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# Synthesis and Spectral Properties of *N*-Aryl-5-hydroxy-1,4-naphthoquinone 4-Imines

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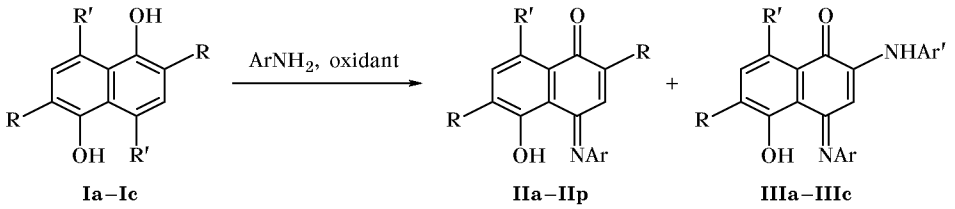
**Abstract**—1,5-Dihydroxynaphthalene, 2,6-dibromo-1,5-dihydroxynaphthalene, and 2,4,6,8-tetrabromo-1,5-dihydroxynaphthalene react with aromatic amines in the presence of an oxidant to afford the corresponding *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines.

Derivatives of *N*-arylquinonemonoimines have been proposed as dyes for optical data storage devices [1], antioxidants [2], anticarcinogenic compounds [3], and synthons for the preparation of dyes for liquid crystalline materials [4]. We previously showed that oxidative coupling of 1,5-dihydroxynaphthalene (**Ia**) with some aromatic amines leads to formation of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines whose yield depends on the substituent in arylamine and the nature of oxidant [5].

With the goal of extending the series of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imine derivatives, in the present work we performed a comparative study of the oxidative amination of 1,5-dihydroxynaphthalene (**Ia**), 2,6-dibromo-1,5-dihydroxynaphthalene (**Ib**), and 2,4,6,8-tetrabromo-1,5-dihydroxynaphthalene (**Ic**) with arylamines in the presence of $K_3Fe(CN)_6$, $HIO_3$, and $NaIO_4$ (Scheme 1, Table 1) and examined the effect of electronic and steric factors in the arylamine on the yield and spectral properties of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines thus obtained (compounds **IIa**–**IIp** and **IIIa**–**IIIc**; Tables 2, 3).

We have found that compounds **Ia**–**Ic** react with aryl- amines in aqueous alcohol at 20°C in the presence of $K_3Fe(CN)_6$ (method *a*) [optimal reactant ratio **I**:**II**:$K_3Fe(CN)_6$ = 1:1:4] to afford the corresponding *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines **IIa**–**IIp** and that the product yield decreases from 85 to 3% in parallel with the basicity of arylamines [6, 7]. In the presence of $K_3Fe(CN)_6$, compounds **IIa**–**IIp** are likely to be formed according to the radical cation mechanism which requires 4 mol of the oxidant per mole of quinone imine (Scheme 2), by analogy with the synthesis of indophenols and indoanilines [8]. Arylamines having electron-donor substituents in the aromatic ring stabilize intermediate radical cations; therefore, the products are formed in a fairly high yield (85–50%). By contrast, the yield of *N*-aryl-5-

**Scheme 1.**




**Ia–Ic** **IIa–IIp** **IIIa–IIIc**

**I**, R = R′ = H (**a**); R = Br, R′ = H (**b**); R = R′ = Br (**c**); **II**, R = R′ = H, Ar = 4-$Me_2NC_6H_4$ (**a**); R = R′ = H, Ar = 4-$BuOC_6H_4$ (**b**); R = R′ = H, Ar = 4-$MeOC_6H_4$ (**c**); R = R′ = H, Ar = Ph (**d**); R = R′ = H, Ar = 2,4,6-$Me_3C_6H_2$ (**e**); R = R′ = H, Ar = 4-$IC_6H_4$ (**f**); R = R′ = H, Ar = 3-$NO_2C_6H_4$ (**g**); R = R′ = H, Ar = 4-$BuOCOC_6H_4$ (**h**); R = R′ = H, Ar = 2-$MeOCOC_6H_4$ (**i**); R = R′ = H, Ar = 2-MeOCO-4-$IC_6H_3$ (**j**); R = R′ = H, Ar = 4-$NO_2C_6H_4$ (**k**); R = R′ = H, Ar = $C_6F_5$ (**l**); R = Br, R′ = H, Ar = 4-$BuOC_6H_4$ (**m**); R = Br, R′ = H, Ar = 2,4,6-$Me_3C_6H_2$ (**n**); R = R′ = Br, Ar = 4-$BuOC_6H_4$ (**o**); R = R′ = Br, Ar = $C_6F_5$ (**p**); **III**, R = R′ = H, Ar = Ar′ = Ph (**a**); R = R′ = H, Ar = 4-$IC_6H_4$, Ar′ = Ph (**b**); R = R′ = Br, Ar = Ar′ = 4-$BuOC_6H_4$ (**c**).

