C=O and C=N groups, *viz.*, λ_{\max} 3-NO₂ > 1-NO₂ > 1-NO₂ > 2-NO₂ and 4-NO₂ > 6-NO₂ > 5-NO₂.

The small shifts resulting from substitution in the naphthalene ring by a nitro group are in accord with those observed in disubstituted benzenes where both substituents have similar polar effects, *viz.*, the shift approximates (28-30) to that shown by the more polar substituent. Thus, compared to naphthalene (31), nitronaphthalenes

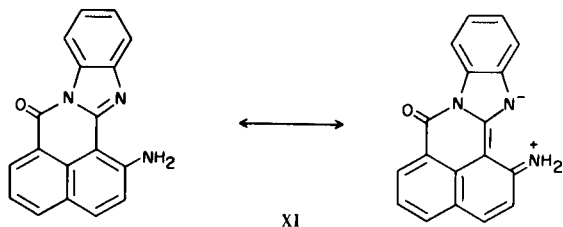
TABLE I

Electronic Spectra Data of Substituted I.
 λ max (nm) ($\log_{10} \epsilon$) in (a) ethanol or (b) glacial acetic acid.

Substituent								
H	(a)	272s (4.45)	283 (4.22)	293 (4.26)			382 (4.11)	
	(b)	271 (4.02)	282 (4.13)	292 (4.17)			384 (4.07)	
1-NO ₂	(b)		281 (4.11)	291 (4.08)			387 (4.06)	
2-NO ₂	(b)	273 (4.33)	281 (4.23)	292 (4.38)			385 (4.03)	
3-NO ₂	(b)		283 (4.18)		343s (4.00)		403 (4.27)	
4-NO ₂	(b)		288 (4.21)		347 (3.79)		404 (3.81)	
5-NO ₂	(b)		282 (4.41)	292 (4.44)			397 (3.93)	
6-NO ₂	(b)		284 (4.32)	294 (4.34)	344 (3.81)		299 (3.97)	
2-Br	(b)		283 (4.17)	294 (4.18)		358 (4.03)	390 (4.11)	
5-Br	(a)	269 (4.32)	284 (4.26)	296 (4.26)	344 (3.83)		390 (4.03)	
	(b)		284 (4.26)	295 (4.26)	343s (3.88)		386 (4.07)	
1-NH ₂	(a)	273 (4.47)		303 (4.26)	335 (3.90)		440 (4.11)	456 (4.11)
1- <i>p</i> -Tosylamino	(b)			297 (4.17)	341 (3.89)	358 (3.96)	405 (4.14)	426s (4.03)
6- <i>p</i> -Tosylamino	(b)			301 (4.17)	346 (4.02)	364 (4.18)	413 (4.17)	436s (3.99)
10-OMe	(a)			306 (4.33)			409 (4.03)	
11-OMe	(a)		289 (4.32)	299 (4.43)	344 (4.03)		373 (4.05)	
	(b)		289 (4.33)	299 (4.41)	344 (4.06)		371 (4.07)	

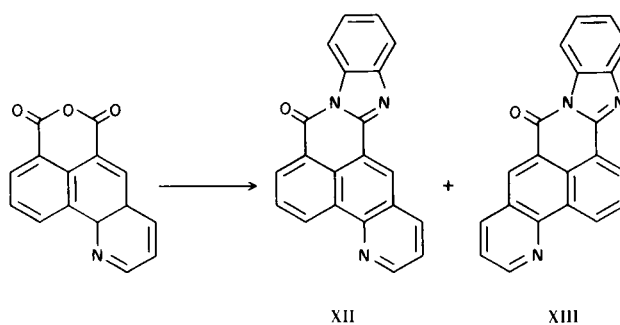
Footnotes: λ max in hexane: 1-NO₂ 383 and 399; 2-NO₂, 290 and 406; 3-NO₂, 394s, 415, and 448s; 4-NO₂, 414; 5-NO₂; 401 and 420s; 6-NO₂, 405 and 420s nm. In chloroform (11): 2-NO₂ 389; 3-NO₂, 410; 5-NO₂, 405 nm.

are bathochromic by approximately 70 nm (32), whilst introduction of the heterocyclic ring in I gives a bathochromic shift of approximately 100 nm. In the nitro derivatives of I, the overall shift approximates more to that of the heterocyclic residue, and is not additive as in the case of conjugated electron donor-acceptor chromophores. As with 1,8-naphthalimides, the presence of an amino group (giving a donor-acceptor system) is necessary for greater bathochromicity, e.g., 1-amino-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (XI) shows λ max 440 and 456 nm.



