Effect of substituents on the tautomeric equilibrium of 5-hydroxy-1,4-naphthoquinon-4-imines

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Tautomeric equilibria of *para*- and *ana*-quinoid forms of 5-hydroxy-1,4-naphthoquinone-4-imines in solutions were studied by UV and ^{1}H NMR spectroscopy. The *ana*-form is stabilized by electron-donating substituents at positions 2 and 8 and at nitrogen atom and by electron-withdrawing substituents at position 6.

Key words: 1,4-naphthoquinon-4-imines, 1,5-naphthoquinones, tautomerism.

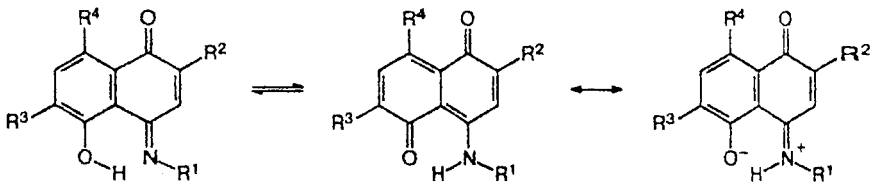
1,5-Naphthoquinone (*ana*-naphthoquinone) is a very unstable compound. Only 4,8-diamino-1,5-naphthoquinones and their derivatives are known as stable *ana*-quinoid compounds, which are used in optical information recording systems[1] and liquid-crystal devices.[2]

Previously, we have demonstrated that in organic solvents, 5-hydroxy-1,4-naphthoquinon-4-imines occur as tautomeric mixtures of *para*- and *ana*-quinoid forms.[3] The *ana*-form is stabilized by an alkyl substituent at the nitrogen atom of the imino group. The use of protic solvents also stabilizes the *ana*-form.[3]

In this work, we studied the dependence of the tautomeric equilibrium on the type of substituents at positions 2, 6, and 8 and at the nitrogen atom in 5-hydroxy-1,4-naphthoquinon-4-imines **1**—**10** (Scheme 1).

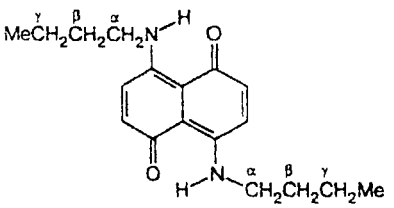
We have established that compounds in the OH-form A are characterized by the presence of one band in the

Scheme 1



A **B** **B'**

1: R^1 = Ph; R^2 = R^3 = Br; R^4 = H
2: R^1 = Ph; R^2 = R^3 = R^4 = Br
3: R^1 = Bu; R^2 = BuNH; R^3 = *p*-Bu^{t}C$_6$H$_4$S; R^4 = H
4: R^1 = Bu; R^2 = PhNH; R^3 = *p*-Bu^{t}C$_6$H$_4$S; R^4 = H
5: R^1 = Ph; R^2 = PhNH; R^3 = Br; R^4 = H
6: R^1 = Ph; R^2 = PhNH; R^3 = R^4 = Br
7: R^1 = Ph; R^2 = PhNH; R^3 = NO_2; R^4 = H
8: R^1 = Ph; R^2 = PhNH; R^3 = *p*-Bu^{t}C$_6$H$_4$S; R^4 = H
9: R^1 = Bu; R^2 = PhNH; R^3 = Br; R^4 = H
10: R^1 = Bu; R^2 = BuNH; R^3 = Br; R^4 = H



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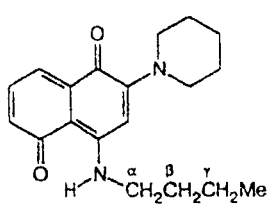

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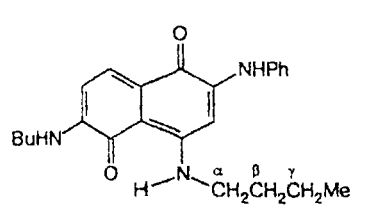

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 358—362, February, 1997.

1066-5285/97/4602-0344 $18.00

visible region (440—470 nm). The position of this band depends little on polarity of the solvent.[3] The band of the *ana*-quinoid tautomeric NH-form **B** is observed at 570—670 nm and exhibits negative solvatochromism,[3—5] *i.e.*, the ground state of the molecule is more polar than the excited state. Therefore, this state is more adequately described by the bipolar structure **B'**.

