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Synthesis of 2-Amino(alkylamino)-3-nitro-1,4-naphthoquinones

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Abstract—The reaction of 2-amino(alkylamino)-1,4-naphthoquinones with nitrating mixture in concentrated sulfuric acid leads to the formation of 2-amino(alkylamino)-3-nitro-1,4-naphthoquinones.

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1,4-Naphthoquinone derivatives having a nitro group in the quinoid part of the molecule are poorly understood. The nitration of 1,4-naphthoquinone [1] and 2,3-dichloro-1,4-naphthoquinone [2] in fairly stringent conditions afforded the corresponding 5-nitro-1,4-naphthoquinones. The nitration of 2-hydroxy-1,4-naphthoquinone and its derivatives with conc. nitric acid or with nitrating mixture results in the corresponding 2-hydroxy-3-nitro-1,4-naphthoquinones [3]. When oxidation-sensitive fragments are present in the benzene ring of the 2-hydroxy-1,4-naphthoquinone the nitration into the position *3* is carried out with nitronium tetraborate in acetonitrile [4].

2-Hydroxy-3-nitro-1,4-naphthoquinone was first obtained [5] by a reaction of 2,3-dichloro-1,4-naphthoquinone with sodium nitrite in a water-alcohol environment. 1,4-Naphthoquinone containing nitro and amino groups in the quinoid part of the molecule has not been known up till now.

We have found that 2-amino-1,4-naphthoquinone (**Ia**), and also 2-alkyl(dialkyl)amino-1,4-naphthoquinones **Ib–Ig** readily react with the nitrating mixture in conc. sulfuric acid furnishing the corresponding 2-amino(alkylamino)-3-nitro-1,4-naphthoquinones **IIa–IIg** (Scheme 1).

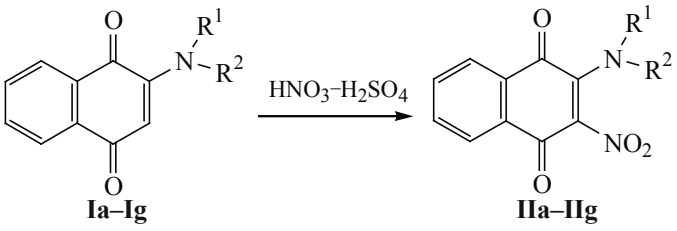
The reaction of compounds **Ia–Ig** with nitrating mixture in acetic acid is nonselective. For instance, 2-(propylamino)naphthoquinone (**Id**) gave as a main product 1-hydroxy-2-ethyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (**IIId**) (Scheme 2).

The conversion **Id** → **IIId** is accompanied with nitrogen oxides liberation. Apparently this process like the heterocyclization of 2-benzylamino-1,4-naphthoquinone to 1-hydroxy-2-aryl-1*H*-naphtho[2,3-*d*]-imidazole-4,9-dione [6] occurs by the radical mechanism and is initiated by the reaction of R-amino-1,4-naphthoquinones **I** with nitronium cation (Scheme 3).

The structure of hydroxyimidazole **IIId** was confirmed by physicochemical methods. In its ^{1}H NMR spectrum the proton signal of the hydroxy group appears in the weak field (12.7 ppm) like in the spectrum of 1-hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (13.2 ppm).

In the mass spectrm of hydroxyimidazole **IIId** the most intensive peak (*m/z* 57) corresponds apparently to the acylium cation $C_2H_5CO^+$. The fragmentation of

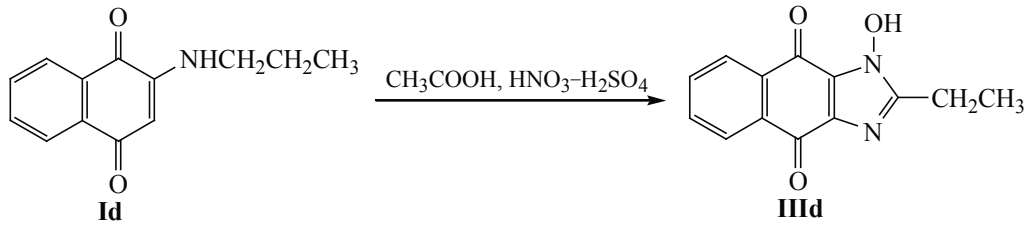
Scheme 1.



