

## Heterocyclic Derivatives of Naphthalene-1,8-Dicarboxylic Anhydride. Part I. Nitro-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-ones.

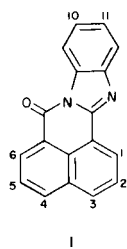
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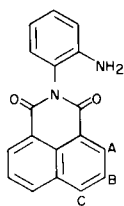
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Condensation of *o*-phenylenediamine with 2-, 3- and 4-nitronaphthalene-1,8-dicarboxylic anhydrides gives, in each case, an isomer mixture. Separation of the mixtures into the six isomeric mononitro-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-ones is described and the isomers characterised in respect of previously reported data on some isomers; ir and mass spectrum data are reported, the latter showing fragmentation ions which may be used in characterising dyes based on this chromophore. Other new derivatives of 7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one are also described.

Nitro derivatives of 7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (I) have been obtained (2) by condensation of 3- and 4-nitronaphthalene-1,8-dicarboxylic anhydrides with *o*-phenylenediamine, but no separation of the isomer mixtures described. Nitration of I occurs (3) preferentially in the 10-position, in accord with theoretical calculations (4) based on the electronic spectra of I. Unambiguous syntheses of some nitro derivatives of I in which the nitro group is in the phenyl (5) or naphthalene (6,7) ring have been described.



I



IIa: A - NHSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>p; B - C - H  
 IIb: A - NO<sub>2</sub>; B - C - H  
 IIc: B - NO<sub>2</sub>; A - C - H  
 IId: C - NO<sub>2</sub>; A = B = H

The synthesis of 2-nitronaphthalene-1,8-dicarboxylic anhydride has been recently described (8) and condensation of this, and of 3- and 4-nitronaphthalene-1,8-dicarboxylic anhydrides with *o*-phenylenediamine, gave yellow products, separated into individual isomers by recrystallization from glacial acetic acid and benzene or by preparative layer chromatography on silica gel.

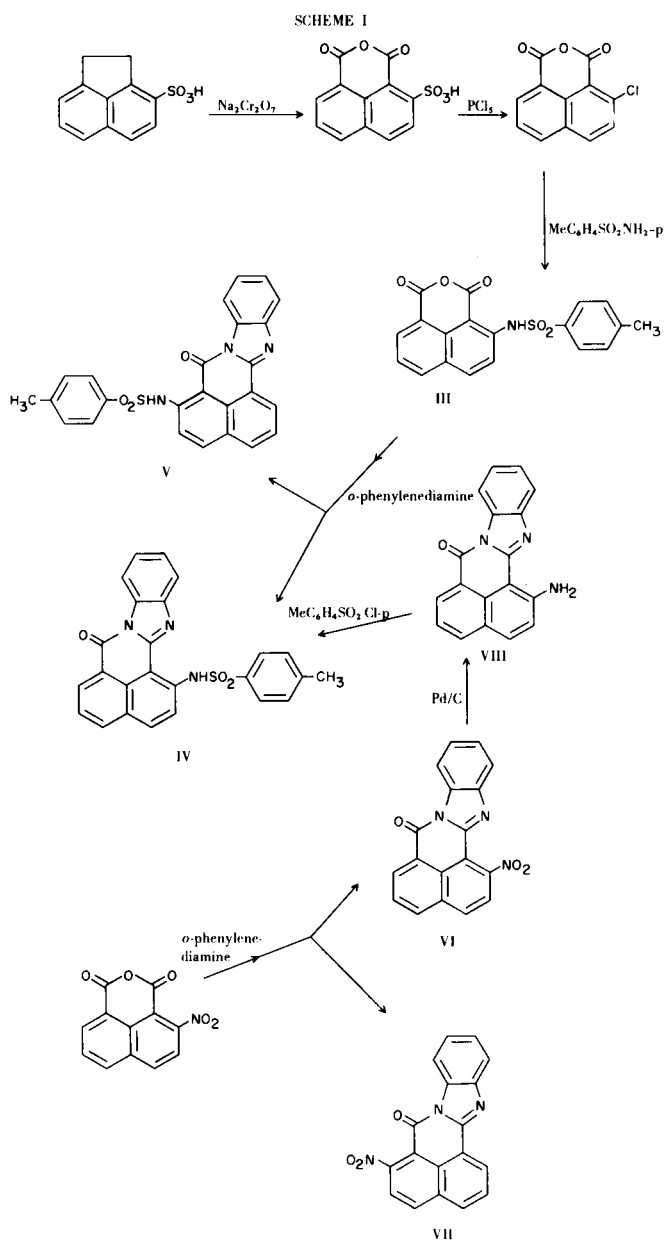
2-(*p*-Toluenesulphonamidonaphthalene)-1,8-dicarboxylic anhydride (III) (prepared from 2-chloronaphthalene-1,8-dicarboxylic anhydride and *p*-toluenesulphonamide)