Compounds **1—10** can be divided into three groups depending on the character of their UV spectra (Table 1).

Compounds **1** and **2** occur almost entirely in the form **A**, because only bands at 440—470 nm are observed in the visible region. In addition, we have demonstrated previously that *N*-aryl-5-hydroxy-1,5-naphthoquinon-4-imines containing NHAr, $NAlk_2$, SO_2Ar, and SAr substituents at position 2 of naphthoquinone, and 2,8-di(arylsulfonyl)-, 2,6-, and 2,8-di(*p-tert*-butylphenylthio)-*N*-aryl-5-hydroxy-1,4-naphthoquinon-4-imines occur predominantly in the *para*-quinoid form regardless of the nature of the solvent.[3,6—9]

In the UV spectra of compounds **3** and **4**, a band at 440—470 nm is absent, but an intense band at 570—670 nm is observed, which indicate that these compounds occur in the *ana*-quinoid form **B**.

The occurrence of two tautomeric forms is typical of compounds **5—10**. In the visible region of the spectra of these compounds, both absorption bands are observed. In going from non-polar solvents to chloroform and ethanol, the intensity of absorption of the *ana*-quinoid NH-form **B** increases with concomitant decrease in the intensity of the band of the *para*-quinoid OH-form **A**. Previously, an analogous behavior has been observed for *N*-phenyl-5-hydroxy-2,6,8-tri(*p-tert*-butylphenylthio)-1,4-naphthoquinon-4-imine[9] and *N*-alkyl-5-hydroxy-1,4-naphthoquinon-4-imines.[3]

The relative intensities of the *para*- and *ana*-quinoid forms indicate that in CCl_4, compounds **5—8** occur predominantly in the OH-form **A**, whereas in $CHCl_3$ and EtOH, the forms **A** and **B** are present in comparable amounts. When the N-aryl group is replaced by an alkyl group, the equilibrium is shifted further to the *ana*-quinoid NH-form (*cf.* compounds **8** and **4** and compounds **5** and **9**).

The ^1H NMR spectra of all compounds under study show a singlet of a proton of the OH(NH) group in the region of δ 12.92—18.06. This proton is bonded to the C=N (C=O) group through a strong intramolecular hydrogen bond and is averaged due to the 1,5-prototropic rearrangement rapid within the NMR time scale. For compounds containing the N-alkyl group, the concentration of the *ana*-quinoid NH-form can be determined from the value of the spin-spin coupling constant $^1J_{^{15}N-H}$ (see Ref. 3) or $^3J_{NHCH}$ (see Ref. 10). For 4,8-dimethylamino-1,5-naphthoquinone, the directly observed $^3J_{NHCH}$ was 5.3 Hz.[4] In the case of compound **11**, which was synthesized according to the known procedure[11] and which occurs in the *ana*-quinoid NH-form, $^3J_{NHCH}$ was determined by ^1H NMR spectroscopy using selective spin decoupling. When the signal of the proton at δ 12.92 was selectively suppressed, a doublet of triplets of the α-CH_2 group at δ 3.53 is transformed into a triplet, which unambiguously indicates that this proton is associated with the NBu group. When the signals of protons of the β-CH_2 group at δ 1.65—1.80 were suppressed, the signal of protons of the α-CH_2 group was transformed into a doublet with $^3J_{NHCH}$ = 5.3 Hz. Therefore, this spin-spin coupling constant is typical of the *ana*-quinoid NH-form of the model 4,8-diamino derivatives of 1,5-naphthoquinone, whereas for the *para*-quinoid OH-form, this constant is equal to zero. Under the conditions of the rapid exchange, the concentration of the form **B** is described by the following formula:

$$P_B = {}^3J_{obs}/{}^3J_B \cdot 100\%,$$

where $^3J_{obs}$ is the observed spin-spin coupling constant $^3J_{NHCH}$, and ^3J_B = 5.3 Hz.

