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Synthesis of 2,4,6,8-Tetrasubstituted 1,5-Naphthoquinones

L.V. Ektova, A.D. Bukhtoyarova, and V.V. Shelkovnikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia (3832) 308752
e-mail: vsh@nioch.nsc.ru

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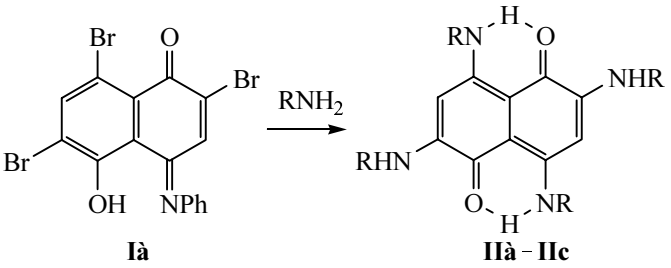
Abstract—Derivatives of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines react with primary amines to afford 2,4,6,8-tetrasubstituted 1,5-naphthoquinones.

1,5-Naphthoquinone (*ana*-naphthoquinone) is an extremely unstable compound [1]. Among its known stable derivatives 4,8-di(alkylamino)- [2] and 4,8-di-(arylamino)-1,5-naphthoquinones [3, 4] and also 2,6-bis-[alkyl(aryl)amino]naphthazarins [4] can be cited. The latter were suggested for use as molecular media for nonlinear optical materials [4, 5] and as dichroic dyes in the liquid-crystal compositions for electrooptics of the "guest-host" type [6]. The initial compounds in the synthesis of these 1,5-naphthoquinone derivatives were naphthazarin and 4,8-di(amino)-1,5-naphthoquinone [4].

In extension of the research on the reactivity of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines a new approach is developed in the present study to the preparation of versatile tetrasubstituted 1,5-naphthoquinones. The essence of the approach is based on the fact that the possibility of existence in the 1,5-naphthoquinoid form is inherent to the structure of 5-hydroxy-1,4-naphthoquinone 4-imine due to a prototropic tautomeric rearrangement [7]. Taking into account the data on stabilization of the *ana*-quinoid form by introducing electron-donor substituents into position *8* [7], we set as the goal of this study the preparation of 1,5-naphthoquinone derivatives by amination of substituted *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines.

N-Aryl-5-hydroxy-1,4-naphthoquinone 4-imines in contrast to N-aryl-1,4-naphthoquinone imine lacking the hydroxy group react with arylamines at both rings of the naphthoquinone imine [8].

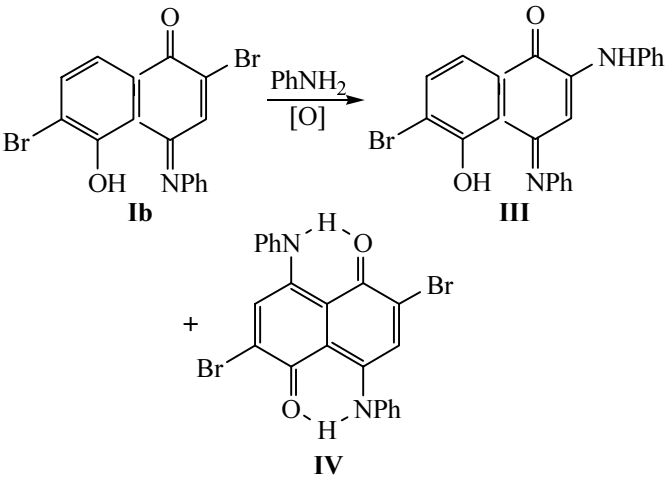
We found that 2,6,8-tribromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinone 4-imine (**Ia**) prepared formerly from 2,4,6,8-tetrabromo-1,5-dihydroxynaphthalene [9] at boiling with *n*-butylamine or *n*-heptylamine in ethanol under basic catalysis (in the presence of K_2CO_3) or with excess aniline afforded 2,4,6,8-tetrabutylamino- (**IIa**), 2,4,6,8-tetraheptylamino- (**IIb**), or 2,4,6,8-tetraphenylamino-1,5-naphthoquinone (**IIc**) respectively.



