SHORT PAPER

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Reactions of isomeric dinitronaphthalic-1,8-anhydrides with alkylamines

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In the reaction products of 4,5-dinitronaphthalic-1,8-anhydride and of the 3,6-dinitro analogue with 1-butylamine only nitro groups in the former compound undergo reaction. 2,5-Dinitronaphthalic anhydride reacted partially. 4,5-Dibutylaminonaphthalic-N-butyl-1,8-imide was moderately fluorescent by comparison with 4-butylamino-N-butyl-1,8-imide, (FBYR). The ease of nucleophilic replacement of the nitro group in mononitro substituted rings increases with ring size and appears to be related to the stability of a Meisenheimer intermediate.

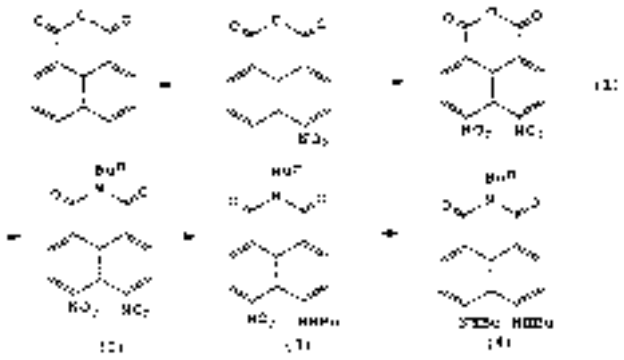
Keywords: isomeric dinitronapthalic-1-8-anhydrides, alkylamines

In the previous paper the influence of extending the conjugated system at the imide N atom to increase the 'pulling' effect by increasing the aromatic conjugation has been described in the exploration of the relationship between structure and fluorescence .

The present work had the objective of potentially increasing the 'pushing' effect further compared with the monobutylamino substituent in FBYR. Thus a number of isomeric dinitronaphthalic-1,8-anhydrides have been prepared so as to then obtain their dialkylamino analogues by nucleophilic displacement.

Firstly, the reactions of 3,6-dinitro,[10] 4,5-dinitro-[11] and the previously unknown 2,5-dinitronaphthalic-1,8-anhydrides with 1-butylamine were examined.

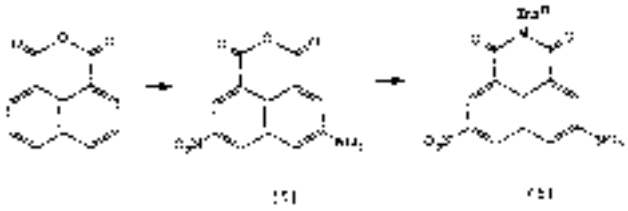
4,5-Dinitronaphthalic-1,8-anhydride (**1**) obtained by the nitration of 4-nitronaphthalic anhydride reacted at 0°C with 1-butylamine to give solely 4,5-dinitronaphthalic-1,8-*N*-butylimide (**2**) while at ambient temperature with an excess of 1-butylamine a mixture of 4-nitro-5-butylaminonaphthalic-1,8-*N*-butylimide (**3**) and 4,5-dibutylaminonaphthalic-1,8-*N*-butyl-imide (**4**) resulted as shown (Scheme 1).



Scheme 1

3,6-Dinitronaphthalic-1,8-anhydride (**5**) reacted as expected with 1-butylamine to give only 3,6-dinitronaphthalic-1,8-*N*-butylimide (**6**) (Scheme 2).

The preparation of 2,5-dinitronaphthalic-1,8-anhydride (**9**) was attempted by the oxidation of 3,6-dinitroacenaphthene (**7**) but was found to result in mainly the formation of 3,6-dinitroacenaphen-2-one (**8**) and the required anhydride (**9**) was a minor product (Scheme 3). Nevertheless, with 1-butylamine a mixture of 2-nitro-5-butylaminonaphthalic-1,8-*N*-butylimide



Scheme 2

(**12**) and 2-butylamino-5-nitronaphthalic-1,8-*N*-butylimide (**11**) was obtained by way of the the N-butyl intermediate (**10**).