Decreasing the donor nature of the amino group, by tosylation (Table I) or by a Skraup reaction, results in significant hypsochromic shifts.

Condensation of naphthalene-1,8-dicarboxylic anhydrides with *o*-phenylenediamines produces isomer mixtures, e.g., XII, XIII.



Whilst some isomer separations or unambiguous isomer synthesis have been reported (33-35), commercial dye-stuffs are normally the isomer mixtures formed during the condensation. The isomer ratios are influenced by polarity factors in the intermediate *N*-aryl-1,8-naphthalimide; thus, 4-nitro-*o*-phenylenediamine gives (33) predominantly the 10-nitro derivative. The isomer mixture of 10-nitro- and 11-nitro- I shows (10) λ max 375s and

TABLE II
Dyeing and Fastness Properties of Substituted I

Substituent	(a) Polyester		Dyebath Exhaustion	Colour of Dyeing	(b) Polyamide		
					Light Fastness		
H	(a)		5,5,3	greenish-yellow	7,	6-7,	6-7
	(b)		5,4,2	pale greenish-yellow	4-5,	4,	4
1-NO ₂	(a)		4,3,1	yellow	5-6,	4-5,	4-5
	(b)		4,2,2	pale yellow	1,	1,	1
2-NO ₂	(a)		5,3,2	greenish-yellow	5-6,	5-6,	5-6
	(b)		4,2,1	pale yellow-brown	1,	1,	1
3-NO ₂	(a)		5,3,2	reddish-yellow	3,	3,	3
	(b)		4,3,2	dull pink	2,	2,	2
4-NO ₂	(a)		5,3,1	orange-yellow	4,	5,	6
	(b)		4,3,2	dull yellow	2,	2,	2
5-NO ₂	(a)		4,3,1	greenish-yellow	7,	7,	7
	(b)		4,3,2	dull brown-yellow	1,	1,	1
6-NO ₂	(a)		4,3,1	yellow	5-6,	6-7,	7
	(b)		4,3,2	dull yellow	1,	1,	2
1-NO ₂ & 6-NO ₂ *	(a)		5,3,2	yellow	5-6,	6,	6-7
	(b)		5,3,2	dull yellow	1,	1,	2
2-NO ₂ & 5-NO ₂ *	(a)		5,4,3	bright yellow	6,	5-6,	5-6
	(b)		5,3,2	yellowish-brown	2,	2,	2
3-NO ₂ & 4-NO ₂ *	(a)		5,4,3	reddish yellow	4,	3-4,	3-4
	(b)		5,4,2	dull yellow-brown	2-3,	2,	2
2-Br & 5-Br*	(a)		5,4,4	bright greenish yellow	6-7,	6-7,	6
3-Br & 4-Br*	(a)		5,4,4	bright greenish yellow	6-7,	6,	5-6
1-NH ₂	(a)		5,4,3	orange yellow	2-3,	2-3,	2-3
1- & 6- <i>p</i> -Tosylamino*	(a)		5,4,3	pale greenish yellow	5,	4-5,	4-5
10-NO ₂ & 11-NO ₂ *	(a)		3,1,1	pale dull yellow	7,	5-6,	5-6
	(b)		4,2,2	dull pink	3-4,	3,	3
10-OMe & 11-OMe*	(a)		5,5,4	bright yellow	7,	7,	7
	(b)		5,5,4	bright yellow	4,	4,	3
10-COOMe & 11-COOMe*	(a)		3,2,1	pale bright yellow	7,	7,	7
	(b)		5,2,1	pale greenish yellow	2,	2-3,	2-3
2,5-(NO ₂) ₂	(a)		4,3,1	yellow	5-6,	5,	4-5
XII & XIII	(a)		5,4,3	bright greenish yellow	5-6,	6,	6

*Isomer mixtures; values for dyebath exhaustion and light fastness for 0.1%, 1% and 2.5% dyeings, respectively.

385 nm, values of a similar order to those resulting from introduction of the nitro group into the naphthalene ring (Table I). From consideration of the structures in Scheme I, a nitro group in the phenyl ring will enhance the contribution of VI by a donor-acceptor effect, this being most significant for substitution at the 11 position;

this will, however, decrease the electron availability at the saturated nitrogen atom and hence decrease the contribution of structures involving this nitrogen atom, *i.e.* III and V, resulting in a relatively small overall colour change.

