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Annulations of 2-Aminonaphthoquinone with Aldehydes and Acetals

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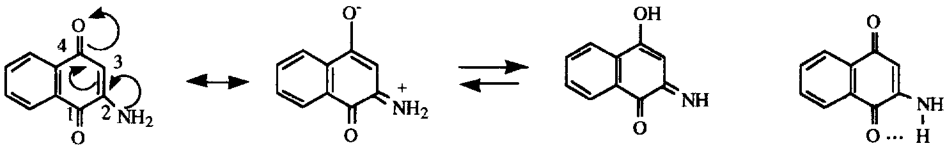
Abstract.- One-pot annulations between 2-amino-1,4-naphthoquinone (**1**) and aldehydes or acetals give either 6,13-dihydro-6-azapentacene-5,7,12,14-tetraones (**4**) or 1*H*-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-diones (**5**). These reactions constitute new examples of Hantzsch synthesis of 1,4-dihydropyridines and 6-*endo-trig* ring closures, respectively.

INTRODUCTION

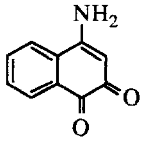
Oxidative additions of nucleophiles to quinones constitute one of the oldest areas of conjugate addition.[1] Very useful annulation procedures have been derived, being the most important the Nenitzesku reaction[2] and the addition of ketene acetals.[3] In high contrast, the use of 2-aminonaphthoquinones as bidentate nucleophiles is very scarce. Comparative experiments with primary and secondary 2- and 4-aminonaphthoquinone compounds (derived from **1** and **2** respectively) have shown that the reactivity against electrophiles such as methyleniminium salts, is higher in the *ortho*-quinoid compounds.[4] 2-Amino-1,4-naphthoquinone (**1**) gives by kinetic control the *N*-aminomethyl compounds, which subsequently generate the thermodinamically more stable *C*-Mannich reaction products, while under the same conditions, its isomer 4-amino-1,2-naphthoquinone (**2**), as well as secondary or tertiary 2-amino-1,4-naphthoquinones, directely give the *C*-aminomethyl derivatives.

We have previously shown that the nucleophillicity of the amino group in **1** is greater than that expected for its amide-like structure. Thus, 2-amino-1,4-naphthoquinone (**1**), and also 6- and 7-aminoquinoline-5,8-quinones, react as *N*-nucleophiles giving with some bis-dielectrophiles, useful intermediates that may be later cyclized to 2- or 4-oxo-1*H*-1-azaanthraquinones.[5] On the other hand, Michael additions between **1** and activated unsaturated bonds differ from those generally found in β-amino-α,β-unsaturated carbonyl compounds such as **3**[6]. These results indicate that the mesomeric interaction between the nitrogen lone pair and the C_4=O group in **1** is not very important and, consequently, *C*-alkylations proceeding on the enol tautomer **1′** through the electronic interaction of the electron pair on the nitrogen atom with the quinoid structure, are less favoured than in related systems.

The mesomeric effect above mentioned might explain the shift of the $E_{1/2}$ value of **1** at pH 7.0 of *ca.* 225 mV to more negative potential, as compared with unsubstituted naphthoquinone.[7] However, this value might be also explained if a hydrogen bond interaction between the C_1=O and NH_2 groups took place stabilizing the quinoid form (**1′′**).[8] Both arguments could explain the $E_{1/2}$ values of the *N*-methyl- (still more negative than that of 2-amino-1,4-naphthoquinone) and *N,N* -dimethyl- (less negative) analogues, since in the last case stabilization of the quinoid form by hydrogen bond is impossible but, at the same time, steric effects also cause a poor ovelapping between the quinone nucleus and the nitrogen lone pair.



1 **1'** **1''**



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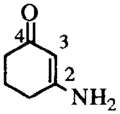

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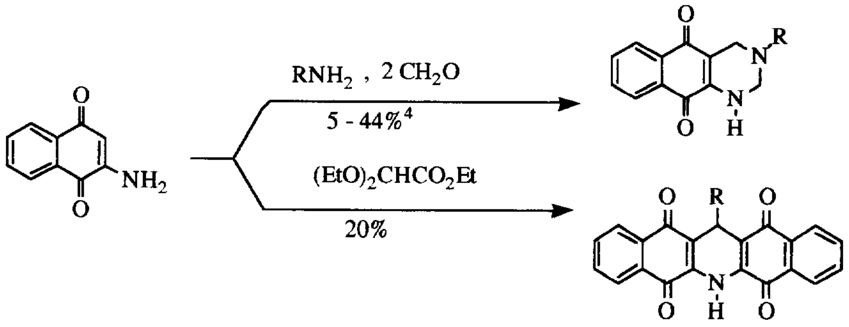
CHEMISTRY

