SHORT PAPER

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Fluorescent compounds from reactions of nitrobenzimidazylbenzisoquinolines from 4-nitronaphthalic anhydride with alkylamines

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The nitro group in the isomeric condensation products of 4-nitronaphthalic-1,8-anhydride with 1,2-diaminobenzene namely 3-nitro and 4-nitro-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one is displaced by reaction with 1-octylamine, to give in the case of the 4-nitro compound the highly fluorescent 4-octylamino derivative. The condensation product from 4,5-dinitronaphthalic-1,8-anhydride and 1,2-diaminobenzene afforded, by nitro group displacement with either 1-butylamine or 1-octylamine, complex mixtures without exhibiting significant fluorescence.

Keywords: fluorescent compounds, nitrobenzimidazylbenzisoquinolines, alkylamines

The fluorescent derivatives based on the naphthylimides remain a prominent group of compounds with a wide variety of applications in the diverse fields of technical, electronic and medicinal chemistry as for example in crack detection in metal and ceramic structures,[1,2] for laser activity,[3] in luminescent devices,[4] in cancer studies[5] and in antiviral applications.[6] The synthesis of such derivatives from nitronaphthalic-1,8- and halogenonaphthalic-1,8-anhydrides has been described[7,8] and their fluorescent and spectral properties examined.[9]

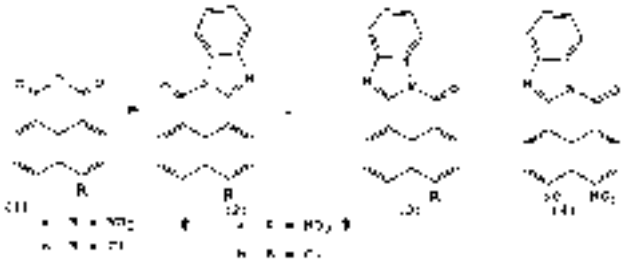
A strategy in the synthesis of highly fluorescent naphthylimide derivatives can be based on using a 4-alkylamino electronic 'pushing' group and an N-alkyl (CON(R)CO moiety) or conjugated aryl 'pulling' group This approach is in fact favoured by the practical fact that aryl substitution at the 4-position is difficult but straightforward at the anhydride group in naphthalic anhydride. Thus 4-nitronaphthalic-N-phenyl-1,8-imide is formed readily with aniline nearly quantitatively at little more than ambient temperature whereas 4-phenylaminonaphthalic-1,8-imide is unknown and the N-methyl analogue was obtained[10] only in very low yield with a vast molar excess of aniline or in only moderate yield with sodioaniline at elevated temperature.

It was of interest to examine the effect of extending the conjugated system at the imide N atom to increase the 'pulling' or 'electronic 'sink' by also involving one of the adjacent C=O groups of the imide system and to complete the 'pushing' effect by introducing the usual 4-alkylamino group.

In other directed work extended conjugated systems have been derived from 4-nitronaphthalic-1,8-anhydride by reaction with 1,2-diaminobenzene.[11] In the present application similar structures have been synthesised and the nitro group in the condensation products has then been displaced by reaction with alkylamines.

4-Nitronaphthalic-1,8-anhydride (**1a**) condensed with 1,2-diaminobenzene to afford a mixture of the isomers, 3-nitro-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one (**2a**) and the 4-nitro analogue (**3a**) (Scheme 1). In a similar way 4,5-dinitronaphthalic-1,8-anhydride afforded the 3,4-dinitro- analogue, 3,4-dinitro-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one (**4**). 4-Nitro-7H-benzimidazo[2.1-a]benz[de]isoquinolin-7-one (**3**) reacted with 1-octylamine to give the 4-octylamino analogue (**6**) by nitro group displacement (Scheme 1).

The 3-nitro isomer appeared to give predominantly under the same conditions a coloured product which may be related



Scheme 1

to a Meisenheimer adduct, and only a minor proportion of an octylamino compound (**5**) by nitro group displacement. This, however, was not characterised although fluorescent components were present.