Ià **IIà – IIc**

R = *n*-C_4H_9 (**a**), *n*-C_7H_{15} (**b**), Ph (**c**).

The reaction of 2,6-dibromo-5-hydroxy-N-phenyl-1,4-naphthoquinone 4-imine (**Ib**) [7] with aniline in the presence of an oxidant gave rise to a mixture of 6-bromo-5-hydroxy-2-phenylamino-N-phenyl-1,4-naphthoquinone 4-imine (**III**) and 2,6-dibromo-4,8-di(phenylamino)-1,5-naphthoquinone (**IV**).



Ib **III** **IV**

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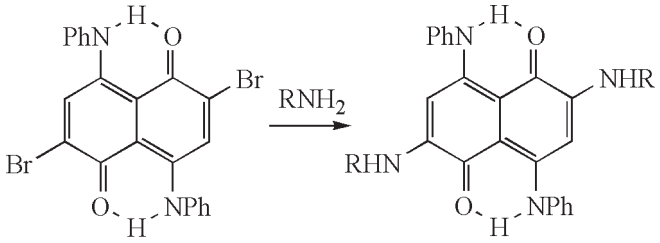
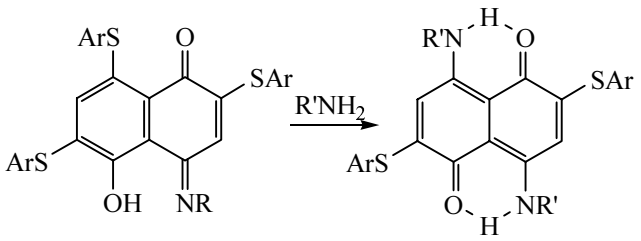
2,6-Di(butylamino)- (**Va**) and 2,6-di(heptylamino)-4,8-di(phenylamino)-1,5-naphthoquinone (**Vb**) were obtained by replacement of bromine in 2,6-dibromo-4,8-di-(phenylamino)-1,5-naphthoquinone (**IV**) by *n*-alkylamino groups.



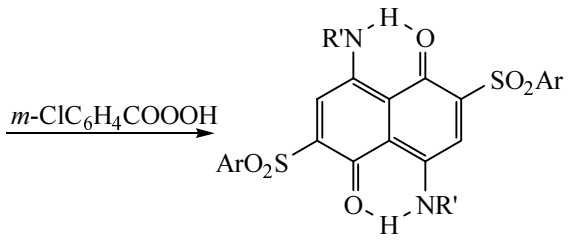
IV **Va, Vb**

R = *n*-C_4H_9 (**a**), *n*-C_7H_{15} (**b**).

Previously *N*-aryl-2,6,8-tri(4-*tert*-butylphenylthio)-5-hydroxy-1,4-naphthoquinone 4-imines **VIa** and **VIb** were reacted with aniline to obtain 2,6-di(4-*tert*-butylphenylthio)-4,8-di(phenylamino)-1,5-naphthoquinone (**VIIa**) [10].



VIà–VIc **VIIà, VIIc, VIId**



VIIIà, VIIIc

Ar = 4-$(CH_3)_3CC_6H_4$, R = Ph (**a**), 4-$Et_2NC_6H_4$ (**b**), 4-$C_4H_9OC_6H_4$ (**c**); R' = Ph (**a**), 4-$C_4H_9OC_6H_4$ (**c**), 4-$C_6H_{13}C_6H_4$ (**d**).

Similarly from compounds **VIb** and **VIc** with 4-butoxyaniline and 4-hexylaniline were obtained the corresponding 4,8-di(arylamino)-1,5-naphthoquinones **VIIc** and **VIId** containing two arylthio groups in the positions *2* and *6*.

The oxidation of arylthio groups in 4,8-di(arylamino)-2,6-di(4-*tert*-butylphenylthio)-1,5-naphthoquinones **VIIa** and **VIIc** with *m*-chloroperbenzoic acid in chloroform by procedure [11] afforded tetrasubstituted 1,5-naphthoquinones **VIIIa** and **VIIIc** having in positions *2* and *6* electron-withdrawing substituents SO_2Ar.