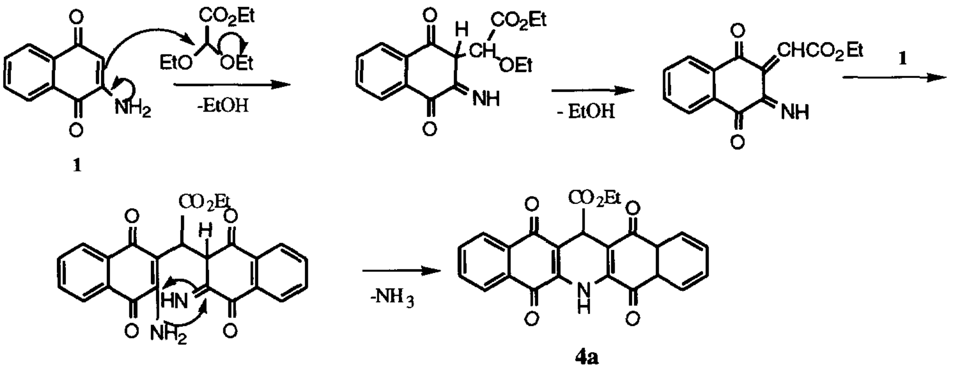
Taking into account that 2-amino-1,4-naphthoquinones behave as bidentate nucleophiles in condensations with 1 equivalent of primary amine and 2 equivalents of formaldehyde to give 3-substituted 1,2,3,4-tetrahydrobenzo[g]chinazoline-5,10-diones in poor to moderate yields (Scheme 1),[4] we studied the reactivity of **1** with acetals and aldehydes in order to find new annulation procedures. In the thermal cyclization of **1** with ethyl 2,2-diethoxyacetate, ethyl diquinone-13-carboxylate (**4a**) was obtained. The acid promoted reaction (TFA, 80 °C, 15 min.) worked better than the thermal cyclization (xylene, reflux, 5h). This transformation constitutes a new example of the Hantzsch synthesis of 1,4-dihydropyridines[9] and has to involve a nucleophillic substitution of **1** at C-3 . This means that **1** is acting here as an enamine compound, which is interesting from both synthetic and theoretical points of view.



4a, R = CO_2Et

Scheme 1

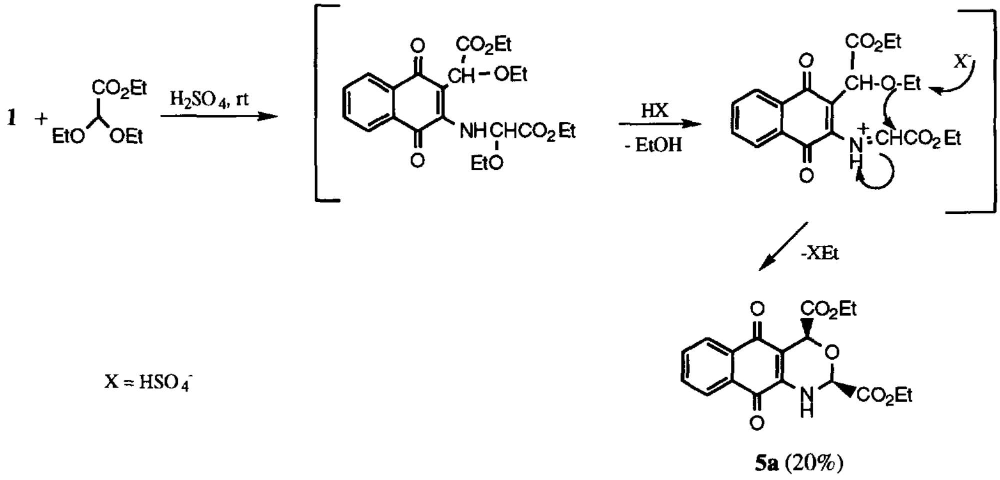
A plausible reaction mechanism involves C-3-alkylation, ethanol elimination, Michael addition of a second molecule of **1** and cyclization (Scheme 2). A precedent of the final elimination of ammonia can be seen in the reported cyclization of the 2-amino-1,4-naphthoquinone dimer to give 6*H*-dibenzo[b,i]carbazole-5,13:7,12-diquinone.[10]



Scheme 2

The use of an excess of **1**, instead of improving the yields of **4a** gave an intractable mixture, probably arising from autocondensation of the aminoquinone **1**. The reaction with triethyl orthoformate in acetic anhydride, which was expected to give 6-azapentacene-5,7,12,14-tetraone[11] failed, possibly because of the lower reactivity of the 4-ethoxy-1-azadiene intermediate as a Michael substrate.