condensed with *o*-phenylenediamine to give a yellow product, separated by column chromatography on alumina into a smaller fraction IV (higher R<sub>f</sub> on tlc) and a more abundant fraction V (lower R<sub>f</sub>).

The formation of I through an intermediate aminonaphthalimide stage II has been established (9,10); cyclisation of IIa will proceed preferentially through the more reactive (electron deficient) or less hindered carbonyl group. The electron donor nature of the *p*-toluenesulphonamide substituent in IIa increases the electron density on the adjacent carbonyl group, and further hinders cyclisation at this carbonyl group by possible steric effects and by hydrogen bonding. The presence of hydrogen bonding is indicated in the lower  $\nu$  (C=O) at 1655 cm<sup>-1</sup> in V compared with 1704 cm<sup>-1</sup> in IV. A similar lowering of  $\nu$  (C=O) occurs in III (1759 and 1690 cm<sup>-1</sup>) compared to naphthalene-1,8-dicarboxylic anhydride (1771 and 1741 cm<sup>-1</sup>) and 2-nitronaphthalene-1,8-dicarboxylic anhydride (1781 and 1748 cm<sup>-1</sup>). Compound I shows  $\nu$  (C=O) at 1694 cm<sup>-1</sup> and a wide range of substituted I show (11)  $\nu$  (C=O) in the region 1684-1715 cm<sup>-1</sup>, with the exception of 2-substituted derivatives in which hydrogen bonding can occur, e.g. V and VIII.

Further evidence supporting the structural assignments above is found in the electronic spectra (in glacial acetic acid) of V ( $\lambda$  max 413, 436 nm) and IV ( $\lambda$  max 405, 426 nm), the bathochromic shift in V being in accord with that expected on the basis of ortho electron acceptor-donor substitution.

Condensation of 2-nitronaphthalene-1,8-dicarboxylic anhydride and *o*-phenylenediamine, and separation of the higher R<sub>f</sub> isomer from the resulting product, gave a nitro



derivative of I, which, on reduction to the amine and condensation with *p*-toluenesulphonylchloride, gave a product identical with IV. The higher  $R_f$  nitro isomer is thus established as 1-nitro-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (VI), and the other isomer (lower  $R_f$ ) must be the 6-nitro derivative (VII). The amine resulting from reduction of VI is similarly confirmed as 1-amino-7*H*-benzimidazo[2,1-*a*]benz[*de*]isoquinolin-7-one (VIII).

By analogy, condensation of *o*-phenylenediamine and 3-nitronaphthalene-1,8-dicarboxylic anhydride gave the 2-nitro (higher  $R_f$  component) and 5-nitro (lower  $R_f$ ) isomers, and 4-nitronaphthalene-1,8-dicarboxylic anhydride gave the 3-nitro (higher  $R_f$  component) and 4-nitro (lower  $R_f$ ) isomers.

Compounds VI and VII have not been previously described and earlier reported data (3,6,7) for the 2-nitro, 3-nitro and 5-nitro isomers is not consistent.

The lower  $R_f$  value of VII compared to VI indicates the higher polarity of VII. On the basis of substitution in I in the naphthalene ring containing the carbonyl group giving the more polar isomer, the  $R_f$  values of isomer pairs resulting from each condensation (Table I) assist in characterisation of the isomer. The relative polarity of isomer pairs, *viz.*, VII > VI; 5-nitro > 2-nitro; 4-nitro > 3-nitro is further indicated by electronic spectra data (12) and additional evidence supporting the characterisation of isomers as reported here results from isomer ratios formed in each condensation. During the condensation of *o*-phenylenediamine with the mononitronaphthalene-1,8-dicarboxylic anhydrides, the intermediate naphthalimides (IIb) (IIc) and (IId) will cyclise preferentially at the more electron deficient carbonyl group, *viz.*, that attached to the nitrated ring. Ratios of isomers formed in each condensation (see Experimental) were found to be in this anticipated order, *viz.*, VI > VII, 2-nitro > 5-nitro and 3-nitro > 4-nitro.