The structure of compounds obtained was established from spectral and analytical data. In the mass spectra of compounds synthesized strong molecular ions peaks were registered with *m/z* values corresponding to the calculated ones. In the IR spectra of 1,5-naphthoquinones obtained the absorption bands of stretching vibrations of the C=O groups are strongly displaced to the low frequency region (1620–1580 cm^{-1}) in keeping with the characteristic pattern for the carbonyl groups located in different rings of a fused system [3, 12]. In the ^1H NMR spectra of the 1,5-naphthoquinone derivatives the proton signals from NH groups attached to positions *4* and *8* appear downfield (12.16–14.45 ppm) due to formation of strong hydrogen bonds as has been also observed in the spectra of the described 4,8-di[alkyl(aryl)amino]-1,5-naphthoquinones [2, 3] whereas the proton signals from the NHR groups in the *2* and *6* positions are observed at 6.60–8.40 ppm

The study of 4,8-di(alkylamino)-1,5-naphthaquinones tautomerism by means of ^1H [2, 3, 7] and ^{13}C [13] NMR spectroscopy revealed that these compounds exist in the *ana*-quinoid and not in the *ana*-quinone imine form.

The electron absorption spectra of 2,4,6,8-tetrasubstituted 1,5-naphthoquinone derivatives like those described for 4,8-diamino-1,5-naphthoquinones [2, 3] contain in the visible region a strong absorption band with a pronounced vibronic structure. Depending on the character of the substituents the position of the strongest absorption maximum varies from 577 nm for 2,4,6,8-tetraalkylamino-1,5-naphthoquinones **IIa** and **IIb** to 763 nm for 4,8-di(arylamino)-2,6-di(4-*tert*-butylphenyl-sulfonyl)-1,5-naphthoquinone (**VIIIc**). The comparison with the spectra of 4,8-di(methylamino)-1,5-naphtho-quinone (λ_{max} 606, 657 nm [2]) and 4,8-di(phenylamino)-1,5-naphthoquinone (λ_{max} 625, 667 nm [3]) showed that introduction of the electron-donor substituents (NHAlk) into positions *2* and *6* resulted in a blue shift of the long-wave absorption band accompanied with growing intensity, whereas the electron-acceptor groups $ArSO_2$ exerted the opposite influence. The presence in positions *2* and *6* bromine atoms or 4-*tert*-butylphenylthio groups possessing *–I* and *+M*-effects caused the red shift of λ_{max} with the simultaneous increase in the intensity of the absorption band.

In the electron absorption spectra of compound **Va** registered in solvents of different polarity (CCl_4, $CHCl_3$, and EtOH) a negative solvatochromism of the long-wave absorption band was observed, similar to that described for 4,8-diamino derivatives of 1,5-naphthoquinone [2, 3].

Compounds **IIc**, **IV**, **VIIa**, **VIIc**, and **VIId** were tested as dichroic dyes in the liquid-crystal composites [14]. It was shown that the introduction of 4-*tert*-butylphenylthio groups into positions *2* and *6* of 4,8-di(arylamino)-1,5-naphthoquinones (compounds **VIIa**, **VIIc**, and **VIId**) resulted in increased value of the order parameter *S* and increased contrast of the composites.

Thus the amination of derivatives of *N*-aryl-5-hydroxy-1,4-naphthoquinone 4-imines provided a possibility to go from compounds with the *para*-quinoid structure to the derivatives with the *ana*-quinoid structure.

EXPERIMENTAL

IR spectra were recorded on spectrophotometers UR-20 and Vector- 22 from samples pelletized with KBr, the electron absorption spectra in the visible region were measured on spectrophotometers Hewlett Packard 4853 and Beckmann DU-8. ^{1}H NMR spectra were registered on spectrometers Bruker WP-200 SY and AM-400 in $CDCl_3$. Molecular mass and elemental composition of compounds was determined from the precision measurement of molecular ions mass on Finnigan MAT 8200 and Finnigan AEI MS-900 instruments.