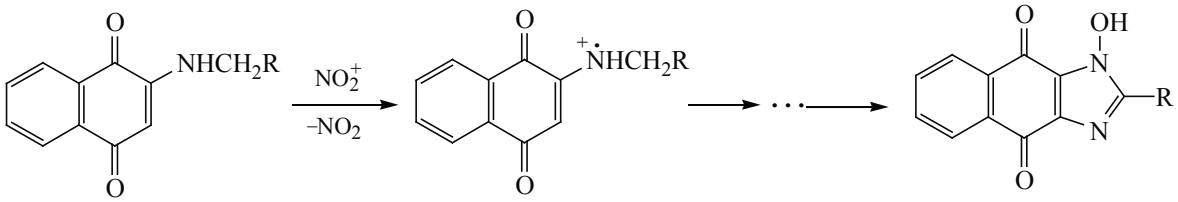
Ia–Ig **IIa–IIg**

R^1 = H, R^2 = H (**a**), CH_3 (**b**), C_2H_5 (**c**), $CH_2CH_2CH_3$ (**d**), C_4H_9 (**e**), $CH_2CH(CH_3)_2$ (**f**); R^1 = R^2 = CH_3 (**g**).

Scheme 2.



Scheme 3.



molecular ions of 1-hydroxy-2-aryl-1*H*-naphtho[2,3-*d*]-imidazole-4,9-diones proceeds also with the formation of aroyl cations [6].

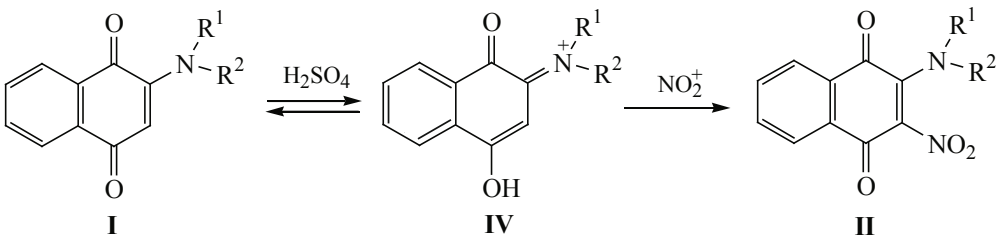
During the nitration of alkylaminoquinones **I** in conc. sulfuric acid apparently the nitronium cations react with protonated forms **IV** along the electrophilic substitution process (Scheme 4).

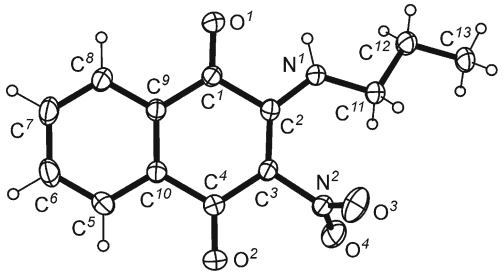
The protonation of aminoquinones **I** occurs at the carbonyl and not at the amino group as prove the data of UV spectroscopy. In the UV spectrum of aminoquinone **Ia** taken in ethanol the longwave band of the charge transfer from the amino group to the carbonyl group is present at 450 nm; in 30% sulfuric acid the absorption band in the visible region is retained (λ_{max} 450 nm), whereas the spectral curves in the region 250–400 nm suffer notable alterations. If the protonation of compound **Ia** occurred at the amino group the UV spectrum of the protonated amines would lack the longwave charge transfer band. The absorption caused by the charge transfer from the hydroxy group to the immonium fragment is also observed in the UV spectra of solutions of the other aminoquinones **Ia–Ig** in sulfuric acid.

