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Unusual Photocyclization of 1-(2-Pyridylamino)-8-chloronaphthalene

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Photocyclization of 1-(2-pyridylamino)-8-chloronaphthalene **3** results in the formation of the novel heterocyclic system 7*H*-7,8-diazabenz[*d*,*e*]anthracene **4** and the previously unknown pyrido[1,2-*a*]perimidine **5**.

The photocyclization of 2-anilinopyridine proceeds with C—C bond formation leading to α-carboline. However, an analogous process does not take place for either 2-(1- and 2-(2-naphthylamino)pyridines or naphthylphenyl ether.[1] In the latter case the presence of a chlorine atom in the aromatic ring assists the reaction. Thus, *o*-chlorophenyl naphthyl ether[1] and 1-naphthyl-4-(tetrachloropyridyl)sulfide[2] undergo cyclization on irradiation to give benzo[*b*]naphtho[2,1-*d*]furan or the corresponding thiophene. In both examples cyclization occurs at the β-position of the naphthalene ring.

We have observed the same regioselectivity in the photoreaction of 2-(1-naphthylamino)-3,5-dichloropyridine **1**. This reac-

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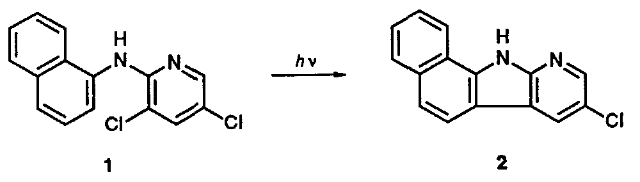


Scheme 1

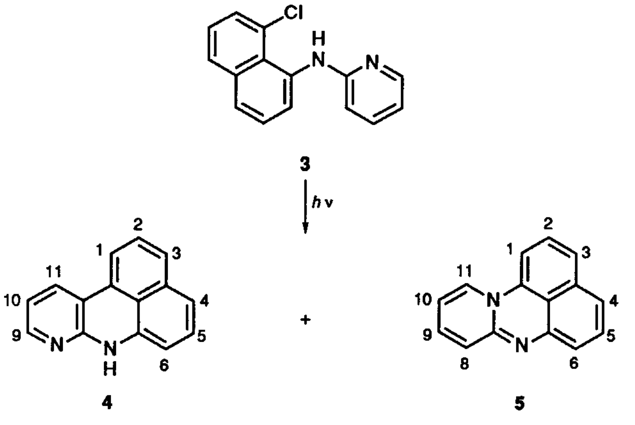
tion results in the formation of the tetracyclic compound **2** (Scheme 1).[†,‡]

No cyclization occurred at the *peri*-position of the naphthalene ring in any of the above-mentioned examples.

We stated above that the presence of a halogen atom in the 8-position of the naphthalene ring, as in 1-(2-pyridylamino)-8-chloronaphthalene **3**, irradiation resulted in cyclization at the *peri*-position with the formation of C—C and C—N bonds, the products being the novel heterocyclic system 7*H*-7,8-diazabenz[*d*,*e*]anthracene **4** and the previously unknown pyrido[1,2-*a*]perimidine **5** (Scheme 2). This reaction of compound **3** with the formation of pyridoperimidine **5** is the first example of photocyclization at a nitrogen atom leading to the closure of a fused pyrimidine ring.

After irradiation of a degassed solution of 0.005 mol of compound **3** in 800 cm^3 aqueous Me$_3$COH with the full spectrum light from a mercury lamp (400 W) for 5 h, followed by chromatography on aluminium oxide, the coloured compounds **4** and **5** were obtained.

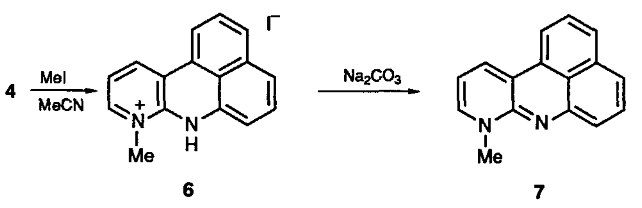
Compound **4** was isolated as brown–orange needles (from CHCl$_3$), m.p. 220–224 °C,[‡,§] showing a green luminescence in EtOH solution. ^{1}H NMR {100 MHz, [^{2}H$_7$]dimethylformamide (DMF)} δ 7.61 (dd, 1H, *J* 7 and 2 Hz, 1-H), 7.27 (dd, 1H, *J* 8 and 7 Hz, 2-H), 7.41 (dd, 1H, *J* 8 and 2 Hz, 3-H), 7.00 (dd, 1H, *J* 8 and 2 Hz, 4-H), 7.17 (dd, 1H, *J* 8 and 2 Hz, 5-H), 6.71 (dd, 1H, *J* 7 and 2 Hz, 6-H), 8.15 (dd, 1H, *J* 7.5 and 2 Hz, 9-H), 6.81 (dd, 1H, *J* 7.5 and 5 Hz, 10-H), 8.04 (dd, 1H, *J* 5 and 2 Hz, 11-H), 10.12 (s, 1H, NH); IR ν_{max}/cm^{-1} (CHCl$_3$) 3580 (OH), 3430 (NH); UV λ_{max}/nm (lg ε) (EtOH) 262 (4.34), 318 (3.92), 331 (4.07), 430 (4.08); yield 35% (all yields are given for the initial amine which had undergone the reaction).