Initial 2,6,8-tribromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinone 4-imine (**Ia**) and 2,6-dibromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinone 4-imine (**Ib**) were obtained as described in [7], 2,6,8-tribromo-*N*-(4-butoxyphenyl)-5-hydroxy-1,4-naphthoquinone 4-imine (**Ic**) was prepared by procedure from [9].

The monitoring of reaction progress and the checking of the products purity was carried out by TLC on Silufol plates, eluent $CHCl_3$.

Synthesis of 2,4,6,8-tetraalkylamino-1,5-naphthoquinones IIa and IIb. A mixture of 0.5 mmol of 2,6,8-tribromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinone 4-imine (**Ia**), 2 mmol of *n*-butylamine or *n*-heptylamine, 0.2 g of K_2CO_3, and 40 ml of EtOH was heated at reflux for 20 h. The reaction mixture was poured into water and neutralized with 5% HCl, the precipitate was filtered off, washed with water, dried, and subjected to chromatography on a column packed with Al_2O_3, eluent CCl_4.

2,4,6,8-Tetrabutylamino-1,5-naphthoquinone (IIa). Yield 68%, mp 131–135°C (benzene–heptane, 1:5). IR spectrum, ν, cm^{-1}: 1605 (C=O), 2857, 2870, 2924, 2952 (CH), 3288 (NH). ^{1}H NMR spectrum, δ, ppm: 0.96 t (12H, $4CH_3$), 1.45–1.52 m (8H, $4CH_2$), 1.68–1.74 m (8H, $4CH_2$), 3.21 m (4H, $2CH_2$), 3.39 m (4H, $2CH_2$), 5.56 s (2H, H^{3,7}), 6.60 br.s (2H, 2NH), 12.22 br.s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 400 (4.30), 546 (4.08), 577 (4.38). Found: [*M*]$^+$ 442.33075. $C_{26}H_{42}N_4O_2$. Calculated: *M* 442.33076.

2,4,6,8-Tetraheptylamino-1,5-naphthoquinone (IIb). Yield 57%, mp 130–131°C (benzene–heptane, 1:5). IR spectrum, ν, cm^{-1}: 1604 (C=O), 2852, 2919, 2955 (CH), 3276 (NH). ^{1}H NMR spectrum, δ, ppm: 0.86 t (12H, $4CH_3$), 1.05–1.51 m (32H, $16CH_2$), 1.52–2.00 m (8H, $4CH_2$), 3.19 m (4H, $2CH_2$), 3.36 m (4H, $2CH_2$), 5.53 s (2H, H^{3,7}), 6.60 br.s (2H, 2NH), 12.16 br.s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 400 (4.35), 536 (4.15), 577 (4.42). Found: [*M*]$^+$ 610.51835. $C_{38}H_{66}N_4O_2$. Calculated: *M* 610.51855.

Synthesis of 2,4,6,8-tetraphenylamino-1,5-naphthoquinone (IIc). A mixture of 0.5 mmol of compound **Ia** and 1 mmol of aniline was heated at 150°C for 0.5 h. The reaction mixture was poured into water and neutralized with 5% HCl, the precipitate was filtered off, washed with water, dried, and subjected to chromatography on a column packed with SiO_2, eluent $CHCl_3$. Yield 73%, mp 303–304°C (benzene). IR spectrum, ν, cm^{-1}: 1620 (C=O), 3030, 3060 (=CH), 3230 (NH). ^{1}H NMR spectrum, δ, ppm: 6.86 s (2H, H^{3,7}), 7.07–7.43 m (10H, $2C_6H_5$), 8.40 s (2H, 2NH), 13.97 s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 445 (4.62), 581 (4.49), 624 (4.64). Found: [*M*]$^+$ 522.20654. $C_{34}H_{26}N_4O_2$. Calculated: *M* 522.20556.