Compounds **IIa–IIg** comprise a new group of quinoid compounds. Their structure was investigated by X-ray diffraction (XRD) (see the figure). According to XRD data there is a steric strain in the **IId** molecule, the C^1–C^2 bond length of 1.523(2) Å is considerably longer than this bond in the unsubstituted 1,4-naphthoquinone (1.472 and 1.476 Å [7]) and in 2-amino-1,4-naphthoquinone (1.488 Å [8]). The atoms N^1 and N^2 deviate from the plane of the bicyclic skeleton by +0.191(2) and –0.122(2) Å respectively. The nitro group is strongly turned with respect to the plane, the torsion angle $C^2C^3N^2O^3$ is 69.8(2)°, resulting in a decrease in its conjugation with the naphthoquinone skeleton. The bond length C^2–C^3, 1.369(2) Å, coincides with the length of its bond in the 2-[(3-methoxycarbonyl)propylamino]-1,4-naphthoquinone, 1.367 Å [9].

In the crystal **IId** molecules are connected into chains along the *b* axis by the hydrogen bonds N^1–H···O^2 [N–H 0.86(2), H···O 2.53(2) Å, N–H···O 157(2)°]. Among the intermolecular interactions the interactions of carbonyl groups C^1=O^1···C^4=O^2 [O^1···C^4 3.051(2) Å] and N^2–O^4···π(C^1–C^4) [distance O–centroid 2.991(1) Å] should be noted.

Scheme 4.





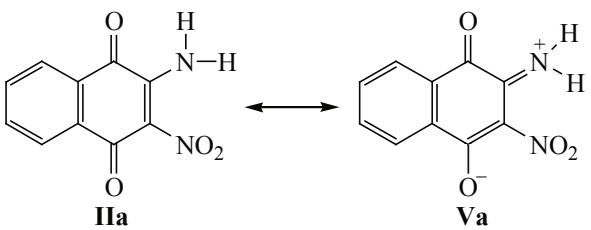
The structure of the molecule of 2-propylamino-3-nitro-1,4-naphthoquinone (**IId**).

The electron absorption spectra of 2-amino-3-nitronaphthoquinones **IIa–IIg** are distinguished from the spectra of initial amines **Ia–Ig** by the absorption band at ~290 nm, and also by the blue shift of the longwave absorption maxima by 20–50 nm. Evidently the blue shift of the longwave absorption maxima in the spectra of quinones **IIa–IIg** is caused by the displacement of the amino group from the coplanarity with the naphthoquinoid moiety, and also by the electron-withdrawing effect of the nitro group.

In the IR spectra of compounds **IIa–IIg** the stretching vibrations of the nitro group give rise to bands at 1516–1521, 1338–1342 cm^{-1} in compliance with the IR spectra of *o*-nitroanilines [10]. The bands of the stretching vibrations of the carbonyl groups appear at 1680–1690 cm^{-1}.

In the ^1H NMR spectra of compounds **II** the signals of protons at the nitrogen atom are shifted downfield by 1–1.5 ppm with respect to analogous signals of initial compounds, and the proton signals of the benzene ring of the molecule, by 0.05–0.15 ppm. In the ^1H NMR spectrum of compound **IIa** at 20°C the protons of the primary amino group are observed as two separate singlets (8.95 and 9.15 ppm), and at 60°C, as one signal at 8.75 ppm. Evidently the protons of the primary amino group are fixed due to the formation of intramolecular hydrogen bonds with the carbonyl and the nitro groups. It is also possible that the formation of two signals originates from the contribution of polar structure **Va**, like it is observed in primary amides [11]. At heating to 60°C the effect of these factors weakens (Scheme 5).

Scheme 5.