Scheme 2

Compound **5** was obtained as red crystals, m.p. 142–143 °C.[‡,¶] ^{1}H NMR (100 MHz, CDCl$_3$) δ 7.27 (dd, 1H, *J* 7 and 2 Hz, 1-H), 6.98 (dd, 1H, *J* 8 and 7 Hz, 2-H), 7.10 (dd, 1H, *J* 8 and 2 Hz, 3-H), 6.68 (dd, 1H, *J* 8 and 2 Hz, 4-H), 6.79 (dd, 1H, *J* 8 and 7 Hz, 5-H), 6.57 (dd, 1H, *J* 7 and 2 Hz, 6-H), 7.13–7.21 (m, 2H, 8-H, 9-H), 6.15 (td, 1H, *J* 7 and 2 Hz, 10-H), 7.39 (dd, 1H, *J* 7 and 2 Hz, 11-H); IR ν_{max}/cm^{-1} (KBr) 3060 (CH); UV λ_{max}/nm (lg ε) (EtOH) 314 sh (3.26), 353 (3.99), 383 (3.90), 402 (3.86), 457 (3.16), 483 (3.14), 515 sh (2.99); yield 28%. Neither the IR nor ^{1}H NMR spectra of compound **5** show any signal corresponding to an NH-group.

After alkylation of compound **4** with MeI in MeCN, 7*H*-8-methyl-7-aza-8-azoniabenz[*d*,*e*]anthracene iodide **6** was formed as a carmine powder: m.p. >260 °C,[‡] λ_{max}/m (lg ε) (EtOH) 270 (4.12), 276 sh (4.10), 310 sh (3.59), 355 (3.66), 420 (3.34), 522 (3.67), 548 sh (3.66). When the latter was treated with an aqueous solution of Na$_2$CO$_3$, followed by diethyl ether extraction and chromatography on aluminium oxide, 8-methyl-7,8-diazabenz[*d*,*e*]anthracene **7** was obtained as a violet powder (from a mixture of hexane–CHCl$_3$, 1:1).[‡,||] ^{1}H NMR (100 MHz, [^{2}H$_7$]DMF) δ 3.55 (s, 3H, NMe), 7.45–7.59 (m, 2H, 1-H, 11-H), 7.16 (dd, 1H, *J* 8 and 7 Hz, 2-H), 7.37 (dd, 1H, *J* 8 and 2 Hz, 3-H), 6.93 (dd, 1H, *J* 8 and 2 Hz, 4-H), 7.10 (dd, 1H, *J* 8 and 7 Hz, 5-H), 6.66 (dd, 1H, *J* 7 and 2 Hz, 6-H), 7.75 (dd, 1H, *J* 7 and 2 Hz, 9-H), 6.10 (t, 1H, *J* 7 Hz, 10-H); IR ν_{max}/cm^{-1} (KBr) 2930, 2860 (NMe); UV λ_{max}/nm (lg ε) (EtOH) 279 (4.03), 289 sh (3.94), 340 sh (3.59), 355 (3.66), 420 (3.34), 522 (3.67), 548 sh (3.66) (Scheme 3).



Scheme 3

The alkylation of compound **4** at the pyridine-type N^8 is confirmed by a considerable bathochromic shift (118 nm) of the long-wave band in the electronic spectrum of the *N*-methyl derivative **7** relative to that of the initial diazabenzanthracene **4**. The given direction of alkylation is also supported by the increase in the chemical shift of the pyridine ring protons H^9-H^{11} in the ^{1}H NMR spectrum of the base **7** compared with the non-methylated product **4**.

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[†] Degassed solution of 0.005 mol of dichloro derivative **1** in 800 cm^3 aqueous Me$_3$COH was irradiated for 20 h using a mercury lamp (400 W). From the mixture obtained by chromatography on aluminium oxide the major product 11*H*-8-chloro-10,11-diazabenzo[*i*]fluorene **2** was isolated as colourless plates (recrystallized from toluene or EtOH): m.p. 330–332 °C (in a sealed capillary); IR ν_{max}/cm^{-1} (KBr) 3200 sh, 3160, 3130 sh (NH), 3060 (CH); UV λ_{max}/nm (lg ε) (EtOH) 275 (4.27), 315 (4.45), 368 (3.40); Mass spectrum *m*/*z* 252 (C$_{15}$H$_9$ClN$_2$). No product of cyclization at the *peri*-position was observed.

[‡] Satisfactory elemental analyses were obtained for all new compounds.

[§] The product contains about 3 H$_2$O molecules per molecule of compound **4**. Mass spectrum, *m*/*z* 218 [M$^+$], 190 [M$^+$ − H$_2$CN], 164 [M$^+$ − H$_2$CN − C$_2$H$_2$], 109 [M^{2+}].

[¶] Mass spectrum: *m*/*z* 218 [M$^+$], 190 [M$^+$ − H$_2$CN], 164 [M$^+$ − H$_2$CN − C$_2$H$_2$], 152 [M$^+$ − H$_2$CN − C$_3$H$_2$], 139 [M$^+$ − C$_5$H$_5$N], 125 [M$^+$ − C$_5$H$_5$N$_2$], 109 [M^{2+}].

[||] M.p. 120–130 °C, after drying in vacuum (10 mmHg) at 100 °C over P$_2$O$_5$ m.p. was 140–180 °C. The product contains about 3H$_2$O molecules per molecule of compound **7**. Mass spectrum, *m*/*z* 232 [M$^+$], 217 [M$^+$ − Me], 190 [M$^+$ − Me − HCN], 116 [M^{2+}].