Analogously, the selectively decoupled NMR spectrum (in $CDCl_3$) of 4-butylamino-2-piperidino-1,5-naphthoquinone (**12**) synthesized previously[3] gave $^3J_{NHCH}$ = 3.0 Hz, which corresponds to the concentration of the NH-form of ~57% (it should be noted that the concentration of the NH-form determined from the spin-spin coupling constant $^1J_{^{15}NH}$ is 62%).

The UV spectra of compounds **9** and **10** in CCl_4 and $CHCl_3$ are substantially different. In nonpolar CCl_4, two bands at 440—450 and 600 nm (the intensities of these bands are approximately equal) are observed, which indicates that the forms **A** and **B** occur in comparable amounts. In $CHCl_3$ and EtOH, a short-wavelength band typical of the *para*-quinoid form virtually disappears. The compositions of the tautomeric mixtures of compound **10** in CCl_4 and $CDCl_3$ were determined according to the procedure described above. The value of $^3J_{NHCH}$ of the α-CH_2-group changes from 3.2 Hz in CCl_4 to 5.2 Hz in $CDCl_3$, which corresponds to the concentrations of the *ana*-quinoid NH-form of 60 and 90%, respectively. For compound **9** containing a weaker electron-donating PhNH group instead of the BuNH group at position 2, $^3J_{NHCH}$ = 4.8 Hz in $CDCl_3$, which corresponds to the concentration of the NH-form of 90%.

N-Aryl-5-hydroxy-1,5-naphthoquinon-4-imines react with amines at positions 2, 6, and 8 to form the corresponding amino derivatives, which, according to the UV spectra, are similar to the *ana*-quinones[6,7] obtained previously. In this work, we determined the value of $^3J_{NHCH}$ for 2-anilino-4,6-di(*n*-butylamino)-1,5-naphthoquinone **13** [7] (5.3 Hz), which is additional evidence that compound **13** and 2,4,6- and/or 8-amino derivatives, which have analogous structures, occur in the *ana*-quinoid form.

When the inductive effect of a substituent is analyzed within the framework of the theory of excited molecular orbital,[12—14] the change in the π-electron density on the atom to which the substituent is attached is consid-

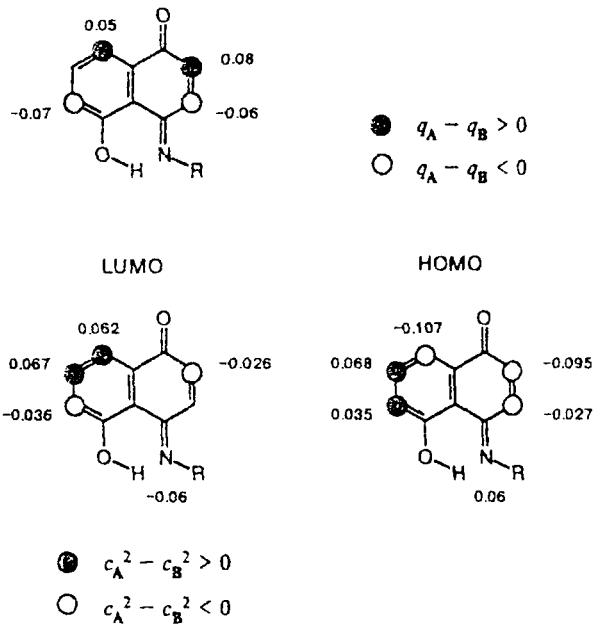
Table 1. Spectral characteristics of compounds **1**—**11**