10-Methoxy- and 11-methoxy- I show λ_{\max} 409 and

373 nm, respectively. From Scheme I, a donor substituent at the 10-position, conjugated to the pyridino nitrogen atom, will increase the contribution of VII without affecting significantly the other resonance forms, and a significant bathochromic shift results. Presence of a donor group in the 11 position is hypsochromic, presumably by lowering the contribution of VI (on a conjugated donor-donor basis).

In general therefore, to significantly deepen the colour of I, introduction of strong donor substituents in the naphthalene ring is necessary; substitution in the phenyl ring can be bathochromic or hypsochromic, depending on the nature and orientation of the substituent.

Dyeing Behaviour.

Compound I has virtually no affinity for cellulose secondary acetate, as has been observed (36) with some derivatives of I. Dyeing tests were therefore restricted to polyester and polyamide substrates, general dyeing properties and light fastness assessments being given in Table II. Light fastness assessments were made by standard methods (37); data in Table II referring to dyebath exhaustion is an empirical assessment of the residual dye liquor, *viz.*, 5, excellent exhaustion, graded to 1, very poor exhaustion.

On polyester fibres, I gave fluorescent greenish-yellow shades of moderate build-up. The nitro derivatives of I containing the nitro group in the naphthalene ring gave yellow shades, all redder in hue than I and showing good clarity of shade; the dull yellow-brown shades previously reported (36) were not obtained, these differences presumably being relatable to the purity of the dyestuffs under test.

The nitro derivatives showed distinct differences in both colour and build-up, the latter factor showing the order $1\text{-NO}_2 \equiv 2\text{-NO}_2 < 5\text{-NO}_2 < 6\text{-NO}_2 < 3\text{-NO}_2 \equiv 4\text{-NO}_2$; both the 3- and 4-nitro derivatives gave very good colouration of polyesters. Isomer mixtures in general tended to be superior to the individual isomers. The presence of two nitro groups, as in 2,5-dinitro- I, gave dyeings superior to either the 2-nitro- or 5-nitro derivatives.

Presence of nitro or carbomethoxy groups in the phenyl ring gave poor dyes, but the 10- and 11-methoxy- I isomer mixture and the individual isomers had excellent dyeing properties.

The halogeno isomer mixtures 2-bromo- and 5-bromo- I, and 3-bromo and 4-bromo- I both gave satisfactory intense greenish-yellow dyeings, but 1- and 6-*p*-toluenesulphonamido- I, and the isomer mixture (XII and XIII) were poor dyes. 1-Amino- I dyed well, but had poor light fastness.

Light fastness generally of dyes with halogen substituents in the naphthalene ring or methoxy in the phenyl ring was excellent and the presence of these substituents

can be considered particularly advantageous in combinations of good dyeing and fastness properties.

On polyamide fibres, dyeings were generally poor, with the exception of the 10- and 11-methoxy- I isomer mixture, although light fastness is lower than on polyesters. The nitro derivatives of I showed a tendency to degrade during dyeing, the extent of the degradation varying from 1-nitro and 4-nitro (dull yellow), through 2-nitro (yellow-brown) to 3-nitro (pink). The reduction of nitro derivatives of I to amines during the mass colouration of polyamides has been reported (36), and the effect is here observed to occur during the lower temperatures of conventional dyeing procedures. The degradation is progressive, initial stages of the dyeing process giving bright yellow dyeings with all isomers. Differences in degradation colours of the isomers is compatible with the formation of amines, *viz.*, 2-amino- I is yellow, and 3-amino- I is pink (36,38).

EXPERIMENTAL

Preparation of isomer mixtures of 1-nitro and 6-nitro, 2-nitro and 5-nitro, and 3-nitro and 4-nitro- I, and separation into individual isomers, and of 1-amino- I, 1- and 6-*p*-tosylamino- I are reported in Part I. Other dyes prepared as below; analytical data are given for new compounds only.

10- and 11-Nitro- (XIV), Carbomethoxy- (XV) and Methoxy-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (XVI).