IIa **Va**

In compounds **IIc–IIf** the signal of the protons of the methylene group linked directly to the amino group is a broadened singlet both because of the fast intermolecular proton exchange and the changes in the molecule conformation [12].

In the ^{13}C NMR spectra of compounds **IIa, IIf** the signals of the carbonyl carbon atoms are shifted upfield by 2 and 8 ppm with respect to the signals in the spectra of compounds **Ia, If**.

EXPERIMENTAL

NMR spectra were recorded on a spectrometer Bruker DRX (500 MHz) in DMSO-d_6, internal reference TMS. Mass spectra were taken on an instrument Finnigan MAT 8200 (EI, 70 eV). Electron absorption spectra were recorded on a spectrophotometer Evolution 300 (cells 10 mm) in EtOH (layer thickness 1 cm, c 2 × 10^{-4} mol L^{-1}). IR spectra were registered on a spectrophotometer Shimadzu IRAffinity-1 from pellets with KBr. Melting points were measured on a heating microblock Boëtius. The elemental analysis was carried out on an analyzer Euro EA 3000. In the synthesis of compounds **Ia–Ig** commercial 1,4-naphthoquinone (Acros organics) was used. The reaction progress and the purity of compounds obtained were monitored by TLC on Silufol UV-254 plates (eluent toluene–acetone, 10 : 1). XRD experiment was carried out on a diffractometer Bruker APEX-II CCD [graphite monochromator, λ(MoK_α) 0.71073 Å, φ,ω-scanning, 2θ° < 56.6°, 200 K].

X-ray diffraction study of compound IId. Single crystals of compound **IId** were obtained after passing the benzene solution of compound **IId** through a column packed with silica gel (layer thickness 15 cm) followed by concentrating the eluate at 20–25°C and atmospheric pressure. mp 196°C. $C_{13}H_{12}N_2O_4$. Monoclinic crystal system, space group $C2/c$, a 20.2191(8), b 7.9146(2), c 15.8395(7) Å, β 109.137(2)°, V 2394.7(2) $Å^3$, Z 8, d_{calc} 1.444 g/cm^3, μ 0.109 cm^{-1}, number of measured reflections 10127, among them independent 2987 (R_{int} 0.0478), number of reflections with $I \geq 2\sigma(I)$ 2410. The correction for absorption was performed empirically using program SADABS (T_{min}/T_{max} 0.872/0.980). The structure was solved by the direct method. The positions and thermal parameters of atoms were refined in the anisotropic approximation by full matrix least-squares

procedure. The hydrogen atom of the amino group was localized from the difference maps and refined isotropically, the other hydrogen atoms were placed in the geometrically calculated positions and were included in the refinement in the riding model. The number of refined parameters 178, wR_2 0.1325, S 1.012 (for all reflections), R_1 0.0456 [$I \geq 2\sigma(I)$]. All calculations were carried out applying SHELX software. The data obtained were deposited in Cambridge Crystallographic Data Center, CCDC 948698.

2-Amino-1,4-naphthoquinone (Ia) was obtained from 1,4-naphthoquinone and sodium azide in acetic acid [13]. UV spectrum, λ_{max}, nm (log ε), in EtOH: 226 (4.28), 330 (3.41), 444 (3.42); in 30% H_2SO_4: 227 (4.49), 263 (4.34), 300 (4.00), 356 (3.43), 468 (3.48). ^{1}H NMR spectrum, δ, ppm: 5.80 s (1H, H^3), 7.2 br.s (2H, NH_2), 7.72 t [1H, H$^{6(7)}$, *J* 7.5 Hz], 7.81 t [1H, H$^{7(6)}$, *J* 7.5 Hz], 7.92 d [1H, H$^{5(8)}$, *J* 7.6 Hz], 7.98 d [1H, H$^{8(5)}$, *J* 7.6 Hz]. Mass spectrum, *m/z* (I_{rel}, %): 173 (80.6) $[M]^+$, 105 (70.9), 76 (100), 50 (86.2), 41 (68.3).