Previous syntheses of the 2-nitro- and 5-nitro isomers by fractional crystallisation of the condensate of *o*-

TABLE I

 $R_f$  Values of Nitro Derivatives of I

	Benzene	Benzene:acetone (95:5)	Benzene:acetone (75:25)	Toluene:ethyl acetate (75:25)
1 - NO <sub>2</sub>	0.38	0.48	0.75	0.66
2 - NO <sub>2</sub>	0.20	0.46	0.74	0.64
3 - NO <sub>2</sub>	0.19	0.44	0.72	0.54
4 - NO <sub>2</sub>	0.18	0.40	0.69	0.49
5 - NO <sub>2</sub>	0.08	0.22	0.59	0.31
6 - NO <sub>2</sub>	0.07	0.20	0.56	0.28

TABLE II  
Mass Spectra Data of Nitro Derivatives of I

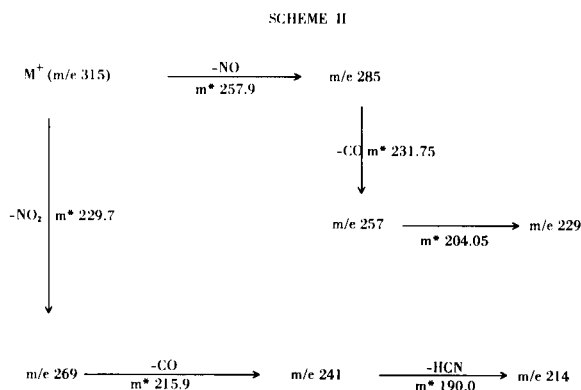
m/e	Relative abundance							Molecular constitution
	1-NO <sub>2</sub>	2-NO <sub>2</sub>	3-NO <sub>2</sub>	4-NO <sub>2</sub>	5-NO <sub>2</sub>	6-NO <sub>2</sub>		
315 (P <sup>+</sup> )	100	100	100	100	100	100	C <sub>18</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>	
285 (P-NO)	18.8	4.6	23.6	10.7	5.8	11.7	C <sub>18</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>	
269 (P-NO <sub>2</sub> )	35.3	55.9	27.2	34.2	47.4	18.5	C <sub>18</sub> H <sub>9</sub> N <sub>2</sub> O	
275 (P-NO, CO)	22.0	8.1	11.3	15.1	5.8	12.8	C <sub>17</sub> H <sub>9</sub> N <sub>2</sub> O	
241 (P-NO <sub>2</sub> , CO)	19.6	17.5	11.9	26.7	34.7	44.3	C <sub>17</sub> H <sub>9</sub> N <sub>2</sub>	
214	10.2	11.4	8.9	8.0	11.0	10.6	C <sub>16</sub> H <sub>8</sub> N	
151	3.1	2.5	3.0	3.6	5.8	2.9	C <sub>11</sub> H <sub>5</sub> N	

phenylenediamine and 3-nitronaphthalene-1,8-dicarboxylic anhydride (3) or by indirect synthesis from nitro derivatives of 8-bromo-1-naphthoic acid (6,7) report m.p. considerably lower (3) than in this current work, indicating incomplete separation, or agreement with this present work in the case of the 5-nitro isomer only (6,7). Earlier condensations of 4-nitronaphthalene-1,8-dicarboxylic anhydride with *o*-phenylenediamine gave (3) only the 3-nitro isomer, m.p. in agreement with this current work. Other indirect syntheses (6,7) also report a 3-nitro-derivative of lower m.p.

On the basis of the above data on tlc, electronic spectra, polarity and isomer ratios, orientation of the isomers as described in this present investigation is substantiated.