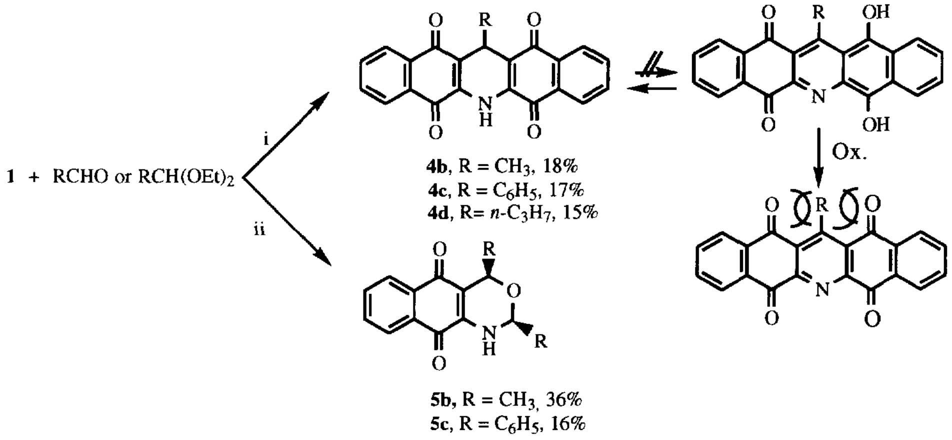
The above reaction did not work at room temperature, but when it was run at very low pH (H_2SO_4), (±)-*cis*-diethyl 5,8-dioxo-1*H*-2,4-dihydronaphtho[2,3-d]1,3-oxazine-2,4-dicarboxylate (**5a**) was obtained after 6 days. The full process can be understood through the participation of a *N,C*-dialkylated intermediate and subsequent 6-*endo-trig* ring closure (Scheme 3).



Scheme 3

The stereochemistry of **5a** was determined by NOE experiments. Thus, irradiation of H-2 signal (5.75 ppm) in a NOE difference experiment produced significant enhancement to the H-4 (5.55 ppm) and NH (6.65 ppm) proton resonances.

We also assayed the synthesis of compounds **4** and **5** by reaction of **1** with other acetals and aldehydes, obtaining similar results. Compounds **5**, in spite of their hemiaminal structure, are surprisingly stable in an acid medium.[4,12] On the other hand, compounds **4** are deeply coloured and, in contrast with the easy oxidation of some related compounds such as 5,12-dihydro-5,12-diazanaphthazene-6,11-diones[13] or 2,3,4,5,6,7,9,10-octahydroacridine-1,8-diones, which are NADH models,[14] all attempts to oxidize them were unsuccessful and their possible tautomers 7,12-dihydroxy-6-azapentacene-5,14-quinones were not observed. The interaction between the substituent at C_{13} and the C_{12} and C_{14} carbonyl groups in the planar aromatic structure is responsible of the dificult aromatization in compounds **4** (Scheme 4).



4b, R = CH_3, 18%
4c, R = C_6H_5, 17%
4d, R= n-C_3H_7, 15%

5b, R = CH_3, 36%
5c, R = C_6H_5, 16%

i: TFA, 80 °C, 5-10 min
ii: conc. H_2SO_4, r.t., 6-8 days

Scheme 4

Compounds **4** can be related with the 1,4-dithiane and 1,4-thiazine derivatives obtained by Katritzky and coworkers from 2,3-disubstituted naphthoquinones,[15] or with pentacene-5,7:12,14-diquinone obtained in the basic dimerization of 2-methylnaphthoquinone.[16]

This work widens the applications of 2-amino-1,4-naphthoquinone in organic synthesis through one-pot annulations. The ease which the reactions occur and the availability of the reactants render them attractive even though the yields are low.