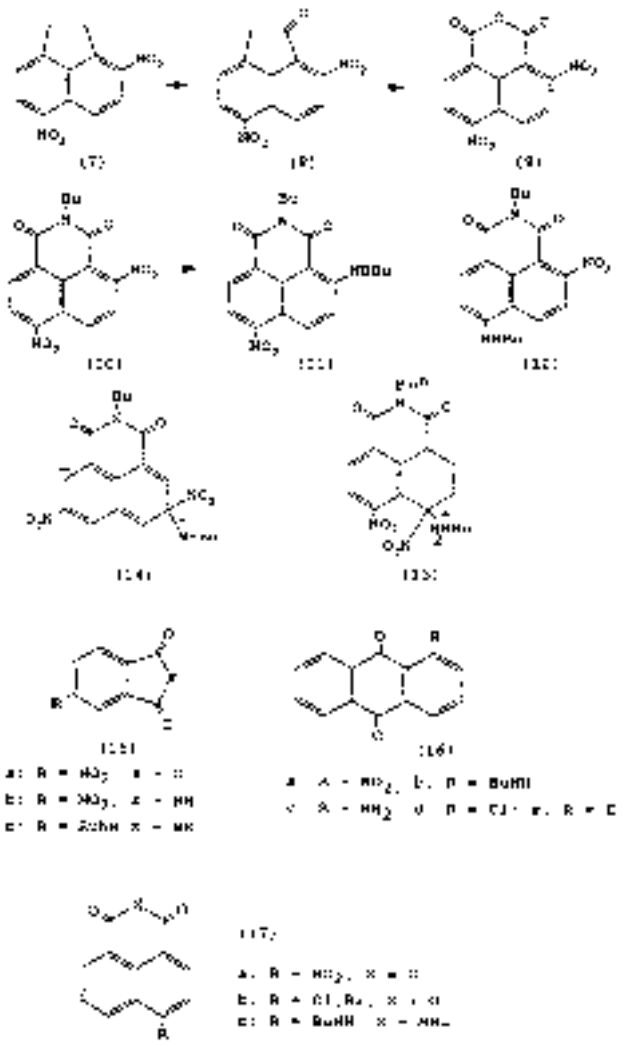
With the 4,5-dinitro compound a more stable Meisenheimer intermediate contribution containing both a benzenoid ring and an α carbanion (**13**) can result, while that from the 3,6-dinitro isomer (**14**) lacks both these structural features. In the case of 2,5-dinitronaphthalic anhydride steric hindrance may partially impede reaction towards the intermediate structure.

It was of interest to compare the nucleophilic activity of the nitro group in the aryl monocyclic, bicyclic and tricyclic compounds towards amines and the relative reactivity of phthalic anhydride (**15a**), 4-nitronaphthalic anhydride (**17a**) and 1-nitroanthraquinone (**16a**) towards 1-n-butylamine was examined. 1-Nitroanthraquinone (**16a**) under mild conditions in DMF formed mainly 1-butylaminoanthraquinone (**16b**) together with a number of other coloured products.[8] (**16b**) has also been synthesised but generally in lower yields by a variety of other methods; thus it has been obtained from 1-bromobutane and 1-aminoanthraquinone[15] (**16c**), by reductive alkylation[16] of (**16c**) with 1-butanal, from 1-chloroanthraquinone[17] (**16d**) by reaction with 1-aminobutane, by direct amination of anthraquinone (**16e**) with 1-aminobutane in the presence of rhodium (I) complexes[18] and by Ullmann reaction[19] of (**16d**) with 1-aminobutane catalysed by copper (I) salts with simultaneous formation of 1,4-bis(butylamino)anthraquinone. By contrast 4-nitronaphthalic anhydride (**17a**) under much more drastic reaction conditions underwent negligible nitro group displacement and merely formed 4-nitrophthalimide (**15b**) and only a trace of a fluorescent material believed to be 4-butylaminphthalimide (**15c**).