The high stability of I is reflected in its mass spectrum, the molecular ion (base peak) being considerably more abundant than the principal fragment ions resulting from initial loss of CO (m/e 242, C<sub>17</sub>H<sub>10</sub>N<sub>2</sub>, 7% relative abundance), followed by loss of HCN (m/e 215, C<sub>16</sub>H<sub>9</sub>N, 5% relative abundance). Further fragmentation involves formation of low intensity ions at m/e 152 (C<sub>11</sub>H<sub>6</sub>N) and m/e 126 (C<sub>10</sub>H<sub>6</sub>). This fragmentation pattern has been found (11) to be characteristic of a wide range of substituted I; fragment ions, usually of low abundance, occur at m/e 269, 241, 214, 152 and 126 for I substituted in the phenyl ring and at m/e 269, 241, 214, 151 and 125 for I substituted in the naphthalene ring. The presence of these ions can thus be used in identification of dyes based on this chromophore.

The nitro derivatives of I fragment as above, "metastable peaks" confirming loss of CO after partial or complete loss of the nitro group (Scheme II). Relative abundance of the fragment ions are shown in Table II.



The daughter ion at m/e 229, arising from fragmentation of the ion at m/e 257 is present in very low relative abundance, although "metastable peaks" at m\* 204.05 are apparent in the spectrum of most isomers.

#### EXPERIMENTAL

Melting points are uncorrected. Microanalyses were performed by Research Laboratorium Dr. C. Janssen, Beerse, Belgium. Mass spectra were run, using a direct insertion probe, on an AEI MS-902 instrument (source 250° C; 70 eV ionising energy; 100 μ A emission); high resolution measurements were within 5 ppm; using perfluoro-tri-*n*-butylamine as reference.

1-Nitro- (VI) and 6-Nitro-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (VII).

2-Nitronaphthalene-1,8-dicarboxylic anhydride (5 g.), prepared as previously described (8), and *o*-phenylenediamine (2.2 g.) were refluxed in glacial acetic acid (250 ml.) for 30 minutes and the cooled liquor filtered to give deep yellow needles, m.p. 280-290° (88%); mother liquors, on adding to water, gave a further 10%, m.p. 250-270°. Recrystallizations from glacial acid gave a fraction containing predominantly a higher R<sub>f</sub> com-

ponent, the mother liquors containing mainly a lower  $R_f$  component. Further purification of each fraction by thick layer plate chromatography (applied from acetone solution to 2 mm. thick plates of Kieselgel 60 PF<sub>254</sub> + 364, Merck; eluted with benzene-acetone 95:5), afforded VI (higher  $R_f$ ) yellow plates, m.p. 298-299°; ir 1711  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_3$ : C, 68.6; H, 2.9; N, 13.3. Found: C, 68.7; H, 2.9; N, 13.2.

Compound VII (lower  $R_f$ ) orange-yellow needles gave m.p. 295-296°; ir 1694 and 1707  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_3$ : C, 68.6; H, 2.9; N, 13.3. Found: C, 68.5; H, 2.9; N, 13.2.

5-Nitro- (IX) and 2-Nitro-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (X).

3-Nitronaphthalene-1,8-dicarboxylic anhydride, reacted as above, gave orange needles, m.p. 264-290° (96%), and a further 4%, m.p. 266-272° from the mother liquors. Separation as above gave, as higher  $R_f$  component X, orange needles, m.p. 312-313° (lit. (3) 271°; (7) 292-294°); 1705  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_3$ : C, 68.6; H, 2.9; N, 13.3. Found: C, 68.3; H, 2.9; N, 13.5.

Lower  $R_f$  component was IX yellow needles, m.p. 302° (lit. (3) 242°; (7) 300-302°); ir 1708  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_3$ : C, 68.6; H, 2.9; N, 13.3. Found: C, 68.45; H, 2.9; N, 13.5.

3-Nitro- (XI) and 4-Nitro-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (XII).

4-Nitronaphthalene-1,8-dicarboxylic anhydride similarly gave orange needles, m.p. 248-266° (72%) and a further 28%, m.p. 210-224° from the mother liquors. From this were separated XI, orange-yellow needles, m.p. 294° (lit. (3) 295°; (7) 259-260°); ir 1707  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_3$ : C, 68.6; H, 2.9; N, 13.3. Found: C, 68.9; H, 2.9; N, 13.5.

The lower  $R_f$  component, (XII) red plates, gave m.p. 268° (lit. (7) 285-286°); ir 1696  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_9\text{N}_3\text{O}_3$ : C, 68.6; H, 2.9; N, 13.3. Found: C, 68.5; H, 2.8; N, 13.5.