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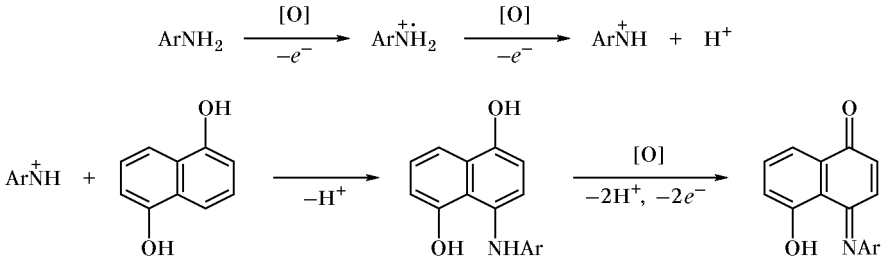
**Scheme 2.**



hydroxy-1,4-naphthoquinone 4-imines with electron-acceptor substituents in the *N*-aryl fragment is poor (3–40%).

It was shown previously that oxidative amination of 1,5-dihydroxynaphthalene with arylamines using $NaIO_4$ as oxidant affords with a satisfactory yield quinone imines containing both electron-donor and electron-acceptor substituents. The reaction is likely to follow a ionic mechanism involving electrophilic attack by $NaIO_4$ on the hydroxy group in 1,5-dihydroxynaphthalene to give a complex (cf. [9]) which then reacts with $ArNH_2$. The yield of the resulting *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imine depends on the reactivity of arylamine [5].

In this work we have found that the reaction of **Ia**–**Ic** with arylamines in the presence of $HIO_3$ or $NaIO_4$ (methods *b* and *c*, respectively) at a reactant ratio of 1:1:1 is characterized by greater yields of products **IIa**–**IIp**. Exceptions were the reactions of 1,5-dihydroxynaphthalene (**Ia**) with 4-dimethylaminoaniline and aniline and of 2,4,6,8-tetrabromo-1,5-dihydroxynaphthalene (**Ic**) with 4-butoxyaniline. In the first case, decrease in the yield of **IIa** may be explained by competing oxidation of 4-dimethylaminoaniline (cf. [9]). The low yield of *N*-phenyl-5-hydroxy-1,4-naphthoquinone 4-imine (**IId**) may be due to formation of *N*-phenyl-5-hydroxy-2-phenylamino-1,4-naphthoquinone 4-imine (**IIIa**) [10] and iodine-containing compounds **IIf** and **IIIb** as by-products. Taking into account published data [11], compounds **IIf** and **IIIb** could result from iodination of aniline with a mixture of iodine (released during the process) and $HIO_3$ and from the reaction of 4-iodoaniline thus formed with initial compound **Ia**. This was confirmed by independent synthesis of **IIf** from **Ia**, aniline, and $I_2$. In keeping with the spectral data, product **IIIb** has the structure of *N*-(4-iodophenyl)-5-hydroxy-2-phenylamino-1,4-naphthoquinone 4-imine. It should