With the 4-nitro compound (**3**) the intermediate Meisenheimer transition states (Fig.1) (**7**), (**8**) and (**9**) appear to possess more stability through benzenoid, enolic or carbanion contributions compared to those from the 3-nitro isomer (**2**), shown in Fig. 2, namely (**10**), (**11**) and (**12**).

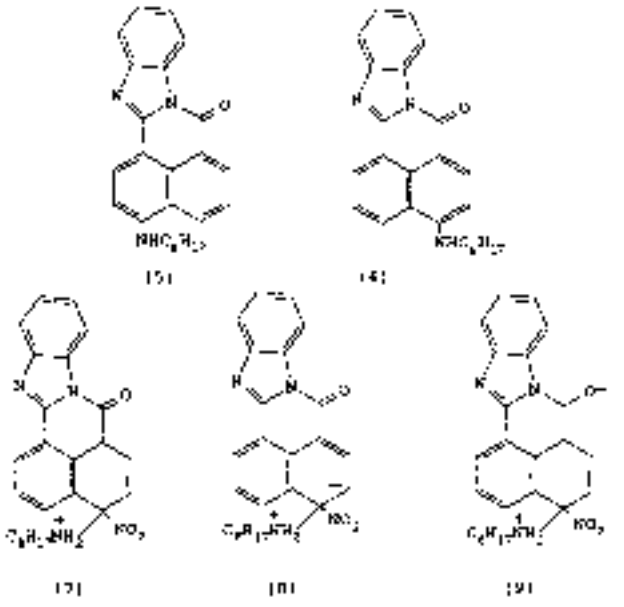


Figure 1

* To receive any correspondence.

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

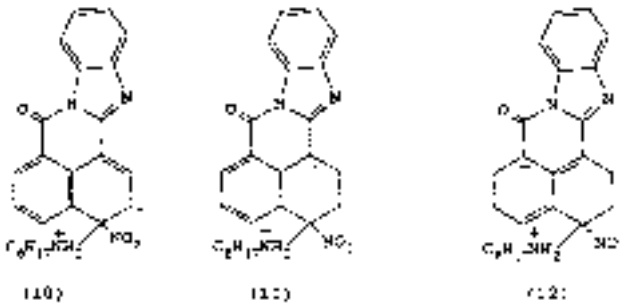


Figure 2

3,4-Dinitro-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one (4) with either 1-octylamine or 1-butylamine afforded complex mixtures.

Work is continuing on the reaction of 1,2-diaminobenzene with 4-chloronaphthalic anhydride (1b) to synthesise the 4-chloro- and 3-chloro- analogues of (3b) and (2b) respectively and to examine their nucleophilic reactions with alkylamines in N-methylpyrrolidinone by analogy with those of 4-chloronaphthalic anhydride.[8b]

No reaction of 1,2-diaminobenzene with the 4-nitro group in 4-nitronaphthalic anhydride was observed and likewise 4-nitronaphthalic anhydride only underwent reaction at the anhydride group with 4-methoxyaniline to afford simply the N-aryl product. 2,4-Dimethoxyaniline did not yield a characterisable product.

The fluorescence[9] of the octylamino derivative (**6**) indicates near comparability with that of FBYR with quantum yields of 0.72 and 0.81 respectively. It is unfortunate that it did not prove possible to obtain compound (**5**) in a pure state although it clearly possessed distinct intense fluorescence in the crude state. By contrast the supposed 4,5-dibutylamino product from (**4**) even in the crude state was devoid of fluorescence possibly attributable to steric interaction at the 4- and 5-positions resulting in loss of coplanarity.

Experimental

Spectroscopic determinations, chromatography and characterisations were effected as described.[7a] 4-Nitronaphthalic anhydride was obtained from the oxidation of 5-nitroacenaphthene as decribed.[7a]

Preparation and reactions of nitro-7H-benzimidazo [2,1-a] benz[de]isoquinolin-7-ones.

