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Novel 2-amino-3-(2,4-dinitrophenylamino) derivatives of 1,4-naphthoquinone

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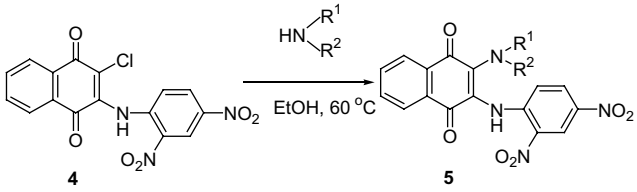
Abstract—The strong electron withdrawing nature of a 2,4-dinitrophenylamino group when attached to a chloro-naphthoquinone enhances the displacement of the chlorine atom by various aliphatic, cyclic and aromatic amines. A new series of 2-amino-3-(2,4-dinitrophenylamino) derivatives of 1,4-naphthoquinone were prepared. Three absorption maxima in the UV–vis spectra were typical, including one at 430–550 nm assigned to a CT transition.

Aliphatic amines as well as aryl amines of enhanced nucleophilicity can react with 2,3-dichloro-1,4-naphthoquinone, substituting one chlorine atom and yielding 2-alkyl (aryl)-amino-3-chloro-1,4-naphthoquinones[1] which are vinylogous amides. Electronic enrichment of the quinone system renders it less reactive to nucleophiles and inhibits the substitution of the second chlorine atom. In order to enable such a substitution and to obtain 2,3-diamino-1,4-naphthoquinones, an electron withdrawing effect must be imposed on the quinone ring, for which three methods are known (Fig. 1): (a) *N*-acylation of the quinone as in **1**[2,3] renders the chlorine atom reactive to oxygen and nitrogen nucleophiles. (b) *N*-nitrosation as in **2**, has a similar effect. Both the acyl and the nitroso groups can be easily installed and then removed after the substitution.[4] (c) Pyridinium salts **3**, formed by reacting 2,3-dichloro-1,4-naphthoquinone with pyridine, also have enhanced reactivity for the substitution of the second chlorine by aromatic amines.[5]

We have now prepared 2-chloro-3-(2,4-dinitrophenylamino)-1,4-naphthoquinone **4** (Scheme 1) by direct nitration of the aniline derivative. We found that the strong electron withdrawing nature of the dinitrophenylamino group made the quinone system sufficiently electron-poor that the second chlorine could be easily displaced by various aliphatic and aromatic amines. Thus, reacting **4** with pyrrolidine (pK_a of the conjugated



Scheme 1.

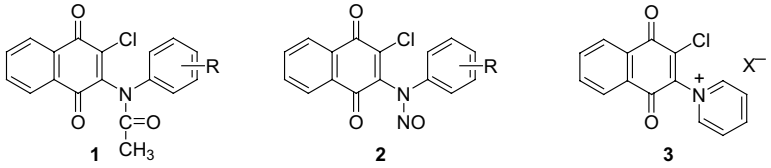


Figure 1.

Keywords: Naphthoquinones; Dinitrophenylamino-quinones; UV–vis.
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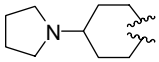
Table 1. Reactant ratio and yields of compounds **5a**–**h**

Entry	R^1	R^2	Compd	Ratio [4:amine]	Yield (%)
1	H	H	**5a**	Excess NH_3	52
2	H	$CH_3(CH_2)_4CH_2$	**5b**	1:6	63
3	CH_3CH_2	CH_3CH_2	**5c**[a]	1:5	58
4			**5d**	1:2	65
5			**5e**	1:3	63
6			**5f**	1:3	77
7	H	*p*-HO-C_6H_4	**5g**	1:4	78
8	H	*p*-CH_3O-C_6H_4	**5h**	1:9	75

[a] Solvent DCM.

acid in aqueous solution, 11.26) yielded **5d** in 65% yield. The reaction was performed at room temperature using ethanol as solvent. Comparable reactions with ammonia, primary, secondary, cyclic and electron-rich aromatic amines, gave the di-aminated naphthoquinones (**5a**–**h**) in average in good yields (Table 1).[6]

The reaction does not proceed with amines of lower nucleophilicity, for example, *p*-toluidine and *p*-aminostilbene. The reaction also does not proceed when 2-chloro-3-phenylamino-1,4-naphthoquinone was used. The usual reaction time (tlc) was 2–4 h and in several cases the reaction temperature was raised to 60 °C. Under these reaction conditions, the 2,4-dinitrophenylamino group was not substituted by the added amines. All the products **5** were previously unknown and were characterized by IR, UV–vis, ^{1}H NMR, ^{13}C NMR and HR-MS.[7,8]