Reaction of 2,6-dibromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinone 4-imine (Ib) with aniline in the presence of $Na_2S_2O_8$. To a dispersion of 1 mmol of compound **Ib** and 10 mmol of aniline in 200 ml of EtOH was added dropwise at stirring a solution of 2 mmol of $Na_2S_2O_8$ in 20 ml of water, and the mixture was kept at 20°C for 7 days with intermittent stirring. The reaction mixture was poured into water and neutralized with 5% HCl, the precipitate was filtered off, washed with water, dried, then it was dissolved in $CHCl_3$ and subjected to chromatography on plates with SiO_2, eluent CCl_4–$CHCl_3$, 1:1. From the brown zone initial compound **Ib** was isolated. Yield 5%. From the green zone was isolated **2,6-dibromo-4,8-di(phenylamino)-1,5-naphthoquinone (IV)**. Yield 24%, mp 324–325°C (benzene). IR spectrum, ν, cm^{-1}: 1577 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.24–7.50 m (10H, 2 C_6H_5), 7.94 s (2H, H^{3,7}), 14.43 s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (lgε): 641 (4.49), 686 (4.69). Found: [*M*]$^+$ 495.94225. $C_{22}H_{14}N_2O_2Br_2$. Calculated: *M* 495.94230. From the violet zone was isolated **2-anilino-6-bromo-5-hydroxy-**

***N*-phenyl-1,4-naphthoquinone 4-imine (III).** Yield 59%, mp 259–260°C (chloroform).

Synthesis of 2,6-di(alkylamino)-4,8-di(phenylamino)-1,5-naphthoquinones Va and Vb. A mixture of 0.3 mmol of 2,6-dibromo-4,8-di(phenylamino)-1,5-naphthoquinone (**IV**) and 1.5 mmol of *n*-butylamine or *n*-heptylamine in 30 ml of EtOH was heated at reflux for 15 h. The reaction mixture was evaporated to the half of its volume, then it was poured into water, the precipitate was filtered off, washed with water, dried, and subjected to column chromatography on Al_2O_3, eluent CCl_4–$CHCl_3$, 1:1.

2,6-Di(butylamino)-4,8-di(phenylamino)-1,5-naphthoquinone (Va). Yield 62%, mp 221–223°C (benzene). IR spectrum, ν, cm^{-1}: 1605 (C=O), 2869, 2939, 2955 (CH), 3037, 3060 (=CH), 3277 (NH). ^1H NMR spectrum, δ, ppm: 0.89 t (6H, $2CH_3$), 1.30–1.48 m (4H, $2CH_2$), 1.52–1.66 m (4H, $2CH_2$), 3.09 m (4H, $2CH_2$), 6.03 s (2H, $H^{3,7}$), 6.61 t (2H, 2NH), 7.19–7.45 m (10H, $2C_6H_5$), 13.99 br.s (2H, 2NH). Electronic spectrum, λ_{max}, nm (lgε) (CCl_4): 412 (4.14), 550 (4.12), 598 (4.40); ($CHCl_3$): 416 (4.31), 550 (4.20), 592 (4.48); (EtOH): 415 (4.23), 550 (4.19), 584 (4.42). Found: $[M]^+$ 482.26811. $C_{30}H_{34}N_4O_2$. Calculated: *M* 482.26816.

2,6-Di(heptylamino)-4,8-di(phenylamino)-1,5-naphthoquinone (Vb). Yield 67%, mp 213–215°C (benzene). IR spectrum, ν, cm^{-1}: 1607 (C=O), 2870, 2930, 2950 (CH), 3030, 3060 (=CH), 3280 (NH). ^1H NMR spectrum, δ, ppm: 0.86 t (6H, $2CH_3$), 1.18–1.42 m (16H, $8CH_2$), 1.52–1.69 m (4H, $2CH_2$), 3.08 m (4H, $2CH_2$), 6.03 s (2H, $H^{3,7}$), 6.63 t (2H, 2NH), 7.16–7.45 m (10H, $2C_6H_5$), 13.95 br.s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (lgε): 419 (4.36), 560 (4.28), 592 (4.51). Found: $[M]^+$ 566.36213. $C_{36}H_{46}N_4O_2$. Calculated: *M* 566.36206.