Nucleophilic reactivity of these three nitro derivatives appears to increase with the number of rings in the reactant. The ease of formation of (**17c**) from either (**17a**) or from (**17b**) lies between that of (**15c**) and (**16a**) and seems to be associated with the relative stability of the intermediate Meisenheimer transition state. For 4-nitrophthalic anhydride three mesomeric structures can be depicted none of which are benzenoid while by contrast, 4-nitronaphthalic anhydride N-butyl-1,8-imide or anhydride has seven contributors three of

* To receive any correspondence.

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



Scheme 3

which are benzenoid. With 2-nitroanthraquinone three of the four possible mesomers are benzenoid.

The results from the examination of the fluorescence and determination of the quantum efficiency of the compounds obtained in the present work enable some correlation to be made between structure and fluorescence in the whole series. Generally it can be concluded that in compounds with reduced coplanarity due to the steric effect of substituents at both 4- and 5-positions such as (**4**), the fluorescence intensity is diminished with respect to FBYR which is devoid of this influence. Compounds even merely substituted in the 4-position by a bulky group e.g. dimethylamino, namely 4-dimethylaminonaphthalic-N-butyl-1,8-imide, in which interaction with the 5-hydrogen atom drastically impedes coplanarity also exhibit weak fluorescence. Thus electron release is not the only factor influencing fluorescence and it would be of interest to prepare 3,6-dibutylaminonaphthalic-N-butyl-1,8-imide, a compound free of any steric interactions, by catalytic reductive amination of (**5**), and examine its fluorescence properties.

Experimental

Spectroscopic determinations, chromatography and characterisations were effected as described.[7a]

Preparation of dinitronaphthalic anhydrides.

4,5-Dinitronaphthalic anhydride (**1**): 4,5-Dinitronaphthalic anhydride was prepared[10] by the nitration of 4-nitronaphthalic anhydride in concentrated sulphuric acid with a mixture of nitric acid (d 1.5) and sulphuric acid and obtained in 36.5% yield, as pale yellow needles, m.p. 325–327°C (lit. 321°C); Found: C, 49.75;H, 1,40;N, 9.63. Calc. for $C_{12}H_4N_2O_7$, C, 50.00;H, 1.39;n, 9.72%; δ_H (DMSO-d_6) 8.91 (4H, s, 2-H,3-H, 5-H, 7-H); υ_{max} (KBr, cm^{-1}) 3120,3090, 1800,1760 (C=O), 1550 (NO_2), 1230, 1160 (C–N), 1050,880, 840, 820, 750).

3,6-Dinitronaphthalic anhydride (**5**): This compound was essentially synthesised[11] by the nitration of naphthalic anhydride dissolved in concentrated sulphuric acid with nitric acid (d 1.5) in concentrated sulphuric acid at below 40°C and obtained as cream-coloured needles in 18% yield, m.p. 214°C(lit. 214°C); Found: C, 49.98;H, 1.50;N, 9.77. Calc. for $C_{12}H_4N_2O_7$, C, 50.00;H, 1.39; n, 9.72%; δ_H (DMSO-d_6) 9.07–9.10 (2H, d, H-2, H-7, *J* 1.8z, 9.77–9.80 (2H, d, 4-H,5-H, *J* 1.8z); υ_{max} (KBr, cm^{-1}) 3080, 1790, (C=O), 1745 (C=O), 1595 C=C), 1350, 1540 (NO_2), 1160 (C-N), 1070, 1010,800,750,690.

2,5-Dinitronaphthalic anhydride.

3,6-Dintroacenaphthene (**7**): 3-Nitroacenaphthene in dichloroethane was nitrated[12] with nitric acid (d 1.36) to give after work-up 3,6-dinitroacenaphthene in 27% yield as yellow needles, m.p. 209–210°C (lit. 209–210°C); Found: C, 59.09;H, 3.41; N, 11.52. Calc. for $C_{12}H_8N_2O_4$, C, 59.02;H, 3.28;N, 11.48%; δ_H ($CDCl_3$) 8.35-8.84 (3H, m, 3-H,5-H), 7.26-7.92 (1H, m, 7-H);υ_{max} (KBr, cm^{-1}) 3100, (CH), 2940 (CH_2), 1615, 1610 (C=C), 1515, 1335 (NO_2) , 830, 800,750.