**Table 1.** Oxidative amination of compounds **Ia**–**Ic**

| Initial comp. no. | Arylamine (p$K_a$ [6]) | Product (yield, %; method) |
|---|---|---|
| **Ia** | 4-$Me_2NC_6H_4NH_2$ (6.59) | **IIa** (85; *a* [5]); **IIa** (59; *b*), **IIa** (74; *c* [5]) |
| **Ia** | 4-$BuOC_6H_4NH_2$ | **IIb** (65; *a*); **IIb** (88; *b*) |
| **Ia** | 4-$MeOC_6H_4NH_2$ (5.31) | **IIc** (65; *a* [5]); **IIc** (73; *b*); **IIc** (71; *c* [5]) |
| **Ia** | $PhNH_2$ (4.60) | **IId** (64; *a*); **IId**, **IIf**, **IIIa**, **IIIb** (41, 2, 6, 6; *b*) |
| **Ia** | 2,4,6-$Me_3C_6H_2NH_2$ [3.89 (2,6-$Me_2C_6H_3NH_2$)] | **IIe** (50; *a*); **IIe** (58; *b*); **IIe** (41; *c*) |
| **Ia** | 4-$IC_6H_4NH_2$ (3.78) | **IIf** (45; *a*); **IIf** (61; *b*); **IIf** (70; *c*) |
| **Ia** | 3-$NO_2C_6H_4NH_2$ (2.50) | **IIg** (40; *a*); **IIg** (68; *b*); **IIg** (69; *c*) |
| **Ia** | 4-$BuOCOC_6H_4NH_2$ (2.47) | **IIh** (24; *a*); **IIh** (76; *b*) |
| **Ia** | 2-$MeOCOC_6H_4NH_2$ (2.23) | **IIi** (23; *a*); **IIi** (41; *b*) |
| **Ia** | 2-MeOCO-4-$IC_6H_3NH_2$ | **IIj** (38; *a*); **IIj** (44; *b*) |
| **Ia** | 4-$NO_2C_6H_4NH_2$ (0.99) | **IIk** (38; *a* [5]); **IIk** (40; *b*); **IIk** (55; *c* [5]) |
| **Ia** | $C_6F_5NH_2$ (–0.28 [7]) | **IIl** (3; *a*); **IIl**, juglone (45, 25; *b*) |
| **Ib** | 4-$BuOC_6H_4NH_2$ | **IIm** (42; *a*); **IIm** (92; *b*) |
| **Ib** | 2,4,6-$Me_3C_6H_2NH_2$ | **IIn** (53; *a*); **IIn** (74; *b*) |
| **Ic** | 4-$BuOC_6H_4NH_2$ | **IIo** (62; *a*); **IIo**, **IIIc** (43, 24; *b*) |
| **Ic** | $C_6F_5NH_2$ | **IIp** (14; *a*); **IIp** (62; *b*) |

**Table 2.** Melting points, IR and electron absorption spectra, and molecular weights of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines **IIb**, **IIe**–**IIj**, **III**–**IIp**, **IIIb**, and **IIIc**

| Comp. no. | mp, °C (solvent) | IR spectrum (KBr), ν, $cm^{-1}$ | UV spectrum[a] ($CHCl_3$), $\lambda_{max}$, nm ($\varepsilon \times 10^{-4}$, $l\ mol^{-1}\ cm^{-1}$ | Found $M^+$ | Formula | Calculated $M$ |
|---|---|---|---|---|---|---|
| **IIb** | 122–123 (benzene–hexane, 1 : 5) | 1657 (C=O), 1619 (C=N) | 490 (0.85) | 321.13649 | $C_{20}H_{19}NO_3$ | 321.13648 |
| **IIe** | 145 (hexane) | 1660 (C=O), 1630 (C=N) | 423 (0.42) | 291.12372 | $C_{19}H_{17}NO_2$ | 291.12592 |
| **IIf** | 210–212 (benzene–heptane, 1 : 3) | 1654 (C=O), 1619 (C=N) | 453 (0.54) | 374.97595 | $C_{16}H_{10}INO_4$ | 374.97581 |
| **IIg** | 224–226 (benzene–hexane, 1 : 5) | 1660 (C=O), 1630 (C=N), 1530 ($NO_2$), 1370 ($NO_2$) | 430 (0.64) | 294.06251 | $C_{16}H_{10}N_2O_4$ | 294.06405 |
| **IIh** | 131–132 ($CHCl_3$–hexane, 1 : 10) | 1719 ($COO^-$), 1660 (C=O), 1620 (C=N) | 442 (0.71) | 349.13128 | $C_{21}H_{19}NO_4$ | 349.13140 |
| **IIi** | 161–162 (benzene–hexane, 1 : 5) | 1720 ($COO^-$), 1660 (C=O), 1620 (C=N) | 432 (0.62) | 307.08405 | $C_{18}H_{13}NO_4$ | 307.08445 |
| **IIj** | 114–115 (benzene–hexane, 1 : 5) | 1717 ($COO^-$), 1657 (C=O), 1620 (C=N) | 443 (0.61) | 432.98117 | $C_{18}H_{12}INO_4$ | 432.98129 |
| **III** | 168–170 (hexane) | 1660 (C=O), 1620 (C=N) | 447 (0.59) | 339.03119 | $C_{16}H_6F_5NO_2$ | 339.03186 |
| **IIm** | 123–124 (benzene–hexane, 1 : 5) | 1660 (C=O), 1600 (C=N) | 508 (0.89) | 476.95857 | $C_{20}H_{17}Br_2NO_3$ | 476.95761 |
| **IIn** | 211–213 ($CHCl_3$–hexane, 1 : 10) | 1671 (C=O), 1600 (C=N) | 440 (0.61) | 446.94764 | $C_{19}H_{15}Br_2NO_2$ | 446.94705 |
| **IIo** | 136–137 (benzene–hexane, 1 : 5) | 1670 (C=O), 1615 (C=N) | 513 (1.09) | 554.87081 | $C_{20}H_{16}Br_3NO_3$ | 554.86818 |
| **IIp** | 223–225 (benzene–hexane, 1 : 5) | 1676 (C=O), 1615 (C=N) | 470 (0.72) | 572.76367 | $C_{16}H_3Br_3F_5NO_2$ | 572.76356 |
| **IIIb** | 250–251 (benzene–hexane, 1 : 5) | 3268 (NH), 1656 (C=O), 1621 (C=N) | 459 (0.89) | 466.01817 | $C_{22}H_{15}IN_2O_2$ | 466.01800 |
| **IIIc** | 124–125 (benzene–hexane, 1 : 5) | 3329 (NH), 1658 (C=O), 1620 (C=N) | 515 (1.10), 551 (1.20), 640 (0.80); 496 (1.13), 550 (0.90), 640 (0.30)[b] | 640.05639 | $C_{30}H_{30}Br_2N_2O_4$ | 640.05732 |