ACKNOWLEDGEMENT

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EXPERIMENTAL

All melting points were obtained using a Reichart hot-stage microscope or a Büchi immersion apparatus in open capillary tubes and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 577 and Buck Scientific 500 spectrophotometers, with all compounds compressed into KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were obtained in $CDCl_3$ solution in 5 mm tubes using TMS as internal standard on Bruker AC-250 (250 MHz for ^{1}H, 63 MHz for ^{13}C) and Varian VXR-300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) spectrometers. Elemental analyses were determined by the Servicio de Microanálisis, Universidad Complutense, on a Perkin-Elmer 2400 CHN microanalyzer. Reactions were monoritored by thin layer chromatography on aluminium plates coated with silica gel with fluorescent indicator (Scharlau Cf 530) or visualized with iodine. Separations by flash chromatography were performed on silica gel (SDS 60 ACC, 230-400 mesh and Scharlau Ge 048) with the indicated eluents.

All solvents were purified if necessary, according to standard procedures[17] and all reagents were purchased from Aldrich and used without further purification unless otherwise noted. Concentration of solutions was accomplished by rotary evaporation at water aspirator pressures. The expresion "petroleum ether" refers to the fraction boiling at 40-60 °C.

Ethyl 5,7,12,14-tetraoxo-6,13-dihydro-6-azapentacene-13-carboxylate (4a).

A solution of 2-amino-1,4-naphthoquinone (0.4 g, 2.31 mmol), ethyl dietoxyacetate (0.44 ml, 2.48 mmol) and trifluoroacetic acid (3 ml) was placed in an Erlenmeyer flask which was immersed in a bath preheated to 80 °C with stirring for 15 minutes. Then the reaction was cooled and water (15 ml) was added. The aqueous phase was extracted with ethyl acetate (30 ml) and the organic phase was dried with Na_2SO_4. Concentration gave the crude product, which was purified on a column of silica gel eluting with ethyl acetate/petroleum ether, 1:1 to afford **4a** (0.1 g, 20%) as red crystals. Melting point: 210-211 °C. IR ν: 3440 (NH), 1750 (C=O ester), 1700 and 1640 (C=O quinone), 1620, 1580, 1470, 1415, 1375, 1315, 1300, 735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.10 and 8.02 (2d, *J* =7.4 Hz and J=7.5 Hz, 4H, H-1, H-11 and H-4, H-8); 7.71 and 7.60 (m, 4H, H-2, H-10 and H-3, H-9); 6.25 (br s, 1H, NH); 5.52 (s, 1H, H-13); 4.22 (q, *J* =7.1 Hz, 2H, CH_2); 1.23 (t, *J* =7.1 Hz, 3H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$) δ: 183.4 and 181.1 (C-5, C-7 and C-12, C-14); 169.6 (CO_2); 148.9 (C-5a, C-6a); 134.8 and 132.3 (C-2, C-10 and C-3, C-9); 133.5 and 130.2 (C-4a, C-7a and C-11a, C-14a); 126.7 and 126.3 (C-1, C-11 and C-4, C-8); 110.5 (C-12a, C-13a); 61.3 (CH_2); 37.6 (C-13); 14.2 (CH_3) ppm. Analysis calc. for $C_{24}H_{15}NO_6$: C, 69.73; H, 3.63; N, 3.38. Found: C, 69.41; H, 3.72; N, 3.65.

13-Methyl-6,13-dihydro-6-azapentacene-5,7,12,14-tetraone (4b).

A solution of 2-amino-1,4-naphthoquinone (0.7 g, 4.04 mmol), 1,1-dietoxyethane (0.62 ml, 4.35 mmol) and trifluoroacetic acid (3 ml) was placed in a Erlenmeyer flask which was immersed in a bath preheated to 80 °C with stirring for 10 minutes. Then the reaction was cooled and the formed precipitate filtered and washed with water and then methanol to give **4b**. A further amount was obtained by concentration of the filtrate. The crude product was purified on a column of silica gel eluting with ethyl acetate/hexane, 1:1 to afford **4b** (0.2 g, 18%) as red crystals. Melting point: 274-275 °C. IR ν: 3440 (NH), 1710 and 1670 (C=O quinone), 1625, 1620, 1600, 1505, 1495, 1300, 750 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.31 (s, 1H, NH); 8.15 (2 overlapped d, 4H, H-1, H-11 and H-4, H-8); 7.75 (m, 4H, H-2, H-10 and H-3, H-9); 4.63 (q, *J* =6.6 Hz, 1H, H-13); 1.31 (d, *J* =6.6 Hz, 3H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$) δ: 182.2 and 179.1 (C-5, C-7, C-12, C-14); 137.5 (C-5a, C-6a); 134.8 and 133.0 (C-2, C-10 and C-3, C-9); 132.7 and 130.2 (C-4a, C-7a and C-11a, C-14a); 126.6 and 126.3 (C-1, C-11 and C-4, C-8); 120.6 (C-12a, C-13a); 29.7 (C-13); 21.9 (CH_3) ppm. Analysis calc. for $C_{22}H_{13}NO_4$: C, 74.36; H, 3.66; N, 3.94. Found: C, 74.03; H, 3.63; N, 3.92.