Condensation of naphthalene-1,8-dicarboxylic anhydride with 1,2-diamino-4-nitrobenzene in glacial acetic acid, addition of the reaction liquor to dilute hydrochloric acid and extraction of unreacted naphthalene-1,8-dicarboxylic anhydride with 5% aqueous sodium hydroxide gave the isomer mixture XIV (78%), m.p. 269-290°. Similar reaction from 3,4-diaminomethylbenzoate gave XV (91%), m.p. 232-262°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_3$: C, 73.2; H, 3.7; N, 8.5. Found: C, 73.1; H, 3.8; N, 8.3.

3,4-Diaminoanisole gave XVI (73%), m.p. 158-164°, separated by thick layer plate chromatography into the higher R_f component, 10-methoxy- I, m.p. 212° (lit. (35) 210-211°), and lower R_f component, 11-methoxy- I, m.p. 197° (lit. (35) 193°).

2-Bromo- (XVII), 5-Bromo- (XVIII), 3- and 4-Bromo- (XIX), and 2,5-Dinitro-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (XX).

o-Phenylenediamine similarly condensed with 3-bromonaphthalene-1,8-dicarboxylic anhydride gave XVII and XVIII (98%), m.p. 231-237°; column chromatography on activated alumina from chlorobenzene solution, eluting with benzene-acetone 95:5, gave (higher R_f component), XVII orange needles, m.p. 296° (lit. (39) 271-272°).

Anal. Calcd. for $\text{C}_{18}\text{H}_9\text{BrN}_2\text{O}$: C, 61.9; H, 2.6; N, 8.0; Br, 22.9. Found: C, 61.8; H, 2.6; N, 7.8; Br, 22.6.

The lower R_f component (XVIII), yellow needles, gave m.p. 275° (lit. (39) 289-290°). The bromo derivatives previously described (39) were prepared from Sandmeyer reaction of amino compounds obtained by reduction of nitro- I; we have discussed characterization of nitro- I in part I.

4-Bromonaphthalene-1,8-dicarboxylic anhydride and *o*-phenyl-

enediamine similarly gave XIX (99%), m.p. 221-223°, showing no apparent isomer separation on tlc. 3,6-Dinitronaphthalene-1,8-dicarboxylic anhydride gave XX (98%), m.p. 306-307° (lit. (40) 301°).

Pyrido[2,3-*g*]-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (XII) and 4,5,2',3'-Pyrido-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (XIII).

Pyrido[2,3-*e*]acenaphthene (12 g.) (prepared (42) by the Skraup reaction on 5-aminoacenaphthene) on oxidation with chromium trioxide (41) gave pyrido[2,3-*c*]naphthalene-1,8-dicarboxylic anhydride (70%) white needles (pyridine) m.p. 324-325° (lit. (42) 317°); condensation of 1 g. with *o*-phenylenediamine (0.43 g.) by refluxing 0.5 hour in glacial acetic acid (100 ml.) gave a mixture of XII and XIII (96%), greenish-yellow needles, m.p. 250-256°.

Anal. Calcd. for C₂₁H₁₁N₃O: C, 78.5; H, 3.5; N, 13.1. Found: C, 78.7; H, 3.4; N, 13.2.

2-Anilino-1,8-*N*-phenylnaphthalimide (XXI) and 2-*p*-Anisidino-1,8-*N*-*p*-anisyl-naphthalimide (XXII).

1,8-Naphthalene dicarboxylic anhydride-2-sulphonic acid (5 g.) (prepared by oxidation of acenaphthene-3-sodium sulphonate (43) was refluxed 4 hours in aniline (50 ml.), the reaction liquor added to dilute hydrochloric acid and filtered. The brown solid was dissolved in chlorobenzene and chromatographed on activated alumina, using benzene-acetone 95:5 as eluant. The principal yellow zone gave XXI (53%), yellow prisms, m.p. 243° (chlorobenzene); ν 1695 and 1638 cm⁻¹ (C=O).

Anal. Calcd. for C₂₄H₁₆N₂O₂: C, 79.1; H, 4.4; N, 7.7. Found: C, 79.2; H, 4.5; N, 7.6.

Similar reaction using *p*-anisidine at 250° gave XXII (56%), brownish-yellow leaflets, m.p. 236° (ethanol); ν 1688 and 1639 cm⁻¹ (C=O).

Anal. Calcd. for C₂₆H₂₀N₂O₄: C, 73.6; H, 4.8; N, 6.6. Found: C, 73.4; H, 4.7; N, 6.4.

Acknowledgment.

The authors thank the Science Research Council for the award of a Research Studentship (to P. H. G.).

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