Synthesis of 2,6,8-tri(4-*tert*-butylphenylthio)-*N*-(4-butoxyphenyl)-5-hydroxy-1,4-naphthoquinone 4-imine (VIc). A mixture of 0.5 mmol of 2,6,8-tribromo-*N*-(4-butoxyphenyl)-5-hydroxy-1,4-naphthoquinone 4-imine (**Ic**) and 6 mmol of 4-*tert*-butylthiophenol in 5 ml of pyridine was stirred at 20°C for 45 min. The reaction mixture was poured on ice, the separated precipitate was filtered off, washed with water, dried, and subjected to column chromatography on SiO_2, eluent benzene. Yield 47%, mp 199–200°C (benzene–hexane, 1:5). IR spectrum, ν, cm^{-1}: 1246 (C–O–), 1583 (C=N), 1605 (C=O), 3431 (OH). ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3), 1.27 s (9H, $3CH_3$), 1.31 s (9H, $3CH_3$), 1.36 s (9H, $3CH_3$), 1.44–1.53 m (2H, CH_2), 1.70–1.78 m (2H, CH_2), 3.87 t (2H, CH_2), 6.45 s (1H, $H^{3(7)}$), 6.68 s (1H, $H^{7(3)}$), 6.73 d (2H, H_{arom}, J_O 9.0 Hz), 6.87 d (2H, H_{arom}, J_O 9.0 Hz), 7.12–7.29 m (8H, H_{arom}), 7.38 C (4H, H_{arom}), 16.53 br.s (1H, OH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 451 (4.60), 600 (4.61), 641 (4.62), 699 (4.63). Found, %: C 73.99; H 6.65; N 1.70; S 11.96. $C_{50}H_{55}NO_3S_3$. Calculated, %: C 73.80; H 6.76; N 1.72; S 11.82.

Synthesis of 2,6-di(4-*tert*-butylphenylthio)-4,8-di-(4-butoxyphenylamino)-1,5-naphthoquinone (VIIc). A mixture of 0.25 mmol of compound **VIc** and 0.50 mmol of 4-butoxyphenylamine in 5 ml of pyridine was heated at 120°C for 24 h. The reaction mixture was cooled, poured into water, neutralized with 5% HCl, the precipitate was filtered off, washed with water, dried, and subjected to chromatography on a column packed with SiO_2, eluent benzene. Yield 43%, mp 310–311°C (benzene–hexane, 1:5). IR spectrum, ν, cm^{-1}: 1230 (C–O–), 1580 (C=C), 1600 (C=O), 2950 (CH). ^1H NMR spectrum, δ, ppm: 1.01 t (6H, $2CH_3$, *J* 7.0 Hz), 1.30 s (18H, $6CH_3$), 1.45–1.57 m (4H, $2CH_2$), 1.70–1.84 m (4H, $2CH_2$), 3.91 t (4H, $2CH_2$, *J* 7.0 Hz), 6.54 s (2H, $H^{3,7}$), 6.76 d (4H, H_{arom}, J_O 10.0 Hz), 6.96 d (4H, H_{arom}, J_O 10.0 Hz), 7.43 br.s (8H, H_{arom}), 14.02 s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 449 (4.16), 640 (4.28), 709 (4.51). Found, %: C 73.82; H 6.99; N 3.50; S 7.90. $C_{50}H_{56}N_2O_4S_2$. Calculated, %: C 73.89; H 6.90; N 3.45; S 7.88.