13-Phenyl-6,13-dihydro-6-azapentacene-5,7,12,14-tetraone (4c).

A solution of 2-amino-1,4-naphthoquinone (1.5 g, 8.67 mmol), benzaldehyde (0.96 ml, 9.42 mmol) and trifluoroacetic acid (5 ml) was refluxed for 5 minutes. The reaction mixture was cooled and the precipitate obtained was filtered and washed with methanol to give **2c** (0.3 g, 17%) as orange crystals. Melting point: >300 °C. IR ν: 3490 (NH), 1730 and 1690 (C=O quinone), 1640, 1625, 1530, 1400, 1345, 1320 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.46 (s, 1H, NH); 8.14 and 8.06 (2d, J =7.0 Hz and J =7.5 Hz , 4H, H-1, H-11 and H-4, H-8); 7.72 (m, 4H, H-2, H-10 and H-3, H-9); 7.47 (d, J =6.7 Hz, 2H (Ph), H-2′ and H-6′); 7.26 (m, 2H, H-3′ and H-5′); 7.20 (m, 1H, H-4′); 5.72 (s, 1H, H-13) ppm. Analysis calc. for $C_{27}H_{15}NO_4$: C, 77.69; H, 3.59; N, 3.35. Found: C, 77.35; H, 3.55; N, 3.55.

13-Propyl-6,13-dihydro-6-azapentacene-5,7,12,14-tetraone (4d).

A solution of 2-amino-1,4-naphthoquinone (0.6 g, 3.46 mmol), butyraldehyde (0.33 ml, 3.77 mmol) and trifluoroacetic acid (3 ml) was heated under reflux with stirring for 20 minutes. Then the reaction was cooled and the precipitate obtained was filtered and washed with absolute ethanol to give **4d** (0,15 g, 15%) as red cystals. Melting point: 272-273 °C. IR ν: 3410 (NH), 1700 and 1670 (C=O quinone), 1615, 1595, 1490, 1480, 1210, 750 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.32 (s, 1H, NH); 8.13 (t, 4H, H-1, H-11 and H-4, H-8); 7.73 (m, 4H, H-2, H-10 and H-3, H-9); 4.67 (t, 1H, H-13); 1.58 (m, 2H, CH_2); 1.23 (m, 2H, CH_2); 0.81 (t, 3H, CH_3) ppm. Analysis calc. for $C_{24}H_{17}NO_4$: C, 75,19; H, 4.43; N, 3.65. Found: C, 75.32; H, 4.39; N, 3.57.

Diethyl 5,10-dioxo-1*H*-2,4-dihydronaphtho[2,3-d]1,3-oxazine-2,4-dicarboxylate (5a).