[a] In the visible region.
[b] In $CCl_4$.

**Table 3.** $^{1}H$ and $^{19}F$ NMR spectra of compounds **IIa**–**IIp**, **IIIb**, and **IIIc**

| Comp. no. | Chemical shifts δ, ppm (*J*, Hz) |
|---|---|
| **IIa** | 3.02 s (6H, 2Me), 6.68 d (1H, 2-H, 10.0), 6.74 d (2H, 2′-H, 6′-H, 8.5), 7.03 d (2H, 3′-H, 5′-H, 8.5), 7.25 d.d (1H, 6-H, 8.0, 2.0), 7.46 t (1H, 7-H, 8.0), 7.48 d (1H, 3-H, 10.0), 7.67 d.d (1H, 8-H, 8.0, 2.0), 14.60 s (1H, OH) |
| **IIb** | 0.97 t (3H, Me, 7.0), 1.49 m (2H, $CH_2$), 1.78 m (2H, $CH_2$), 3.98 t (2H, $CH_2$, 7.0), 6.68 d (1H, 2-H, 10.0), 6.96 m (4H, 2′-H, 3′-H, 5′-H, 6′-H), 7.26 d (1H, 6-H, 8.0), 7.36 d (1H, 3-H, 10.0), 7.50 t (1H, 7-H, 8.0), 7.67 d (1H, 8-H, 8.0), 14.22 s (1H, OH) |
| **IIc** | 3.82 s (3H, Me), 6.67 d (1H, 2-H, 10.5), 6.92–7.03 m (4H, 2′-H, 3′-H, 5′-H, 6′-H), 7.26 d.d (1H, 6-H, 8.0, 2.0), 7.34 d (1H, 3-H, 10.5), 7.48 t (1H, 7-H, 8.0), 7.65 d.d (1H, 8-H, 8.0, 2.0), 14.17 s (1H, OH) |
| **IId** | 6.63 d (1H, 2-H, 10), 7.00 d (2H, 2′-H, 6′-H, 8.5), 7.21 d (1H, 3-H, 10), 7.23 d.d (1H, 6-H, 8.0, 2.0), 7.43 m (3H, 3′-H, 4′-H, 5′-H), 7.47 m (1H, 7-H, 8.0), 7.63 d.d (1H, 8-H, 8.0, 2.0), 13.84 s (1H, OH) |
| **IIe** | 2.04 s (6H, 2Me), 2.31 s (3H, Me), 6.62 d (1H, 2-H, 10.0), 6.88 d (1H, 3-H, 10.0), 6.94 s (2H, 3′-H, 5′-H), 7.39 d (1H, 6-H, 8.0), 7.54 t (1H, 7-H, 8.0), 7.70 d (1H, 8-H, 8.0), 14.12 s (1H, OH) |
| **IIf** | 6.70 d (1H, 2-H, 10.0), 6.77 d (2H, 2′-H, 6′-H, 8.5), 7.20 d (1H, 3-H, 10.0), 7.29 d.d (1H, 6-H, 8.0, 2.0), 7.54 t (1H, 7-H, 8.0), 7.69 d.d (1H, 8-H, 8.0, 2.0), 7.75 d (2H, 3′-H, 5′-H, 8.0), 13.64 s (1H, OH) |
| **IIg** | 6.75 d (1H, 2-H, 10.0), 7.12 d (1H, 3-H, 10.0), 7.29–7.41 m (2H, 6-H, 6′-H), 7.50–7.69 m (2H, 7-H, 5′-H), 7.73 d.d (1H, 8-H, 8.0, 2.0), 7.89 t (1H, 2′-H, 2.0), 8.14 d.t (1H, 4′-H, 8.0, 2.0), 13.28 s (1H, OH) |
| **IIh** | 0.97 t (3H, Me, 7.0), 1.48 m (2H, $CH_2$), 1.75 m (2H, $CH_2$), 4.33 t (2H, $CH_2$, 7.0), 6.69 d (1H, 2-H, 10.5), 7.05 d (2H, 2′-H, 6′-H, 8.0), 7.14 d (1H, 3-H, 10.5), 7.30 d.d (1H, 6-H, 8.0, 2.0), 7.54 t (1H, 7-H, 8.0), 7.69 d.d (1H, 8-H, 8.0, 2.0), 8.11 d (2H, 3′-H, 5′-H, 8.0), 13.46 s (1H, OH) |