Compound	IR (KBr), ν/cm^{-1}	Absorption spectrum in the visible region, λ_{max}/nm ($\varepsilon \cdot 10^4$)			^1H NMR ($CDCl_3$), δ (J/Hz)
		CCl_4	$CHCl_3$	EtOH	
1	1680 (C=O)[a] 1610	444 (0.48)	457 (0.68)	444 (0.56)	7.05 (d, 2 H, H arom., J = 8); 7.29—7.55 (m, 3 H arom.); 7.60 (d, 1 H, H(8), J = 8); 7.74 (s, 1 H, H(3)); 7.79 (d, 1 H, H(7), J = 8); 14.92 (s, 1 H, OH)
2	1660 (C=O) 1610	461 (0.78)	444 (0.48)	461 (0.80)	7.04 (d, 2 H arom., J = 8); 7.30—7.57 (m, 3 H arom.); 7.72 (s, 1 H, H(3)); 8.10 (s, 1 H, H(7)); 16.08 (s, 1 H, OH)
3	3375 (N—H)[a] 1610 1660 (C=O)	602 (0.91) 645 (0.79)		570 (1.09)	0.96 (m, 6 H, 2Me); 1.34 (s, 9 H, 3 Me); 1.32—1.92 (m, 8 H, $4CH_2$); 3.16 (dt, 2 H, CH_2); 5.51 (s, 1 H, H(3)); 6.26 (br.s, 1 H, NH); 6.56 (d, 1 H, H(7), J = 8); 7.30—7.50 (m, 4 H arom.); 15.35 (br.s, 1 H, NH)
4	3345 (N—H)[a] 1600 1630 (C=O)	619 (1.05) 669 (0.89)	607 (1.28) 650sh (1.06)	595 (1.30)	0.92 (t, 3 H, Me); 1.32 (s, 9 H, 3 Me); 1.36—1.47 (m, 2 H, CH_2); 1.60—1.70 (m, 2 H, CH_2); 3.57 (dt, 2 H, CH_2, $^3J_{NHCH}$ = 3.9); 6.38 (s, 1 H, H(3)); 6.56 (d, 1 H, H(7), J = 8); 7.41—7.54 (m, 9 H arom.); 9.41 (s, 1 H, NH); 15.35 (br.s, 1 H, NH)[b]
5	3320 (N—H) 1660 (C=O) 1620, 1600	457 (1.06) 600 (0.03)	468 (0.80) 600 (0.40)	460 (0.70)[c] 498 (0.84) 576 (0.67)	6.59 (s, 1 H, H(3)); 7.06—7.45 (m, 10 H arom.); 7.54 (d, 1 H, H(8), J = 8); 7.63 (br.s, 1 H, NH); 7.78 (d, 1 H, H(8), J = 8); 17.10 (s, 1 H, OH[NH])
6	3320 (N—H) 1660 (C=O) 1630, 1590	468 (1.40) 600sh (0.16)	490 (1.00) 600 (0.68)	494 (0.95) 556 (0.96)	6.59 (s, 1 H, H(3)); 7.04—7.45 (m, 10 H arom.); 7.82 (br.s, 1 H, NH); 8.04 (s, 1 H, H(7)); 18.08 (s, 1 H, OH[NH])
7	3320 (N—H) 1680 (C=O) 1630, 1600, 1540, 1360 (NO_2)	468 (0.58) 600 (0.08)		468 (0.34)[c] 510 (0.84) 600 (0.84)	6.65 (s, 1 H, H(3)); 7.05—7.45 (m, 10 H arom.); 7.59 (d, 1 H, H(8), J = 8); 7.74 (br.s, 1 H, NH); 8.06 (d, 1 H, H(7), J = 8); 17.96 (s, 1 H, OH[NH])
8	3355 (N—H)[a] 1665 (C=O) 1635, 1600	454 (1.10) 610 (0.15)	444 (0.94) 615 (0.54)	417 (0.90) 592 (0.88)	1.36 (s, 9 H, 3 Me); 6.58 (s, 1 H, H(3)); 6.75 (d, 1 H, H(7), J = 8); 7.04—7.65 (m, 15 H arom.); 7.73 (br.s, 1 H, NH); 16.92 (s, 1 H, OH[NH])
9	3310 (N—H) 1670 (C=O) 1630	447 (0.47) 605 (0.48)	450 (0.24)[c] 590 (0.75)	450 (0.35)[c] 568 (0.99)	0.92 (t, 3 H, Me); 1.38—1.60 (m, 2 H, CH_2); 1.65—1.85 (m, 2 H, CH_2); 3.52 (dt, 2 H, CH_2, $^3J_{NHCH}$ = 4.8); 6.38 (s, 1 H, H(3)); 7.23—7.25 (m, 4 H arom.); 7.41—7.45 (m, 2 H arom.); 7.69 (d, 1 H, H(7), J = 8); 7.69 (br.s, 1 H, NH); 16.22 (br.s, 1 H, NH)
10	3380 (N—H)[a] 1670 (C=O) 1630	433 (0.46) 590 (0.53)	450 (0.34)[c] 575 (0.82)	450 (0.43)[c] 555 (0.89)	In $CDCl_3$: 0.96 (t, 6 H, 2 Me); 1.34—1.95 (m, 8 H, 4 CH_2); 3.13—3.30 (m, 2 H, CH_2); 3.60 (dt, 2 H, CH_2, 2 H, CH_2, $^3J_{NHCH}$ = 5.2); 5.56 (s, 1 H, H(3)); 7.24 (br.s, 1 H, NH); 7.19 (d, 1 H, H(8), J = 8); 7.67 (d, 1 H, H(7), J = 8); 16.05 (br.s, 1 H, OH[NH]) In CCl_4: 0.97—1.23 (m, 14 H, 2 Me, 4 CH_2); 1.42—1.49 (m, 2 H, CH_2); 1.53—1.87 (m, 2 H, CH_2); 3.05—3.20 (q, 2 H, CH_2); 3.56—3.66 (dt, 2 H, CH_2, $^3J_{NHCH}$ = 3.2); 5.47 (s, 1 H, H(3)); 5.90 (br.s, 1 H, NH); 7.13 (d, 1 H, H(8), J = 8); 7.55 (d, 1 H, H(7), J = 8); 16.89 (br.s, 1 H, OH[NH])
11	3300 (N—H)[a] 1605 (C=O)	621 (0.77) 666 (1.49)	617 (0.89) 658 (1.74)	606 (0.53) 653 (1.03)	0.96 (t, 3 H, Me); 1.40—1.55 (m, 2 H, CH_2); 1.65—1.80 (m, 2 H, CH_2); 3.53 (dt, 2 H, CH_2, $^3J_{NHCH}$ = 5.3); 7.02 (d, 1 H, H(3), J = 10); 7.23 (d, 1 H, H(2), J = 10); 12.92 (br.s, 1 H, NH)