Isomer distribution in each mixture was determined by the combined thin layer chromatography and spectroscopic analysis based on that described (13) for analysis of nitroanthraquinone-1-sulphonic acids. The ratios obtained were: VI, 55.3% and VII, 44.7%; X, 63.8% and IX 36.2; XI 52.2% and XII 57.8%.

2-*p*-Toluenesulphonamidonaphthalene-1,8-dicarboxylic Anhydride (III).

Sulphonation (14) of acenaphthene (100 g.) at 100° gave 54% acenaphthene-3-sulphonic acid; unsulphonated acenaphthene (12.9 g.) was recovered, also 3,3'-diacenaphthylsulphone (1.8 g.) m.p. 248° (ethanol) (lit. (15), 230-232°); ir 1135  $\text{cm}^{-1}$  (SO<sub>2</sub>).

Dichromate oxidation of acenaphthene-3-sulphonic acid gave naphthalene-1,8-dicarboxylic anhydride-2-sulphonic acid (68%), which on fusion with phosphorus pentachloride gave 2-chloronaphthalene-1,8-dicarboxylic anhydride, m.p. 244° (acetic acid) (lit. (14) 246-247°). 2-Chloronaphthalene-1,8-dicarboxylic anhydride (2 g.) refluxed 12 hours in diethyleneglycol dimethyl ether (200 ml.) with *p*-toluenesulphonamide (4 g.) in the presence of cupric acetate (0.2 g.) and copper powder (0.1 g.), gave, on addition to water, greenish grey III, m.p. 248° (ethanol); ir 1759 and 1690  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{13}\text{NO}_5\text{S}$ : C, 62.1; H, 3.6; N, 3.8; S, 8.7. Found: C, 62.1; H, 2.5; N, 3.7; S, 8.5.

1-*p*-Toluenesulphonamido- (IV) and 6-*p*-Toluenesulphonamido-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (V).

Compound III (1 g.) refluxed 30 minutes in glacial acetic acid (50 ml.) with *o*-phenylenediamine (0.3 g.) and addition of the liquor to water, gave a yellow solid (88%), m.p. 234-245°. Column chromatography (of 0.5 g.) from monochlorobenzene solution on activated alumina (Laporte, Type H, 100/200 mesh), eluting with benzene-acetone 95:5 gave two yellow zones. A higher  $R_f$  zone (eluted) gave 0.03 g. of greenish-yellow needles of IV, m.p. 246° (benzene); ir 1704  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$ : C, 68.3; H, 3.9; N, 9.6; S, 7.3. Found: C, 68.0; H, 3.8; N, 9.7; S, 7.7.

A lower  $R_f$  zone, on extraction with ethanol, gave 0.4 g. of greenish-yellow needles of V, m.p. 309-310° (benzene); ir 1655  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$ : C, 68.3; H, 3.9; N, 9.6; S, 7.3. Found: C, 68.1; H, 3.9; N, 9.8; S, 7.4.

1-Amino-7*H*-benzimidazo[2,1-*a*]benz[*d,e*]isoquinolin-7-one (VIII); and Conversion to IV.

A solution of VI (0.6 g.) in pyridine (25 ml.) at 50° was treated with 10% palladium on charcoal (10 mgm.) and hydrazine hydrate (0.25 ml.) in pyridine (2.5 ml.) added dropwise over 30 minutes. After heating 30 minutes, the liquor was filtered hot, evaporated to dryness *in vacuo* and chromatographed on monochlorobenzene solution on activated alumina as above, using benzene-acetone 95:5 as initial eluant and benzene-acetone 75:25 as final eluant. A lower yellow band yielded 0.39 g. orange-needles, m.p. 219°, showing no  $\nu$  (NH) on ir and P<sup>+</sup> at *m/e* 340 on mass spectrum; a central yellow zone yielded 0.038 g. I and an upper orange-yellow zone gave 0.23 g. orange needles, m.p. 296-297° (ethanol) of VIII; ir 1671 (C=O), 3425 and 3385  $\text{cm}^{-1}$  (NH).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}$ : C, 75.9; H, 3.9; N, 14.7. Found: C, 75.7; H, 3.9; N, 14.7.

This amine (0.3 g.) was refluxed 3 hours with *p*-toluenesulphonylchloride (0.3 g.) in pyridine (10 ml.), the liquor taken to dryness *in vacuo* and the residue purified by column chromatography on activated alumina to give IV, m.p. 247°, identical with the product prepared as described above.

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