Synthesis of 2,6-di(4-*tert*-butylphenylthio)-4,8-di-(4-hexylphenylamino)-1,5-naphthoquinone (VIId). A mixture of 0.5 mmol of compound **VIb** and 3 ml of 4-hexylaniline was heated at 150°C for 2.5 h. The reaction mixture was worked up as described above. Yield 40%, mp 284–286°C (benzene). IR spectrum, ν, cm^{-1}: 1604 (C=O). ^1H NMR spectrum, δ, ppm: 0.89 t (6H, $2CH_3$, *J* 7.0 Hz), 1.30 m (34H, $6CH_3$, $8CH_2$), 2.49 t (4H, $2CH_2$, *J* 7.0 Hz), 6.73 s (2H, $H^{3,7}$), 6.85 d (4H, H_{arom}, J_O 8.0 Hz), 7.04 d (4H, H_{arom}, J_O 8.0 Hz), 7.41 d (4H, H_{arom}, J_O 8.0 Hz), 7.55 d (4H, H_{arom}, J_O 8.0 Hz), 14.26 s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 431 (4.05), 629 (4.28), 680 (4.50). Found, %: C 77.51; H 7.71; N 3.19; S 8.02. $C_{54}H_{64}N_2O_2S_2$. Calculated, %: C 78.41; H 6.58; N 3.38; S 7.75.

Synthesis of 4,8-di(arylamino)-2,6-di(4-*tert*-butylphenylsulfonyl)-1,5-naphthoquinones VIIIa and VIIIc. To a solution of 0.25 mmol of 4,8-di(arylamino)-2,6-(4-*tert*-butylphenylthio)-1,5-naphthoquinone **VIIa** or **VIIc** in 20 ml of $CHCl_3$ was added dropwise a solution of 1.5 mmol *m*-chloroperbenzoic acid in 20 ml of $CHCl_3$,

and the mixture was stirred for 3 h at room temperature. The reaction mixture was washed in a separatory funnel with 40 ml of saturated solution of $NaHCO_3$, then twice with 40 ml portions of distilled water, dried with $CaCl_2$, the solvent was evaporated, and the residue was subjected to column chromatography on SiO_2, eluent chloroform.

2,6-Di(4-*tert*-butylphenylsulfonyl)-4,8-di-(phenylamino)-1,5-naphthoquinone (VIIIa). Yield 38%, did not melt till 360°C (benzene). IR spectrum, ν, cm^{-1}: 1160, 1340 (SO_2), 1580 (C=C), 1590 (C=O), 2970 (CH). ^1H NMR spectrum, δ, ppm: 1.29 s (18H, $6CH_3$), 7.26 d (4H, H_{arom}, J_O 8.0 Hz), 7.44–7.56 m (10H, $2C_6H_5$), 7.96 d (4H, H_{arom}, J_O 8.0 Hz), 8.49 s (2H, $H^{3,7}$), 14.30 br.s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 379 (3.80), 670 (4.01), 744 (4.24). Found, %: N 3.56; S 8.78. $C_{42}H_{40}N_2O_6S_2$. Calculated, %: N 3.83; S 8.75.

2,6-Di(4-*tert*-butylphenylsulfonyl)-4,8-di(4-butoxyphenylamino)-1,5-naphthoquinone (VIIIc). Yield 46%, did not melt till 360°C (benzene). IR spectrum, ν, cm^{-1}: 1150, 1340 (SO_2), 1590 (C=C), 1600 (C=O), 2960 (CH). ^1H NMR spectrum, δ, ppm: 0.80 t (6H, $2CH_3$), 0.95 s (18H, $6CH_3$), 1.17–1.30 m (4H, $2CH_2$), 1.37–1.60 m (4H, $2CH_2$), 3.46 t (4H, $2CH_2$, *J* 6.0 Hz), 6.61 d (4H, H_{arom}, J_O 8.0 Hz), 6.79 d (4H, H_{arom}, J_O 8.0 Hz), 7.12 d (4H, H_{arom}, J_O 8.0 Hz), 8.19 d (4H, H_{arom}, J_O 8.0 Hz), 8.64 s (2H, $H^{3,7}$), 14.45 s (2H, 2NH). Electronic spectrum ($CHCl_3$), λ_{max}, nm (log ε): 433 (3.73), 680 (3.88), 763 (4.27). Found, %: C 68.21; H 6.37; N 3.05; S 7.40. $C_{50}H_{56}N_2O_8S_2$. Calculated, %: C 68.49; H 6.39; N 3.21; S 7.31.

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