| **IIi** | 3.80 s (3H, Me), 6.65 d (1H, 2-H, 10.5), 6.87 d.d (1H, 6′-H, 8.0, 2.0), 7.04 d (1H, 3-H, 10.5), 7.26–7.37 m (2H, 6-H, 4′-H), 7.47–7.62 m (2H, 7-H, 5′-H), 7.68 d.d (1H, 8-H, 8.0, 2.0), 8.08 d.d (2H, 3′-H, 8.0, 2.0), 13.52 s (1H, OH) |
| **IIj** | 3.82 s (3H, Me), 6.61 d (1H, 6′-H, 8.0), 6.63 d (1H, 2-H, 10.0), 7.01 d (1H, 3-H, 10.0), 7.28 d.d (1H, 6-H, 8.0, 2.0), 7.52 t (1H, 7-H, 8.0), 7.66 d.d (1H, 8-H, 8.0, 2.0), 7.84 d.d (1H, 5′-H, 8.0, 2.0), 8.37 d (1H, 3′-H, 2.0), 13.26 s (1H, OH) |
| **IIk** | 6.74 d (1H, 2-H, 10.0), 7.08 d (1H, 3-H, 10.0), 7.14 d (2H, 2′-H, 6′-H, 8.0), 7.33 d (1H, 6-H, 8.0), 7.59 t (1H, 7-H, 8.0), 7.73 d (1H, 8-H, 8.0), 8.33 d (2H, 3′-H, 5′-H, 8.0), 13.09 s (1H, OH) |
| **IIl** | 6.77 d (1H, 2-H, 10.0), 6.97 d.t (1H, 3-H, 10.0, 2.5), 7.32 d.d (1H, 6-H, 8.0, 1.0), 7.59 t (1H, 7-H, 8.0), 7.70 d.d (1H, 8-H, 8.0, 1.0), 12.86 s (1H, OH);<br>$^{19}F$ NMR spectrum, $\delta_F$, ppm: 0.50–0.77 m (2F, 3′-F, 5′-F), 4.46 t.d (1F, 4′-F, 23.1), 12.45 d.d (2F, 2′-F, 6′-F, 23.7, 2.5) |
| **IIm** | 0.99 t (3H, Me, 8.0), 1.50 m (2H, $CH_2$), 1.79 m (2H, $CH_2$), 3.99 t (2H, $CH_2$, 8.0), 6.97 d (2H, 2′-H, 6′-H, 8.0), 7.05 d (2H, 3′-H, 5′-H, 8.0), 7.52 d (1H, 7-H, 8.0), 7.72 d (1H, 8-H, 8.0), 7.83 s (1H, 3-H), 15.28 s (1H, OH) |
| **IIn** | 2.04 s (6H, 2Me), 2.32 s (3H, Me), 6.96 s (2H, 3′-H, 5′-H), 7.33 s (1H, 3-H), 7.63 d (1H, 7-H, 8), 7.82 d (1H, 8-H, 8.0), 15.10 s (1H, OH) |
| **IIo** | 0.99 t (3H, Me, 8.0), 1.50 m (2H, $CH_2$), 1.79 m (2H, $CH_2$), 4.00 t (2H, $CH_2$, 8.0), 7.00 d (2H, 2′-H, 6′-H, 8.0), 7.10 d (2H, 3′-H, 5′-H, 8.0), 7.82 s (1H, 3-H), 8.01 s (1H, 7-H), 16.53 s (1H, OH) |
| **IIp** | 7.42 t (1H, 3-H, 2.5), 8.19 s (1H, 7-H), 14.55 s (1H, OH)<br>$^{19}F$ NMR spectrum, $\delta_F$, ppm: 1.77–2.02 m (2F, 3′-F, 5′-F), 6.77 t (1F, 4′-F, 22), 13.34 d.d (2F, 2′-F, 6′-F, 22.5, 2.5) |
| **IIIb** | 6.58 s (1H, 3-H), 6.82 d (2H, 2′-H, 6′-H, 8.0), 7.02 d (2H, 2″-H, 6″-H, 8.0), 7.13–7.62 m (8H, 3′-H, 5′-H, 3″-H, 4″-H, 5″-H, 6-H, 7-H, NH), 7.75 d.d (1H, 8-H, 8.0, 1.0), 15.05 s (1H, OH) |
| **IIIc** | 0.95 m (6H, 2Me), 1.48 m (4H, $2CH_2$), 1.73 m (4H, $2CH_2$), 3.94 m (4H, $2CH_2$), 6.47 s (1H, 3-H), 6.81–7.13 m (8H, 2′-H, 3′-H, 5′-H, 6′-H, 2″-H, 3″-H, 5″-H, 6″-H), 7.74 s (1H, NH), 8.02 s (1H, 7-H), 18.21 s (1H, OH) |