2-Dimethylamino-1,4-naphthoquinone (Ig) and 2-alkylamino-1,4-naphthoquinones Ib–If were synthesized along procedures described respectively in [14, 15]. The yield of 2-alkylamino-1,4-naphthoquinone **Ib–Ig** can be increased by using as solvent 2-propanol instead of methanol.

2-Isobutylamino-1,4-naphthoquinone (If). Into 50 mL of 2-propanol was charged 8 g (0.05 mol) of 1,4-naphthoquinone, to the solution 6 mL of isobutylamine in 10 mL of 2-propanol was added. The reaction mixture was heated at stirring at 40–50°C for 30 min, then at the same temperature and stirring 40 mL of water was added. The reaction mixture was heated to 70°C and cooled to –10°C within 10 h. The separated precipitate was filtered off, washed with 50 mL of 20% aqueous ethanol, and dried. Yield 7.2 g (63%), mp 124°C. UV spectrum, λ_{max}, nm (log ε): 273 (4.36), 328 (3.32), 457 (3.52). IR spectrum, ν, cm^{-1}: 3323 s (NH), 1678 s (C=O). ^{1}H NMR spectrum, δ, ppm: 0.90 d (6H, $2CH_3$, *J* 6.7 Hz), 1.98 septet (1H, CH, *J* 6.7 Hz), 3.01 br.t (2H, CH_2, *J* 6.7 Hz), 5.70 s (1H, H^3), 7.59 br.t (1H, NH, *J* 6.2 Hz), 7.72 t [1H, H$^{6(7)}$, *J* 7.6 Hz], 7.83 t [1H, H$^{7(6)}$, *J* 7.6 Hz], 7.94 d [1H, H$^{5(8)}$, *J* 7.6 Hz], 7.99 d [1H, H$^{8(5)}$, *J* 7.6 Hz]. ^{13}C NMR spectrum, δ, ppm: 20.2 (2C, $2CH_3$), 26.7 (1C, CH), 49.2 (1C, CH_2), 99.3 (1C, C^3), 125.3 [1C, C$^{8(5)}$], 125.8 [1C, C$^{5(8)}$], 130.4 [1C, C$^{4a(8a)}$], 132.0 [1C, C$^{6(7)}$], 133.2 [1C, C$^{8a(4a)}$], 134.8 [1C, C$^{7(6)}$], 148.7 (1C, C^2), 181.2 [1C, C$^{1(4)}$], 181.6 [1C, C$^{4(1)}$]. Mass spectrum, *m/z* (I_{rel}, %): 229 (26.6) $[M]^+$, 186 (100), 43 (35.4). Found, %: C 73.73; H 6.48; N 6.22. $C_{14}H_{15}NO_2$. Calculated, %: C 73.36; H 6.55; N 6.11.