[a] In $CHCl_3$. [b] The ^1H NMR spectrum was recorded in DMSO-d_6. [c] A maximum or shoulder is absent. The value of ε is given.

ered.[13] According to the results of MNDO calculations, in going from the *para*-quinoid OH-form to the *ana*-quinoid NH-form, the electron density on the C(3,6) atoms increases, and the electron density on the C(2,8) atoms decreases. Unlike the tautomer **A**, the π-electron density on the nitrogen atom of the tautomer **B** is deficient (Scheme 2). Because of this, when the electron-donating substituents are attached at positions 2 and 8 and at the nitrogen atom, the portion of the tautomer **B** increases. When substituents are attached at positions 3 and 6, the portion of the tautomer **A** increases. The effect of the electron-withdrawing substituents is opposite. Because changes in the electron density on the C(7) atoms are small, the attachment of the inductive substituents at this position should cause no substantial shift of the tautomeric equilibrium.

Scheme 2



Previously,[14] it has been demonstrated that a comparison of the squares of the coefficients of the frontier orbitals at the C_i atoms of the tautomers **A** and **B** would suffice to qualitatively estimate the effect of mesomeric substituents. The larger the square of the coefficient (c^2) at the position of attachment of a substituent, the larger the stabilizing interaction. Therefore, electron-donating substituents should increase the relative stability of the tautomer with a larger value of c^2 on LUMO at the position of attachment, and electron-withdrawing substituents should increase the relative stability of the tautomer with a larger value of c^2 on HOMO. In the case of $\pm M$ substituents (for example, a Ph group), it is necessary to compare the values of c^2 both on LUMO and HOMO of the tautomers. A comparison of squares of the coefficients of the frontier MOs of the tautomers (which are represented in Scheme 2 in the graphical form) leads to an unexpected conclusion that the attachment of both electron-donating and electron-withdrawing substituents at position 2 should shift the equilibrium to the NH-form, whereas the attachment of substituents at position 7 should shift the equilibrium to the OH-form. Estimation of the effect of mesomeric substituents, which exhibit a strong inductive effect (Me_2N, NO_2, *etc.*), is more complex. The equations that are used are approximate, and therefore, a direct comparison of contributions of the inductive and mesomeric effects is hardly possible within the framework of the simple theory of excited molecular orbitals. Analysis of the experimental data in combination with the results obtained by the method of excited molecular orbitals makes it possible to reveal the governing effect.