The electronic absorption spectra of **5a**–**h** showed the expected benzene and naphthoquinone bands in the UV region around 264–294 nm (λ_1) and at 342–384 nm (λ_2) (π–π^* electronic transitions). In addition, a third lower energy transition appeared as a broad band in the visible region between 452 nm and 542 nm (λ_3). This absorption is typical of amino-substituted quinones[9,10] and is assigned to CT transitions and weak n–π^* transitions (see Table 2). As can be seen in Table 2, all three absorption maxima of compounds **5** show strong bathochromic shifts relative to the mono-substituted quinone **4**. These result from the electron-donating effects of the substituent amines. It is known that full delocalization of the nitrogen lone pair requires its orthogonality to the plane of the quinone. Thus, the shape of the noncyclic amines and the ring size of the cyclic amines influence their basicity, which in turn influences the degree of the bathochromic shifts of **5**.

Table 2. UV–vis data of compounds **4** and **5a**–**h** in $CHCl_3$

Compds	λ_1 (log ε)	λ_2 (log ε)	λ_3 (log ε)
4	264 (4.09)	334 (4.03)	440 (3.70)
5a	266 (4.14)	342 (4.21)	452 (3.49)
5b	274 (4.49)	352 (4.28)	488 (3.61)
5c	266 (4.32)	342 (4.17)	508 (3.23)
5d	284 (4.33)	352 (4.13)	498 (3.73)
5e	294 (4.33)	360 (4.22)	524 (3.77)
5f	292 (4.29)	360 (4.15)	522 (3.70)
5g	286 (4.23)	380 (3.99)	542 (3.48)
5h	286 (4.41)	384 (4.16)	540 (3.54)

This effect combined with steric considerations might explain the great difference in λ_3 between the diethylamino **5c** and hexylamino **5b** derivatives (λ_3, 508 and 488, respectively). It might also explain the different absorptions obtained with the five- and the six-membered cyclic amines. Thus, the λ_3 of **5d** (five-membered) appears at 498 nm, while the λ_3 of **5e** and **f** (six-membered) appear at 524 and 522 nm, respectively. The λ_3 of the hydroxy- and methoxy-substituted anilines **5g** and **h** appear at the longest wavelengths, 542 and 540 nm, respectively.

In conclusion, 2-chloro-3-(2,4-dinitrophenylamino)-1,4-naphthoquinone **4** was used for the preparation of a new series of quinones. It was shown that the very strong electron withdrawing nature of the 2,4-dinitrophenylamino group allowed the easy displacement of the chlorine atom by various aliphatic, cyclic and aromatic amines. These new quinones have two acceptor and one donor groups and might be expected to show unusual spectroscopic, electrochemical and other properties.

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6. General procedure (not optimized): to a stirred solution of **4** (0.1 g, 0.27 mmol) in ethanol (25 mL) several equivalents (see Table 1) of the amine were added. Some of the reactions were performed at room temperature and others at 60 °C. Stirring was continued for 2–4 h and the mixture was left to cool. The precipitated product was collected by filtration, washed with cold ethanol and purified by recrystallization from CH_2Cl_2.
7. Spectral data for **5d**: red-yellow solid; mp 228–230 °C. IR (KBr): 3331, 2973, 1688, 1349 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 9.62 (br s, 1H), 9.19 (d, 1H, J = 2.7 Hz), 8.23 (dd, 1H, J = 2.7, 9.5 Hz), 8.05 (m, 2H), 7.70 (m, 2H), 6.65 (d, 1H, J = 9.4 Hz), 3.67 (m, 4H), 1.84 (m, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 183.43, 178.24, 146.43, 137.41, 134.51, 132.68, 131.68, 131.53, 131.37, 129.75, 126.57, 125.98, 123.94, 117.03, 113.39, 106.25, 53.21, 25.49. HR-MS (CI in CH_4) (m/z), calcd for $C_{20}H_{16}N_4O_6$ 408.106989. Found: 408.10699.
8. Spectral data for **5h**: dark red solid; mp 220–222 °C. IR (KBr): 3353, 3081, 1664, 1332 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 9.48 (br s, 1H), 8.77 (d, 1H, J = 2.5 Hz), 8.21 (m, 2H), 8.11 (dd, 1H, J = 2.6, 9.2 Hz), 7.78 (m, 2H), 6.50 (m, 5H), 3.70 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 181.53, 179.70, 158.72, 141.80, 138.16, 135.30, 133.77, 133.51, 132.02, 130.37, 128.49, 127.58, 127.05, 126.90, 124.93, 122.81, 119.01, 114.82, 113.23, 102.38, 55.61. HR-MS (CI in CH_4) (m/z), calcd for $C_{23}H_{16}N_4O_7$ 460.10190. Found: 460.10218.
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