3-Nitro (**2**) *and 4-nitro-7H-benzimidazo[2,1,-a]benz[de]isoquinolin-7-one* (**3**): The conditions described[11] were slightly modified.

To 4-nitronaphthalic-1,8-anhydride (2.0g, 0.0082mol) in hot glacial acetic acid (60cm^3) 1,2-diaminobenzene (1.20g, 0.0112mol) in acetic acid (10cm^3) was added and the mixture was refluxed for 30min and then allowed to cool. An orange solid was precipitated and filtered (2.3g) m.p. 245–260°C which TLC indicated contained two isomers, the less polar of which gave a yellow band and the more polar 3-nitro isomer **(2)** an orange band; Found: C, 68.47; H, 2.89; N, 13.23. Cald. for $C_{18}H_{90}N_3O_3$, C, 68.57; H, 2.86;N, 13.33%; the isomers were separated by fractional crystallisation from toluene and the more polar compound obtained as red orange needles in two fractions totalling (0.57g), m.p. 250–251°C, (lit[11] 268°C); δ_H (TFA), 7.72–7.79 (3H, m, 5′-H, 6′-H,7′-H), 7.95–8.22 (1H, dd, 6-H), 8.35–8.48 (1H, d, 3–H), 8.54–8.74 (1H, m, 4′–H), 8.84–9.07 (3H, m, 2-H, 5-H, 7-H); υ_{max} (KBr cm^{-1}), 3100–3025 (ArCH bend), 1690 (C=O), 1540–1515, 1380-1310, (NO_2), 1230 (C–N), 850, 770, 760, 740 (ArCH bend).

The less polar, 4-nitro isomer **(3)** gave a yellow orange solid in two fractions (0.44g) m.p. 291–293°C (lit.[16] 295°C), and (0.42g); δ_H (TFA), 7.76–7.82 (3H, d, 5′–H, 6′–H, 7′–H, *J*, 3.6Hz), 7.96–8.22 (1H, dd, 6-H), 8.41-8.51 (1H, d, 3-H, *J* 6.0Hz), 8.61–8.78 (1H, m, 4′-H), 8.88–8.94 (1H, m, 5-H), 8.98–9.11(2H, m, 2-H,7-H).

4-n-Octylamino-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one (**6**): 4-Nitro-7H-benzimidazo[2,1-a]benz[de]isoquiinolin-7-one (0.5g, 0.00158mol) containing traces of the 3-nitro compound, and 1-octylamine (1.0g, 0.0077mol) in DMF (25cm^3) were warmed at 120°C for 3h. Then, after removal of the solvent from the cooled mixture *in vacuo* the residue was prep TLC separated to give a minor upper crimson band and a lower major yellow-green fluorescent band from which orange-brown needles were recovered, (0.10g) m.p. 153.5–154°C; Found: C, 78.57;H, 6.97; N, 10.63. Reqd. for $C_{26}H_{27}N_3O$, C, 78.59; H, 6.86;N, 10.58%; δ_H ($CDCl_3$), 0.79–0.98 (3H, m, Me), 1.09–1.78 [12H, m, $(CH_2)_6$], 3.0-3.30 (2H, m, CH_2NH), 4.98–5.21 (1H, s,br. exch .HN)., 6.40-6.57 (1H, d, 3-H, *J* 10.2Hz), 7.23–7.85 (5H, m, 6-H, 4′-H,5′-H,6′-H,7′-H), 8.28–8.68 (3H, m, 2-H,5-H,7-H); υ_{max} (KBr cm^{-1}), 3450–3400 (NH), 3050 (ArCH), 2860, 2950 (Me), 2925 (CH_2), 1680 (C=O), 1590 (C=C), 1380–1340 (CH bend), 1240, 1140, 760 (ArCH bend).