The available experimental data confirm the results of analysis. Thus, the replacement of the Ph group at the imine nitrogen atom, which has no pronounced effect (according to the difference maps) on the tautomeric equilibrium, by the Bu group actually increases the relative stability of the NH-form. This is evident from the comparison of the UV spectra of compounds **8** and **4**. As expected, the replacement of the Br atom at position 2 (compounds **1** and **2**) by a stronger electron-donating PhNH group (compounds **5** and **6**) results in stabilization of the *ana*-quinoid tautomer. In the case of 2-anilino-5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine,[6] which occurs completely in the OH-form, the attachment of the NO_2 group at position 6 results in an increase in the relative stability of the NH-form through both the inductive and mesomeric effects. Attachment of the Br or 4-Bu^{t}C$_6$H$_4$S groups, which exhibit $-I$ and $+M$ effects, at position 6 of compounds **8—10** (see Tables 1 and 2) also results in an increase in the relative stability of the *ana*-quinoid tautomer. Apparently, the effect of these substituents on the tautomeric equilibrium is determined by their $-I$ effect.

Experimental

The UV spectra were recorded on Specord UV-VIS and Beckmann DU-8 spectrophotometers. The IR spectra were recorded on a UR-20 instrument (in KBr pellets and in

Table 2. Position of the tautomeric equilibrium in compounds **9—13** according to the data of ^{1}H NMR spectroscopy

Compound	Solvent	$^3J_{NHCH}$ /Hz	*K*[A]/[B]
9	$CDCl_3$	4.8	0.11±0.02
10	CCl_4	3.2	0.67±0.06
	$CDCl_3$	5.2	0.02±0.02
11	$CDCl_3$	5.3	<0.01
12	$CDCl_3$	3.0	0.75±0.06
13	$CDCl_3$	5.3	<0.01

$CHCl_3$). The ^1H NMR spectra were obtained on a Bruker AC-200 instrument. Molecular weights and elemental compositions of the compounds were determined from the precise values of the molecular numbers of ions measured on a Finnigan MAT 8200 mass spectrometer. The course of reactions was monitored by TLC on Silufol UV-254 plates in C_6H_6 and $CHCl_3$. Preparative chromatography was carried out on columns packed with SiO_2 (PKN-200, 100—200 μm) or on plates with a non-fixed sorbent layer (SiO_2 PKN-200, 100—200 μm). Quantum-chemical MNDO calculations[15] were carried out with full optimization of geometry with the use of standard parameters.

2,6-Dibromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine (1) was prepared by oxidation of a mixture of 2,6-dibromo-1,5-dihydroxynaphthalene and aniline by $K_3Fe(CN)_6$ according to the known procedure.[16] The yield of compound **1** was 97%, m.p. 192—193 °C (from benzene). Found, *m/z*: 404.9002 $[M]^+$. $C_{16}H_9Br_2NO_2$. Calculated mol. weight was 404.9001.

2,6,8-Tribromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine (2) and 2-anilino-6,8-dibromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine (6). $K_3Fe(CN)_6$ (0.6 g) was added to a solution of 2,4,6,8-tetrabromo-1-naphthol (0.24 g, 0.5 mmol) and aniline (0.2 mL) in a 2 : 1 MeOH—H_2O mixture (150 mL). The reaction mixture was stirred at 25 °C for 24 h and then poured into water (500 mL). The residue was filtered off, washed with water, and dried. The products were extracted from the filtrate with $CHCl_3$ (3×50 mL). The extract was dried with $CaCl_2$ and evaporated to dryness. The dry residues were combined and chromatographed on a column with SiO_2 (benzene as the eluent). Compound **2** was isolated in a yield of 0.10 g (41%), m.p. 204—205 °C (from EtOH). Found (%): C, 39.18; H, 1.24; Br, 49.35; N, 2.68. $C_{16}H_8Br_3NO_2$. Calculated (%): C, 39.55; H, 1.65; Br, 49.34; N, 2.88. Then compound **6** was isolated in a yield of 0.12 g (48%), m.p. 207—208 °C (from EtOH). Found (%): C, 53.08; H, 2.73; Br, 32.25; N, 5.38. $C_{22}H_{14}Br_2N_2O_2$. Calculated (%): C, 53.05; H, 2.82; Br, 32.09; N, 5.62.