2-Amino-3-nitro-1,4-naphthoquinone (IIa). To the cooled to 5°C solution of 1.73 g (0.01 mol) of 2-amino-1,4-naphthoquinone (**Ia**) in 30 mL of 94% sulfuric acid was added within 5 min the nitrating mixture prepared from 1.6 mL of 60% nitric and 2.4 mL of 94% sulfuric acids. After stirring for 30 min the reaction mixture was poured into 150 g of water with ice. The orange precipitate was filtered off, washed with water to neutral washings, and dried. Yield 1.85 g (84%), mp 228°C (alcohol–benzene, 1 : 1). UV spectrum, λ_{max}, nm (log ε): 249 (4.22), 291 (3.16), 399 (3.45). ^{1}H NMR spectrum, δ, ppm (20°C): 7.82 t [1H, H$^{6(7)}$, *J* 7.6 Hz], 7.93 t [1H, H$^{7(6)}$, *J* 7.6 Hz], 8.05 d [1H, H$^{5(8)}$, *J* 7.6 Hz], 8.08 d [1H, H$^{8(5)}$, *J* 7.6 Hz], 8.92 br.s (1H, NH), 9.15 br.s (1H, NH). ^{1}H NMR spectrum, δ, ppm (60°C): 7.82 t [1H, H$^{6(7)}$, *J* 7.6 Hz], 7.93 t [1H, H$^{7(6)}$, *J* 7.6 Hz], 8.05 d [1H, H$^{5(8)}$, *J* 7.6 Hz], 8.08 d [1H, H$^{8(5)}$, *J* 7.6 Hz], 8.80 br.s (2H, NH_2). ^{13}C NMR spectrum, δ, ppm: 179.4 (1C, C^1), 172.8 (1C, C^4). Mass spectrum, *m/z* (I_{rel}, %): 218 (59.4) $[M]^+$, 89 (100), 76 (80.3), 50 (66.3). Found, %: C 55.64; H 2.74; N 12.87. $C_{10}H_6N_2O_4$. Calculated, %: C 55.15; H 2.75; N 12.84.

2-Methylamino-3-nitro-1,4-naphthoquinone (IIb). To the cooled to 5°C solution of 1.87 g (0.01 mol) of 2-methylamino-1,4-naphthoquinone (**Ib**) in 30 mL of 94% sulfuric acid was added within 5 min the nitrating mixture prepared from 1.6 mL of 60% nitric and 2.4 mL of 94% sulfuric acids. After stirring for 30 min the reaction mixture was poured into 150 g of water with ice. The orange precipitate was filtered off, washed with water to neutral washings, and dried. Yield 2.1 g (92%), mp 234°C. UV spectrum, λ_{max}, nm (log ε): 250 (4.30), 293 (3.96), 331 (3.48), 432 (3.47). ^{1}H NMR spectrum, δ, ppm: 2.80 s (3H, CH_3), 7.81 t [1H, H$^{6(7)}$, *J* 7.6 Hz], 7.92 t [1H, H$^{7(6)}$, *J* 7.6 Hz], 8.05 d [2H, H^{5,8}, *J* 7.6 Hz], 8.68 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 232 (18.0) $[M]^+$, 202 (14.5), 188 (5.1), 76 (83.9), 50 (57.4), 30 (100). Found, %: C 57.08; H 3.50; N 12.10. $C_{11}H_8N_2O_4$. Calculated, %: C 56.89; H 3.44; N 12.07.

3-Nitro-2-ethylamino-1,4-naphthoquinone (IIc). To the cooled to 5°C solution of 1.01 g (0.005 mol) of 2-ethylamino-1,4-naphthoquinone (**Ic**) in 15 mL of 94% sulfuric acid was added within 5 min the nitrating mixture prepared from 0.8 mL of 60% nitric and 1.2 mL of 94% sulfuric acids. After stirring for 20 min the reaction mixture was poured into 150 g of water with ice. The

orange precipitate was filtered off, washed with water. Yield 1.0 g (81%), mp 224°C (alcohol–benzene, 1 : 1). UV spectrum, λ_{max}, nm (log ε): 251 (3.38), 295 (3.97), 431 (3.49). ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3, *J* 7.1 Hz), 3.20 br.s (2H, CH_2), 7.81 t [1H, H$^{6(7)}$, *J* 7.1 Hz], 7.92 t [1H, H$^{7(6)}$, *J* 7.1 Hz], 8.40 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 246 (6.9) [*M*]$^+$, 76 (40.8), 50 (29.0), 30 (100)**.** Found, %: C 58.61; H 3.92; N 11.86. $C_{12}H_{10}N_2O_4$. Calculated, %: C 58.53; H 4.06; N 11.38.