3,6-Dinitroacenaphthene-2-one (**8**): This compound has not been described and the conditions for the oxidation of 3-nitroacenaphthene[13] were used. To 3,6-dinitroacenaphthene (0.6g, 0.00245mol) in hot acetic acid (200cm^3) chromium trioxide (1.52g, 0.0152mol) in the minimum of water was added dropwise. Upon completion of the addition the mixture was refluxed for 1h, the solvent was removed *in vacuo* and the residual green paste acidified with dilute sulphuric acid to remove chromium salts which left yellow needles after filtration, washing and drying (0.60g) m.p. 177–179°C, consisting of 3,6-dinitroacenaphene-3-one; Found: C, 55.51;H, 2.84; N, 10.15; Reqd for $C_{12}H_6N_3O_5$,C, 55.80;H, 2.32; N, 10.85 %; δ_H (DMSO-d_6), 8.25–8.91 (4H, m, 4-H,5-H, 7-H,8-H), 3.78-3.93 (2H, m, CH_2); υ_{max} (KBr cm^{-1}) 3100, 2925, (C-H),1790, 1750 (C=O), 1610,1615 (C–C), 1340,1510 (NO_2), 1045, 830, 800, 750.

The experiment was repeated and the product, considered to contain 2,5-dinitronaphthalic-1,8-anhydride (9) was reacted with 1-butylamine.

Reactions of dinitronaphthalic anhydrides with 1-butylamine.

3,6-Dinitro-N-butylnaphthalic-1,8-imide (**6**): To 3,6-dinitronaphthalic anhydride (1.0g, 0.00347mol) in DMF (50cm^3) , 1-butylamine (0.8g, 0.0109mol) was added and the reaction mixture which changed in colour from orange-brown to purple was then stirred at ambient temperature for 2h when TLC showed no dinitro compound remained. After removal of solvent *in vacuo*, the residual dark red gum was crystallised (MeOH) to give a silver-grey solid (0.53g) which upon recrystallisation afforded off-white felted needles (0.40g, 33.6%), of the N-butyl imide, m.p. 224–225°C; Found: C, 56.10; H, 3.84; N, 12.33. $C_{16}H_{13}N_3O_4$ req. C, 55.98; H, 3.79; N, 12.25%; δ_H ($CDCl_3$) 0.86–1.12 (3H, m, Me), 1.39–1.85 (4H, m, $2CH_2$), 4.13–4.39 (2H, m, CH_2–$N(CO)_2$), 9.34–9.37 (2H, d, 4-H,5-H, *J*, 1.8Hz), 9.47–9.50 (2H, d, 2-H, 7-H, *J*, 1.8Hz);υ_{max} (KBr, cm^{-1}) 3090, (ArCH), 2960 (asymm. Me), 2875 (symm.Me), 1710, 1675 (C=O), 1610 (C=C), 1535, 1360 (NO_2), 1260 (C-N), 1110, 950, 820, 75, 730, 710.

4,5-Dinitro-N-butylnaphthalic-1,8-imide (**2**): Two experiments were necessary to obtain this compound and little more than the theoretical proportion of 1-butylamine was required with a reaction temperature below 0°C.

4,5-Dinitronaphthalic anhydride (0.75g, 0.0026mol) and 1-butylamine (g, 0.0052mol) in DMF (60cm^3) were stirred at –15 to 15°C for 1h when TLC showed that no dinitro compound remained. Dilution of the mixture in ice/water at 0°C gave after filtration a buff solid (0.62g) which upon crystallisation ($CHCl_3$) gave a total of 0.24g (31.6%) of buff needles, m.p. 139–141°C of the N-butylimide; Found: C, 56.18; H, 3.95; N, 11.98. $C_{16}H_{13}N_3O_6$ req. C, 55.98; H, 3.97; N, 12.25%; δ_H (DMSO-d_6) 0.83-1.09 (3H,m, Me), 1.22–1.78 (4H, m, $2CH_2$), 3.89–4.16 (2H, t, $CH_2N(CO)_2$), 8.65 (2H, s, 2-H,7-H), 8.71 (2H, s, 3-H,6-H); υ_{max} (KBr, cm^{-1}) , 3150, 3075 (ArCH), 2960, 2940 (Me,CH_2), 1710,1665 (C=O), 1545 (C=C and NO_2), 1350 (NO_2), 1230 (C–N), 870,820,750 (ArCH bend).