be noted that no iodination of quinone imine **IId** occurs under the given conditions and that compounds **IId** and **IIf** do not give rise to arylamino-substituted quinone imines **IIIa** and **IIIb**. The reaction of 2,4,6,8-tetrabromo-1,5-dihydroxynaphthalene (**Ic**) with 4-butoxyaniline in the presence of $HIO_3$ gave a mixture of compound **IIo** and product of bromine replacement in position *2* by the arylamine residue, 6,8-dibromo-*N*-(4-butoxyphenyl)-2-(4-butoxyphenylamino)-5-hydroxy-1,4-naphthoquinone 4-imine (**IIIc**).

The structure of the products was determined on the basis of their spectral data (Tables 2, 3). In the mass spectra we observed strong molecular ion peaks with *m*/*z* values corresponding to the assumed structures. The IR spectra of all the products contained absorption bands in the region 1600–1700 $cm^{-1}$ due to stretching vibrations of the C=O and C=N bonds; compounds **IIh**–**IIj** and **IIg** additionally showed bands from stretching vibrations of the ester carbonyl and nitro group, respectively. The absence of absorption in the region 3400–3600 $cm^{-1}$ is explained by low-frequency shift of the OH stretching vibrations to the region corresponding to C–H bond vibrations (~3000 $cm^{-1}$) due to formation of strong intramolecular hydrogen bond between the 5-hydroxy group and imino nitrogen atom ($C^4$=N) in the *peri* position (cf. [12]). The existence of strong intramolecular hydrogen bond also follows from the $^1$H NMR spectra of compounds **IIa**–**IIp**, **IIIb**, and **IIIc** (Table 3), where singlets from the hydroxy protons appear in a weak field, at δ 12.86–18.21 ppm, as it was observed in the spectra of 5-hydroxy- and 5,8-dihydroxy-1,4-naphthoquinones [13]. Protons in positions *2* and *3* of the quinone ring in **IIa**–**IIl** give rise to two doublets, the 3-H signal being more sensitive to the position and nature of substituent in the *N*-aryl fragment. Compounds **IIa**–**IIc** having electron-donor groups ($NMe_2$, BuO, and MeO) in the *para* position of the *N*-aryl fragment are characterized by the most downfield 3-H signal (δ 7.48, 7.36, and 7.34 ppm, respectively); as electron-acceptor power of the substituent in the *N*-aryl fragment increases, the 3-H signal shifts upfield (δ 7.12–7.01 ppm; compounds **IIg**–**IIk**). The most upfield 3-H signals are observed for *N*-pentafluorophenyl derivative **IIl** and sterically hindered *N*-(2,4,6-trimethylphenyl)-5-hydroxy-1,4-naphthoquinone 4-imine (**IIe**) (δ 6.97 and 6.88 ppm, respectively).