Reaction of 3-nitro-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one with 1-octylamine attempted preparation of (**5**): The 3-nitro isomer contaminated with a little of the 4-nitro compound in DMF (25cm^3) was reacted with 1-octylamine (1.0g, 0.0074mol) at 120°C for 3h after which the solvent was removed *in vacuo.* The residue was prep TLC separated to give a major crimson band with an orange fluorescence, a band corresponding to the starting material, a dark brown baseline band and a yellow green fluorescent band (R_f 0.11) From the crimson band an orange solid was isolated which seems most probably to be related to a Meisenheimer salt, (0.08g) m.p. 237–239°C; Found: C, 70.02;H, 5.22; N, 12.70. Reqd. for $C_{26}H_{28}N_4O_3$ C, 70.27;H, 6.31; N, 12.61%; δ_H (TFA), 0.80–1.02 (3H, m, Me), 1.32–1.58 (12H, m, $6CH_2$) 4.82–5.11 (2H, m, CH_2NH), 8.51–8.78 (3H, m,), 8.81–8.98 (1H, m,), 9.44–9.64 (1H, m,), 9.83–9.97 (2H,d, *J*,8.4 Hz), 10.56 (1H, s,); υ_{max} (KBr cm^{-1}) 3180–3150 (ArCH), 2960, 2860 (Me), 2925 (CH_2), 1680 (C=O), 1610 (C=C), 1540,1320 (NO_2), 14501350 (CH bend), 1200, 120 (C–N), 765,750 (ArCH bend).

3,4-Dinitro-7H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one (**4**): 4,5-Dinitronaphthalic anhydride was prepared[12] from 4-nitronaphthalic anhydride by nitration in nitric and sulphuric acids.

To 4,5-dinitronaphthalic-1,8-anhydride (0.50g, 0.00174 mol) in hot acetic acid (15cm^3), a solution of 1,2-diaminobenzene (0.30g, 0.0028mol) in acetic acid (15cm^3) was added and the mixture was refluxed for 30min. Upon cooling bronze needles (0.35g, 56%) m.p.>360°C were recovered; Found: C, 59.75; H, 2.29; N, 15.35. Cald. for $C_{18}H_8N_4O_5$ C, 60.00; H, 2.22; N, 15.56%; δ_H (TFA) 8.85–8.88 (3H, m, 3′-H,4′-H,5′-H), 9.54–9.74 (1H, m, 2-H), 9.90–9.90 (1H, m, 5-H), 10.03–10.26 (1H, m, 6′-H), 10.63–10.96 (1H, m, 1-H), 11.06–11.29 (1H, m, 6-H); υ_{max}(KBr, cm^{-1}) 3125 (ArCH) 1710 (C=O), 1550–1535 (NO_2), 1360–1320 (C=C, NO_2), 1230 (C–N), 860, 810, 780, 760 745 (ArCH bend).

Attempted reaction of (**4**) *with alkylamines:* **(4)** (0.1g, 0.00028mol) in DMF (10cm^3) containing 1-octylamine (0.25g, 0.00193mol) was stirred at 120°C during which considerable blackening occurred and TLC after 0.5h indicated that a very complex mixture had formed with a large amount of dark polar material present. Separation was not attempted. Reaction with 1-butylamine at a range of temperatures gave similar rersults.

4-Nitro-N-4-methoxyphenylnaphthalic-1,8-imide: 4-Nitronaphthalic-1,8-imide (0.5g, 0.0021mol) and 4-methoxyaniline (0.5g, 0.0041mol) were dissolved in DMF (40cm^3) and the mixture stirred at 120°C under nitrogen for 3 h. After removal of DMF *in vacuo* the cooled mixture was stirred with warm dilute hydrochloric acid and the residual solid filtered and preparatively TLC separated to give an upper crimson band (0.074g) m.p. 237–140°C (lit.[13] 246–247°C); Found: C, 64.38; H, 4.02; N, 7.92; Calc. for $C_{19}H_{12}N_2O_5$, 65.51; H, 3.45; N, 8.04%. A lower non-fluorescent orange band was recovered as a red-brown solid, m.p. 161–164°C.

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