3-Nitro-2-propylamino-1,4-naphthoquinone (IId). A solution of 1.08 g (0.005 mol) of 2-propylamino-1,4-naphthoquinone (**Id**) in 15 mL of conc. H_2SO_4 was cooled to 5°C and 2 mL of nitrating mixture prepared from 0.8 mL of 60% nitric and 1.2 mL of 94% sulfuric acids was added. After stirring for 20 min the reaction mixture was poured into water with ice. The orange precipitate was filtered off, washed with water. Yield 1.2 g (92%), mp 196°C (alcohol–benzene, 1 : 1). UV spectrum, λ_{max}, nm (log ε): 251 (4.45), 289 (4.10), 434 (3.57). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH_3, *J* 7.4 Hz), 1.59 sextet (2H, CH_2, *J* 7.3 Hz), 3.10 s (2H, $\underline{CH_2}$NH), 7.82 t [1H, H$^{6(7)}$, *J* 7.6 Hz], 7.92 t [1H, H$^{7(6)}$, *J* 7.6 Hz], 8.05 t (2H, H^{5,8}, *J* 7.6 Hz), 8.40 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 260 (24.7) [*M*]$^+$, 76 (70.1), 531.6), 41 (100). Found, %: C 59.85; H 4.55; N 10.68. $C_{13}H_{12}N_2O_4$. Calculated, %: C 60.00; H 4.62; N 10.70.

2-Butylamino-3-nitro-1,4-naphthoquinone (IIe). A solution of 1.15 g (0.005 mol) of 2-butylamino-1,4-naphthoquinone (**Ie**) in 15 mL of conc. H_2SO_4 was cooled to 5°C and 2 mL of nitrating mixture prepared from 0.8 mL of 60% nitric and 1.2 mL of 94% sulfuric acids was added. After stirring for 20 min the reaction mixture was poured into water with ice. The orange precipitate was filtered off, washed with water. Yield 1.2 g (87%), mp 120°C (from alcohol). UV spectrum, λ_{max}, nm (log ε): 260 (4.30), 292 (4.00), 330 (3.54), 432 (3.54). ^{1}H NMR spectrum, δ, ppm: 0.86 t (3H, CH_3, *J* 7.4 Hz), 1.27 sextet (2H, $\underline{CH_2}CH_3$, *J* 7.5 Hz), 1.55 quintet (2H, $\underline{CH_2}CH_2CH_3$, *J* 7.2 Hz), 3.12 br.s (2H, NH$\underline{CH_2}$), 7.82 t [1H, H$^{6(7)}$, *J* 7.0 Hz], 7.92 t [1H, H$^{7(6)}$, *J* 7.0 Hz], 8.04 t (2H, H^{5,8}, *J* 7.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 274 (4.9) [*M*]$^+$, 227 (30.0), 76 (32.6), 41 (100)**.** Found, %: C 61.02; H 4.89; N 10.04. $C_{14}H_{14}N_2O_4$. Calculated, %: C 61.31; H 5.11; N 10.22.

2-Isobutylamino-3-nitro-1,4-naphthoquinone (IIf). A solution of 1.15 g (0.005 mol) of 2-isobutylamino-1,4-naphthoquinone (**If**) in 15 mL of concn. H_2SO_4 was cooled to 5°C and 2 mL of nitrating mixture prepared from 0.8 mL of 60% nitric and 1.2 mL of 94% sulfuric acids was added. After stirring for 20 min the reaction mixture was poured into water with ice. The orange precipitate was filtered off, washed with water. Yield 1.1 g (80%), mp 174°C (from alcohol). UV spectrum, λ_{max}, nm (log ε): 257 (4.27), 295 (3.96), 331 (3.51), 432 (3.49). ^{1}H NMR spectrum, δ, ppm: 0.85 d (6H, $2CH_3$, *J* 6.6 Hz), 1.87 quintet (1H, CH, *J* 6.6 Hz), 2.90 br.s (2H, CH_2, *J* 7.6 Hz), 7.82 t [1H, H$^{6(7)}$, *J* 7.6 Hz], 7.92 t [1H, H$^{7(6)}$, *J* 7.6 Hz], 8.03–8.08 m (2H, H^{5,8}), 8.45 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 19.87 (2C, $2CH_3$), 28.23 (1C, CH), 50.04 (1C, CH_2), 126.07 [1C, C$^{5(8)}$], 126.8 [1C, C$^{8(5)}$], 128.18 [1C, C$^{4a,(8a)}$], 129.74 [1C, C$^{8a,(4a)}$], 131.11 (1C, C^2), 133.29 [1C, C$^{6(7)}$], 135.72 [1C, C$^{7(6)}$], 139.75 (1C, C^3). Mass spectrum, *m/z* (I_{rel}, %): 274 (7.3) [*M*]$^+$, 228 (6.8), 174 (19.6), 50 (8.6), 41 (100). Found, %: C 61.17; H 5.01; N 10.03. $C_{14}H_{14}N_2O_4$. Calculated, %: C 61.31; H 5.11; N 10.22.