4-Nitro-5-butylamino-N-butylnaphthalic-1,8-imide (**3**) *and 4,5-di-n-butylamino-n-butylnaphthalic-1,8-imide* (**4**): 4,5-Dinitronaphthalic anhydride (0.50g, 0.0017mol) and 1-butylamine (0.40g, 0.0055mol) in DMF (40cm^3) were stirred at ambient temperature for 1h. After removal of the solvent TLC indicated the presence of dark polar impurities, some 4,5-dinitronaphthalic anhydride, a yellow-green fluorescent band and a least polar crimson non-fluorescent band. By prep TLC the least polar band gave red-brown needles (0.04g) m.p. 124–125°C consisting of *4-nitro-5-n-butylamino-N-butylimide*;

Found: C,64.91; H, 6.16; N, 11.15. Reqd for $C_{20}H_{23}N_3O_4$, C, 65.04;H, 6.23; N, 11.38; δ_H ($CDCl_3$), 0.83–1.16 (6H m, 2Me), 1.25–1.98 (8H, m, $4CH_2$), 3.14–3.43 (2H , m, CH_2NH), 4.03–4.26 (2H, t, $CH_2N(CO)_2$, 5.02–5.25 (1H, br.exch., NH), 6.83–6.96 (1H, d, 6-H, *J*, 7.8Hz), 7.56–7.69 (1H, d, 3-H, *J*, 7.8Hz), 8.45–8.65 (2H, m, 2-H,7-H); υ_{max} (KBr, cm^{-1}), 3150,3075, 2960 (ArCH), 2940, 2840 (CH_2), 1710,1665 (C=O), 1545, 1350 (NO_2), 1230 (C-N), 870, 820, 750 (ArCH bend).

The yellow-green fluorescent band was recovered as golden-orange needles (0.06g), m.p. 184–185°C consisting of *4,5-di-n-butylamino-N-butylnaphthalic-1,8-imide*; Found: C, 73.04; H, 10.46; N, 10.46. Reqd. for $C_{24}H_{33}N_3O_2$, C,72.91 ;H, 8.35; N, 10.66%; δ_H ($CDCl_3$) 0.78–1.19 (9H, m, 3Me), 1.29–1.88 (12H, m, $6CH_2$), 3.04–3.40 (4H, m, $2CH_2NH$), 3.99–4.22 (2H, t, $CH_2N(CO)_2$) 5.68–5.84 (2H, m, $NHCH_2$, exch.D_2O), 6.60-6.73 (2H, d, 3-H,6-H, *J* 7.8Hz), 8.25–8.38 (2H, d, 2-H, 7-H, *J* 7.8Hz); υ_{max} cm^{-1}, 3340, (NH), 2960, 2870 (Me), 2930 (CH_2), 1670, 1615 (CO), 1600 (C=C),1410,1350 (CH bend), 1090 (C–N), 800,750 (ArCH bend).

2-Nitro-5-butylamino-N-butylnaphthalic-1,8-imide(**12***) or 2-butylamino-5-nitro-N-butylnaphthalic-1,8-imide*(**11**): Crude 2,5-dintronaphthalic-1,8-anhydride (0.50g) in DMF (40cm^3) containing 1-butylamine (0.38g, 0.0052mol) was stirred at 0°C for 1h. After dilution of the mixture with water, both water and DMF were removed *in vacuo* and the dark residue was extracted with ethyl acetate. The combined extracts were concentrated and the residue prep TLC to give four bands, a polar impurity on the baseline, a minor yellow fluorescent band, a major orange fluorescent band and a colourless non-polar band. The orange band (0.03g) had m.p. 204–208°C; Found: C,63.98; H, 6.62; N,11.28. Reqd. for $C_{20}H_{23}N_3O_4$, C, 65.04; H, 6.23; N, 11.38; υ_{max} (KBr,cm^{-1}), 3450 (NH), 2880, 2970 (Me), 2940 (CH_2), 1680, 1640 (C=O), 1580 (C=C),1350, 1520, (NO_2), 1440 (CH bend), 1240, 1220)C–N), 850, 820, 750 (ArCH bend).