A solution of 2-amino-1,4-naphthoquinone (1.0 g, 5.78 mmol), ethyl dietoxyacetate (5 ml, 28.17 mmol), concentrated sulfuric acid (0.2 ml) and $CHCl_3$ (5 ml) was stirred at r.t. for 6 days. The crude product was purified on a column of silica gel eluting with ethyl acetate/petroleum ether, 1:1 to afford **5a** (0.4 g, 20%) as yellow crystals. Melting point: 122-123 °C. IR ν: 3430 (NH), 1750 (C=O ester), 1690 and 1655, (C=O quinone), 1610, 1590, 1505, 1385, 740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.09 (m, 2H, H-6 and H-9); 7.76 and 7.70 (m, 2H, H-7, H-8); 6.68 (s, 1H, NH); 5.77 (s, 1H, H-2); 5.57 (s, 1H, H-4); 4.40 (q, J =7.1 Hz, 2H, CH_2); 4.28 (q, J =7.1 Hz, 2H, CH_2); 1.40 (t, J =7.1 Hz, 3H, CH_3); 1.34 (t, J = 7.11 Hz, 3H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$) δ: 179.7 and 179.3 (C-5, C-10); 169.9 and 166.1 (2 CO_2); 141.4 (C-10a); 135.0 and 132.6 (C-7 and C-8); 132.8 and 130.3 (C-5a and C-9a); 126.5 and 126.4 (C-6 and C-9); 109.2 (C-4a); 75.9 (C-2); 70.2 (C-4); 63.3 and 62.2 (CH_2); 14.2 (CH_3) ppm. Analysis calc. for $C_{18}H_{17}NO_7$: C, 60.16; H, 4.73; N, 3.89. Found: C, 59.85; H, 4.77; N, 3.57.

2,4-Dimethyl-1*H*-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-dione (5b).

A solution of 2-amino-1,4-naphthoquinone (1.0 g, 5.78 mmol), dietoxyethane (4.05 ml, 28.5 mmol), concentrated sulfuric acid (0.2 ml) and $CHCl_3$ (5 ml) was stirred at r.t. for 6 days. The chloroform was evaporated and the crude product was purified on a column of silica gel eluting with ethyl acetate/petroleum ether, 2:8 to afford **5b** (0.5 g, 36%) as orange-red crystals. Melting point: 215-216 °C. IR ν: 3360 (NH), 1730 and 1650, (C=O quinone), 1605, 1550, 1485, 1420, 1400, 1370, 1310, 1260, 760 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.07 and 8.02 (2d, J =7.5 Hz and J =7.5 Hz, 2H, H-6, H-9); 7.72 and 7.61 (2t, J =7.5 Hz and J =7.5 Hz, 2H, H-7, H-8); 5.95 (br s, 1H, NH); 5.10 (m, 2H, H-2, H-4); 1.55 and 1.52 (m, 6H, C_2-$\mathit{CH_3}$ and C_4-$\mathit{CH_3}$) ppm. ^{13}C-

NMR ($CDCl_3$) δ: 180.4 and 180.0 (C-5, C-10); 141.8 (C-10a); 134.7 and 132.0 (C-7 and C-8); 133.2 and 130.3 (C-5a and C-9a); 126.1 and 125.9 (C-6 and C-9); 116.0 (C-4a); 72.6 (C-2); 67.6 (C-4); 20.9 and 20.6 (CH_3) ppm. Analysis calc. for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.34; N, 5.76. Found: C, 69.01; H, 5.19; N, 5.61.

2,4-Diphenyl-1*H*-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-dione (5c).

A solution of 2-amino-1,4-naphthoquinone (1.5 g, 8.67 mmol), benzaldehyde (4.42 ml, 43.35 mmol), concentrated sulfuric acid (0.3 ml) and $CHCl_3$ (7 ml) was stirred at r.t. for 8 days. The crude product was purified on a column of silica gel eluting with ethyl acetate/petroleum ether, 1:1 to afford **5c** (0.5 g, 16 %). Recrystallization from absolute ethanol gave orange crystals. Melting point: 199-200 °C. IR ν: 3370 (NH), 1690 and 1630 (C=O quinone), 1620, 1580, 1495, 1370, 1315, 1260, 1230, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 8.10 (m, 2H, H-6, H-9); 7.75 and 7.66 (m, 2H, H-7, H-8); 7.42 (m, 10H, $2C_6H_5$); 6.24 (s, 1H, H-2); 6.19 (s, 1H, NH); 5.48 (s, 1H, H-4) ppm. ^{13}C-NMR ($CDCl_3$) δ: 180.1 and 180.0 (C-5, C-10); 142.9 (C-10a); 134.8 and 132.2 (C-7 and C-8); 133.1 and 130.5 (C-5a and C-9a); 126.5 and 126.1 (C-6 and C-9); 139.8, 136.8, 129.9, 128.9, 128.7, 128.6, 128.5 and 126.9 (2 C_6H_5) ; 112.2 (C-4a); 78.1 (C-2); 73.3 (C-4) ppm. Analysis calc. for $C_{24}H_{17}NO_3$: C, 78.47; H, 4.63; N, 3.81. Found: C, 78.34; H, 4.64; N, 3.92.

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