The electron absorption spectra of the products are also characterized by considerable differences in the position of the long-wave absorption maxima, depending on the nature of substituent in the *N*-aryl fragment. The absorption maximum of compound **IIa** is located at the longest wavelength, $\lambda_{max}$ = 592 nm [5]; compounds **IIb** and **IIc** having weaker electron-donor groups (BuO and MeO) [5] absorb at λ 490 nm. Electron-acceptor substituents (compounds **IIg**–**IIk**) reduce the absorption intensity, and the long-wave absorption maximum shifts to the blue region. The lowest $\lambda_{max}$ and ε values were observed for sterically hindered *N*-(2,4,6-trimethylphenyl) derivative **IIe**. Among bromine-containing derivatives **IIm**–**IIp**, the largest red shift of $\lambda_{max}$ and the strongest absorption intensity, as well as the most downfield position of the 3-H signal in the $^1$H NMR spectrum, are typical of compounds **IIm** and **IIo** having an electron-donor butoxy group in the *para* position of the *N*-aryl moiety. *N*-(2,4,6-Trimethylphenyl) and *N*-pentafluorophenyl derivatives **IIn** and **IIp** are characterized by lower values of $\lambda_{max}$ and ε and upfield shift of the 3-H signal. The observed variation of the 3-H chemical shift in the $^1$H NMR spectra and of the position of the long-wave absorption maxima in the electron spectra may be explained by effect of the benzene ring which is arranged *syn* with respect to the 2-H and 3-H protons [14] and is turned through an angle θ with respect to the plane of the naphthoquinone fragment [15]. Quantum-chamical calculations of the angle θ in molecules **IIa**, **IIc**–**IIe**, **IIh**, and **IIk** gave values of 54.1, 56.8, 57.7, 62.7, 58.1, and 57.8°, respectively. Donor substituents in position *4* of the *N*-aryl fragment makes the molecule more planar; as a result, the 3-H signal shifts downfield, and $\lambda_{max}$ increases. The angle θ in sterically hindered *N*-(2,4,6-trimethylphenyl) derivative **IIe** is larger; therefore, conjugation between the benzene ring and the C=C–C=O bond sequence through the nitrogen atom is broken, and the 3-H signal shifts upfield while the absorption maximum shifts to the blue region.

Introduction of bromine atoms into positions *2*, *6*, and *8* of the naphthoquinone moiety leads to downfield shift of the 3-H signal, red shift of the long-wave absorption maximum, and increase in the absorption intensity (cf. the spectra of **IIb**, **IIm**, **IIo**, **IIe**, and **IIn**, as well as of **IIl** and **IIp**). A similar effect of electron-acceptor substituents in position *2* of the naphthalene ring was observed previously for *N*-aryl-1,4-naphthoquinone 4-imines [16].

We previously reported that 5-hydroxy-1,4-naphthoquinone 4-imines in organic solvents exist as mixtures of *para*- and *ana*-quinoid tautomers [17, 18]. Compounds **IIa**–**IIp** show only one absorption band in the visible region of the electron spectra. As well as previously synthesized *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines [5], they exist in the *para*-quinoid form. Compound **IIIc** is characterized by appreciably

different electron absorption spectra in solvents with different polarities. In going from $CHCl_3$ to $CCl_4$, we observed a blue shift and increase in intensity of the band belonging to the *para*-quinone imine structure ($\lambda$ ~500 nm) and decrease in intensity of the absorption band at 640 nm. These data suggest that compound **IIIc** in $CHCl_3$ gives rise to a mixture of *para*- and *ana*-quinoid tautomers, as was observed for *N*-phenyl-6,8-dibromo-5-hydroxy-2-phenylamino-1,4-naphthoquinone 4-imine [18].