4-Nitrophthalimide(**15c**): 4-Nitrophthalic anhydride (0.6g, 0.00312 mol) in DMF (30 cm^3) and 1-butylamine (1.14g, 0.0156 mol) were stirred at 120°C and the progress of reaction followed by TLC which showed the presence of 4-nitronaphthalic anhydride, 4-nitrophthalimide and a small amount of a yellow-green fluorescent material. The cooled mixture and the solvent removed to give a residue was prep. TLC (dichloromethane) purified to give 4-nitrophthalic anhydride, 4-nitrophthalimide (crystallised, $CHCl_3$, to give white needles, 0.32g m.p. 99–100°, lit.[14] 95–96°; δ_H [$(CD)_2CO$], 0.73–1.09 (3H, m, Me), 1.19–1.78 (4H, m, $2CH_2$) 3.53–3.76 (2H, t, *J*8.0Hz, $CH_2N(CO)_2$), 7.92–8.05 (1H, d, *J*7.8Hz, 5-H), 8.53–8.63 (2H,m, 3-H,6-H); υ_{max} (KBr, cm^{-1}) 3025-3100 (ArCH bend), 2950 (as, C–H, Me), 2925 (CH_2), 2875 (sMe C-H), 1770,1700 (C=O), 1535 (as NO_2), 1400 (C-H,bend), 1340 (s NO_2) 1180,1070 (C-N),870,720 ArCH bend). A trace fluorescent band (0.019g) was observed, m.p. 106–110°C (to give a yellow liquid) which proved to be a mixture and insufficient after further purification for characterisation.

1-n-Butylaminoanthraquinone (**16b**): 1-Nitroanthraquinone (1.00g, 0.0039mol) in the minimum DMSO and 1-butylamine (1.42g, 0.01mol) were reacted at ambient temperature under nitrogen during 1h when TLC ($CHCl_3$–light petroleum, 80:20) indicated no anthraquinone remained and an array of 20 mostly coloured products. Prep TLC ($CHCl_3$–light petroleum 60:40) afforded a purple solid, 0.03g, m.p. 47–50°C (dec.); (Found: C, 68.85; H, 7.83; N, 5.03%. The second band, a major one was recovered as cherry red needles, 0.35g, 32.1%, m.p. 78–79°C,lit.[20] 80–81°C; (Found: C, 76.35; H, 6.08; N, 4.90. Reqd. for$C_{18}H_{17}NO_2$ C, 77.42; H, 6.01; N, 5.02. δ_H [$(CD_3)_2CO$], 0.82–1.12(3H, m, Me), 1.32–1.81 (4H, m, $2CH_2$), 3.18–3.50 (2H, m, CH_2N), 7.06–7.26 (1H m, 3-H), 7.46–7.66 (2H, m, 2-H, 4-H), 7.19–7.95 (2H, m, 6-H,7-H), 8.15–8.38 (2H, m, 5-H, 8-H), 0.72-0.93 (1H, bs exch. D_2O, NH); υ_{max} (KBr, cm^{-1}), 3275 (Ar strech), 2980 (as Me), 2925 (CH_2), 2860 (sMe), 1660 (as C=O), 1630 (sC=O) 1500,1580 (C=C), 1300 (CH bend), 1260,1000 (C–N), 730,690 (Ar bend).

A violet solid was recovered from the next significant band (0.05g) mp 189–190°C (darkens) melts >360°C; (Found: C, 40.75; H, 3.81; N, 2.39%).

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