2,4-Di(*n*-butylamino)-6-(*p*-*tert*-butylphenylthio)-1,5-naphthoquinone (3). A mixture of compound **10** (0.1 g, 0.26 mmol) and (*p*-*tert*-butyl)thiophenol (0.5 mL) in DMF (6 mL) was stirred at 100 °C for 5 h and then poured into a saturated aqueous solution of $NaHCO_3$. The precipitate was filtered off, washed with water, and dried. The products were separated by chromatography on SiO_2 plates (a 1 : 1 C_6H_6—$CHCl_3$ mixture was used as the eluent). The major violet fraction was collected. The yield was 0.08 g (66%), m.p. 134—135 °C (from heptane). Found (%): C, 72.08; H, 7.73; N, 6.00; S, 6.91. $C_{28}H_{36}N_2O_2S$. Calculated (%): C, 72.39; H, 7.80; N, 6.03; S, 6.90.

2-Anilino-4-(*n*-butylamino)-6-(*p*-*tert*-butylphenylthio)-1,5-naphthoquinone (4). A mixture of 2-anilino-*N*-(*n*-butyl)-1,4-naphthoquinon-4-imine[7] (0.32 g, 1 mmol) and (*p*-*tert*-butyl)thiophenol (1 mL) in DMF (5 mL) was stirred at 90 °C for 13 h and then poured into water (50 mL). The precipitate that formed was filtered off, dried, and chromatographed on SiO_2. The major violet fraction was eluted with C_6H_6. Compound **4** was obtained in a yield of 80 mg (17%), m.p. 175—177 °C (from heptane). Found (%): C, 73.74; H, 6.87; N, 5.47; S, 6.65. $C_{30}H_{32}N_2O_2S$. Calculated (%): C, 74.38; H, 6.61; N, 5.79; S, 6.61.

2-Anilino-6-bromo-5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine (5). A mixture of compound **1** (0.40 g, 1 mmol) and aniline (0.2 mL) in EtOH (30 mL) was boiled for 10 h and then poured into water (200 mL). The precipitate was filtered off, dried, and chromatographed on a column with SiO_2 (C_6H_6 was used as the eluent). Compound **5** was obtained in a yield of 0.38 g (91%), m.p. 259—260 °C (from $CHCl_3$). Found (%): C, 62.65; H, 3.55; Br, 19.10; N, 6.43. *m/z*: 418.0313 $[M]^+$. $C_{22}H_{15}BrN_2O_2$. Calculated (%): C, 63.02; H, 3.61; Br, 19.06; N, 6.68. Mol. weight 418.0317.

2-Anilino-5-hydroxy-6-nitro-*N*-phenyl-1,4-naphthoquinon-4-imine (7). A mixture of compound **5** (0.1 g, 0.25 mmol) and $NaNO_2$ (0.07 g, 1 mmol) in DMF (10 mL) was boiled for 2 h and then poured into water (200 mL). The precipitate that formed was filtered off, dried, and separated by chromatography on SiO_2 plates (plates were developed with $CHCl_3$ five times). The major red-violet fraction was isolated. The yield of compound **7** was 40 mg (43%), m.p. 277—279 °C (from $CHCl_3$). Found (%): C, 68.07; H, 3.87; N, 10.87. *m/z*: 385 $[M]^+$. $C_{22}H_{15}N_3O_4$. Calculated (%): C, 68.57; H, 3.92; N, 10.90. Mol. weight 385.

2-Anilino-6-(*p*-*tert*-butylphenylthio)-5-hydroxy-*N*-phenyl-1,4-naphthoquinon-4-imine (8). A solution of compound **5** (0.40 g, 0.95 mmol) and (*p*-*tert*-butyl)thiophenol (0.32 g) in DMF (30 mL) was kept at 25 °C for 3 days. Then the reaction mixture was poured into a 10% $NaHCO_3$ solution and stirred for 1 h. The precipitate was filtered off, washed with water, and dried. The yield of compound **8** was 0.41 g (85%), m.p. 187—189 °C. Found: *m/z*: 504.1878 $[M]^+$. $C_{32}H_{28}N_2O_2$. Calculated: mol. weight 504.1871.