## EXPERIMENTAL

The IR spectra were recorded on Vector 22 and UR-20 instruments in KBr. The electron absorption spectra of solutions in $CHCl_3$ or $CCl_4$ were measured on Specord UV-Vis, Hewlett–Packard 4853, and Beckmann DU-8 spectrophotometers. The $^1H$ and $^{19}F$ NMR spectra were obtained on a Bruker WP-200SY spectrometer from solutions in $CDCl_3$. The molecular weights and elemental compositions of the products were determined from the high-resolution mass spectra which were obtained using Finnigan MAT 8200 and Finnigan AEI MS-900 instruments. The purity of the products was checked by TLC on Silufol plates using $CHCl_3$ as eluent. Quantum-chemical calculations with full geometry optimization were performed in the AM1 approximation using MOPAC software [19].

**Reaction of 1,5-dihydroxynaphthalenes Ia–Ic with arylamines** (Table 1). *a*. To a suspension of 1 mmol of compound **Ia** or **Ib** in 50 ml of EtOH (for compound **Ic**, in 30 ml of DMF) and 1 mmol of the corresponding arylamine we added dropwise with stirring a solution of 4 mmol of $K_3Fe(CN)_6$ in 50 ml of water (in the reactions with **Ic**, in 10 ml of water). The mixture was stirred for 2 h at 20°C and poured into water, and 5 ml of 5% hydrochloric acid and 10 g of solid sodium chloride were added. The precipitate was filtered off, washed with water, dried, and dissolved in $CHCl_3$, and the solution was subjected to column chromatography on $Al_2O_3$ using $CCl_4$–$CHCl_3$ mixtures (10 to 100 vol. % of the latter) as eluent.

*b*. To a suspension of 1 mmol of compound **Ia** or **Ib** in 30 ml of EtOH (for compound **Ic**, in 30 ml of DMF) and 1 mmol of the corresponding arylamine we added dropwise with stirring a solution of 1 mmol of $HIO_3$ (Aldrich) in 15 ml (for **Ic**, 10 ml) of water, and the mixture was stirred for 2 h at 20°C. It was then treated as described above in *a*. An exception was the reaction of **Ia** with aniline, where the precipitate was subjected to column chromatography on silica gel using $CCl_4$–acetone (gradient elution, 10 to 50 vol % of acetone); compounds **IId**, **IIf**, **IIIa**, and **IIIb** were isolated in the order of elution. In the reaction of **Ic** with 4-butoxyaniline, the precipitate was dissolved in $CHCl_3$ and subjected to column chromatography on $Al_2O_3$ using in succession $CCl_4$ (compound **IIp**) and $CHCl_3$ as eluent (**IIIc**).

*c*. To a suspension of 1 mmol of compound **Ia** and 1 mmol of the corresponding arylamine in 30 ml of EtOH we added dropwise with stirring a solution of 1 mmol of $NaIO_4$ in 15 ml of water, and the mixture was stirred for 2 h at 20°C. It was then treated as described above in *a*.

***N*-Phenyl-5-hydroxy-1,4-naphthoquinone 4-imine (IId) and *N*-(4-iodophenyl)-5-hydroxy-1,4-naphthoquinone 4-imine (IIf).** To a suspension of 2 mmol of $I_2$ in 30 ml of EtOH and 15 ml of water we added 1 mmol of aniline, the mixture was stirred for 1 h, 1 mmol of compound **Ia** was added, the mixture was stirred for an additional 1 h and poured into water, and 5 ml of 5% hydrochloric acid and 5 g of sodium chloride were added. The precipitate was filtered off, washed with water, dried, and dissolved in $CHCl_3$. Thin-layer chromatography on silica gel using benzene–chloroform (1 : 1) as eluent gave (in the order of elution) 35% of compound **IIf** and 12% of compound **IId**.

**Behavior of compounds IId, IIf, and IIo under conditions of oxidative amination.** To a suspension of 1 mmol of compound **IId** or **IIf** in 30 ml of EtOH or of compound **IIo** in 30 ml of DMF and 1 mmol of aniline or 4-butoxyaniline we added dropwise with stirring a solution of 1 mmol of $HIO_3$ in 15 or 10 ml of water, and the mixture was stirred for 2 h at 20°C. The mixture was then treated as described above in *a* to isolate unchanged initial compounds **IId** (95%), **IIf** (90%), or **IIo** (90%).

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