2-Dimethylamino-3-nitro-1,4-naphthoquinone (IIg). A solution of 0.8 g (0.004 mol) 2-dimethylamino-1,4-naphthoquinone (**Ig**) in 15 mL of 94% sulfuric acid was cooled to 5°C and 1.5 mL of nitrating mixture prepared of 0.6 mL of 60% nitric and 0.9 mL of 94% sulfuric acids was added. After stirring for 20 min the reaction mixture was poured into water with ice. The orange precipitate was filtered off, washed with ethanol. Yield 0.75 g (76%), mp 151°C. UV spectrum, λ_{max}, nm (log ε): 251 (4.35), 293 (3.97), 432 (3.49). ^{1}H NMR spectrum, δ, ppm: 3.34 s (6H, $2CH_3$), 7.81 t [1H, C$^{6(7)}$, *J* 7.5 Hz], 7.88 t [1H, C$^{7(6)}$, *J* 7.5 Hz], 7.96 d [1H, C$^{5(8)}$, *J* 7.6 Hz], 8.00 d [1H, C$^{8(5)}$, *J* 7.6 Hz]. Mass spectrum, *m/z* (I_{rel}, %): 246 (29.73) [*M*]$^+$, 158 (45.1), 76 (100), 50 (52.2), 30 (60.9). Found, %: C 58.57; H 3.88; N 11.17. $C_{12}H_{10}N_2O_4$. Calculated, %: C 58.54; H 4.06; N 11.38.

1-Hydroxy-2-ethyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (IIId). To a solution of 1.08 g (0.005 mol) of 2-propylamino-1,4-naphthoquinone in 20 mL of acetic acid was added within 5 min at 20°C nitrating mixture prepared of 1.5 mL of 60% nitric and 2.5 mL of 94% sulfuric acids. The reaction mixture was stirred for 30 min while self-heating to 40°C. The liberation of nitrogen oxides was observed. The reaction mixture was cooled to 20°C and poured into ice mixture with water (~100 g), the orange precipitate was filtered off, washed with water, dried, and recrystallized from alcohol–benzene, 1 : 1. Yield 0.54 g (44%), mp 291°C. UV spectrum, λ_{max}, nm (log ε): 280 (4.49), 375 (3.75), 461 (3.81). ^{1}H NMR spectrum, δ, ppm: 1.29 t (3H, CH_3, *J* 7.6 Hz), 2.80 q (2H,

CH_2, *J* 7.6 Hz), 7.82–7.86 m (2H, $H^{6,7}$), 8.04–8.10 m (2H, $H^{5,8}$). Mass spectrum, *m/z* (I_{rel}, %): 242 (6.3) $[M]^+$, 186 (62.8), 57 (100). Found, %: C 64.03; H 3.94; N 11.13. $C_{13}H_{10}N_2O_3$. Calculated, %: C 64.46; H 4.13; N 11.57.

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