2-Anilino-6-bromo-*N*-(*n*-butyl)-5-hydroxy-1,4-naphthoquinon-4-imine (9). A mixture of compound **5** (0.32 g) and Bu^nNH_2 (1 mL) in EtOH (75 mL) was boiled for 6 h and then poured into water (100 mL). The precipitate was filtered off, dried, and chromatographed on SiO_2 plates (development with $CHCl_3$ was carried out three times). The initial compound **5** was recovered in a yield of 100 mg (31%). 2-Anilino-4,6-di(*n*-butylamino)-1,5-naphthoquinone **13** was isolated in a yield of 40 mg (19%). Compound **9** was isolated in a yield of 170 mg (42%), m.p. 192—194 °C (from $CHCl_3$—hexane). Found: *m/z* 398.06510 $[M]^+$. $C_{20}H_{19}BrN_2O_2$. Calculated: mol. weight 398.06303.

6-Bromo-*N*-(*n*-butyl)-2-(*n*-butylamino)-1,4-naphthoquinon-4-imine (10). A mixture of compound **1** (0.2 g, 0.5 mmol) and Bu^nNH_2 (1 mL) in EtOH (30 mL) was boiled for 1.5 h and then concentrated. The residue was washed with a 1% HCl solution and water and dried. The products were separated by chromatography on a column with SiO_2 (a $CHCl_3$—C_6H_6 mixture was used as the eluent, a $CHCl_3$ gradient from 10 to 100%). Product **10** was isolated from the major blue-violet fraction in a yield of 0.14 g (75%), m.p. 140—141 °C (from EtOH). Found (%): C, 57.30; H, 6.31; Br, 21.00; N, 7.71. $C_{18}H_{23}BrN_2O_2$. Calculated (%): C, 57.00; H, 6.11; Br, 21.07; N, 7.38.

References

1. K. Hasegawa, M. Sakakibara, T. Ishida, and Y. Ueno, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1467.
2. Off. Ger. 3126108, 1983.
3. L. V. Ektova, O. P. Petrenko, I. K. Korobeinicheva, and E. P. Fokin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2572 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2359 (Engl. Transl.)].
4. S. M. Bloom and G. O. Dudek, *Tetrahedron*, 1970, **26**, 1267.
5. S. M. Bloom and G. O. Dudek, *J. Org. Chem.*, 1971, **36**, 235.

6. L. V. Ektova, R. P. Shishkina, and E. P. Fokin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1351 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1247 (Engl. Transl.)].
7. L. V. Ektova, R. P. Shishkina, and E. P. Fokin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1672 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1487 (Engl. Transl.)].
8. L. V. Ektova and A. D. Bukhtoyarova, *Sib. Khim. Zh.* [*Sib. Chem. J.*], 1991, No. 3, 84 (in Russian).
9. L. V. Ektova and A. D. Bukhtoyarova, *Sib. Khim. Zh.* [*Sib. Chem. J.*], 1993, No. 2, 105 (in Russian).
10. K. Klemm, H. Schaefer, and E. Daltrozzo, *Chem. Ber.*, 1979, **112**, 484.
11. Jap. Pat. 1165557.
12. V. V. Lapachev, O. P. Petrenko, and V. P. Mamaev, *Usp. Khim.*, 1990, **59**, 457 [*Russ. Chem. Rev.*, 1990, **59** (Engl. Transl.)].
13. O. P. Petrenko, V. V. Lapachev, and V. P. Mamaev, *Zh. Org. Khim.*, 1988, **24**, 1799 [*J. Org. Chem. USSR*, 1988, **24** (Engl. Transl.)].
14. O. P. Petrenko and V. V. Lapachev, *Zh. Org. Khim.*, 1988, **24**, 1806 [*J. Org. Chem. USSR*, 1988, **24** (Engl. Transl.)].
15. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
16. L. V. Ektova and R. P. Shishkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2851 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2588 (Engl. Transl.)].

Received July 16, 1996