Quinonimines and aminoquinones, the reaction products of 3,6-di(*tert*-butyl)-*o*-benzoquinone with primary and secondary amines

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Reactions of 3,6-di(*tert*-butyl)-*o*-benzoquinone with primary amines occur by the nucleophilic 1,4-addition mechanism and lead to the corresponding 2-hydroxy-*p*-quinonimines, which exist in solutions in equilibrium with tautomeric 4-amino-*o*-quinones. The thermodynamic parameters of this prototropic isomerism were determined by NMR spectroscopy. In the case of a secondary amine (piperidine), a derivative of 4-amino-*o*-quinone was obtained; the corresponding *o*-semiquinone complexes were studied in solution by ESR spectroscopy.

Key words: *o*-quinones, amines, *p*-quinonimines, nucleophilic addition, *o*-semiquinone complexes, ESR spectra.

A new and promising application of the chemistry of *o*-semiquinone metal complexes is the synthesis of coordination compounds with bifunctional ligands.

For sterically hindered 3,6-di(*tert*-butyl)-*o*-benzoquinone (**1**), 1,4-addition of nucleophilic reagents to the conjugated quinone system with participation of one carbonyl group is typical. It affords new 4-substituted *o*-quinones. Earlier, the anions of CH acids (dimedone[1] and malononitrile[2]) and ammonia[3] have been used as nucleophilic reagents.

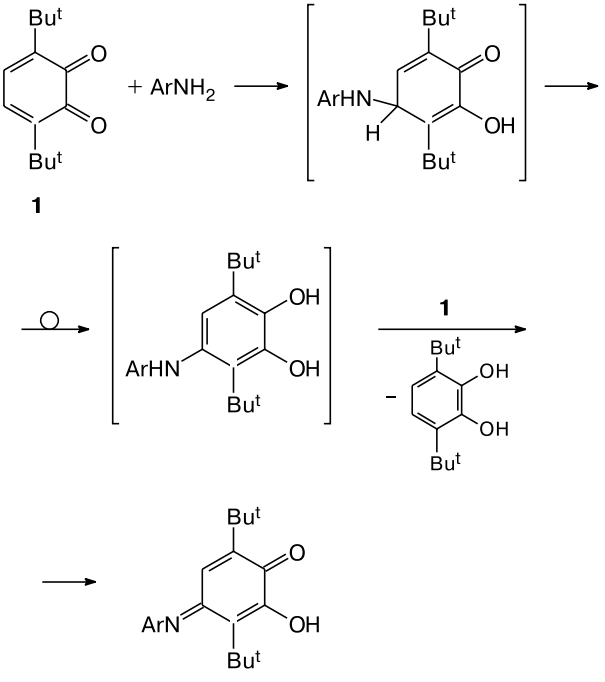
Here we studied reactions of quinone **1** with amines with the aim of obtaining new amino-3,6-di(*tert*-butyl)-*o*-benzoquinones.

Reactions of quinone **1** with a series of primary anilines (aniline, *o*-toluidine, 2,6-dimethylaniline, and 2,6-diisopropylaniline) in methanol in the presence of a catalytic amount of formic acid led to *N*-aryl-3,6-di(*tert*-butyl)-2-hydroxy-*p*-quinonimines **2a—d** but not to substituted *o*-benzoquinones (Scheme 1). This suggests the nucleophilic 1,4-addition of amines onto the *o*-quinone fragment (see Scheme 1).

In all cases, the reaction mixture contained 3,6-di(*tert*-butyl)pyrocatechol in the amount that corresponds to approximately half that of quinone **1** used in the reaction. This is explained by the fact that rearrangement of a primary adduct gives 4-arylamino-3,6-di(*tert*-butyl)pyrocatechol, which is easily oxidized by the starting quinone and partly by atmospheric oxygen. Because of this, the yields of *p*-quinonimines **2** were slightly above 50% with respect to the starting *o*-quinone.

Compounds **2** exist in the *p*-quinonimine rather than *o*-quinone form. The former is stabilized by conjugation of the aryl substituent with the π-system of *p*-quinonimine

Scheme 1



2: Ar = Ph (**a**), 2-MeC_6H_4 (**b**), 2,6-$Me_2C_6H_3$ (**c**), 2,6-$Pr^iC_6H_3$ (**d**)

and, on the other hand, by intramolecular hydrogen bonding between the carbonyl O atom and the OH proton. Their IR spectra show absorption bands characteristic of the C=O (1650 and 1630 cm^{-1}) and O—H stretching vibrations (3350 cm^{-1}). The shapes of the ν(OH) bands

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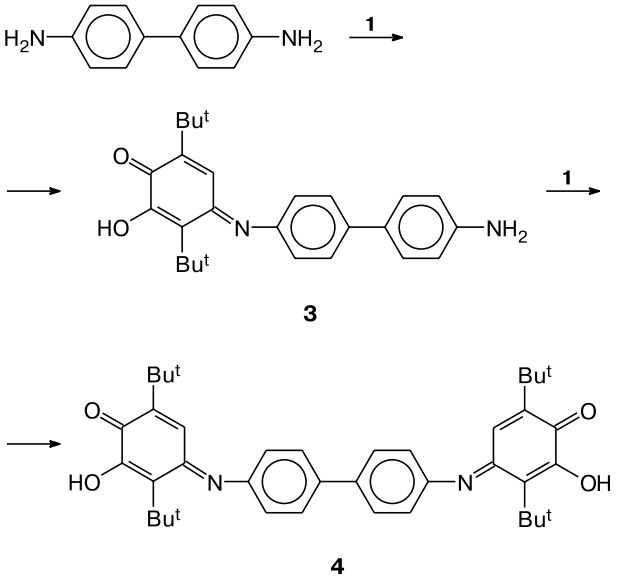
and their frequencies suggest the presence of strong intramolecular hydrogen bonding. It should be noted that these bands become narrower when moving from *p*-quinonimine **2a** to sterically more hindered compound **2d**. Apparently, this is because the shielding of the N atom in *p*-quinonimines with methyl (in **2b,c**) and especially isopropyl substituents (**2d**) hinders intermolecular hydrogen bonding.

In the series of the aromatic amines used, the reaction time increases and the yield of *p*-quinonimine decreases when moving from unsubstituted aniline to 2,6-diisopropylaniline. This can be associated with a substantial role of the steric factor in the reactions of quinone **1** with sterically hindered anilines.

The reaction of compound **1** with benzidine was carried out under the aforementioned conditions; the ratio of the quinone to the diamine was 2 : 1. The course of the reaction was monitored by TLC. As expected, this reaction yielded 1,4-adducts in two steps involving one (monoadduct **3**) and both amino groups of benzidine (bisadduct **4**) (Scheme 2).

Scheme 2



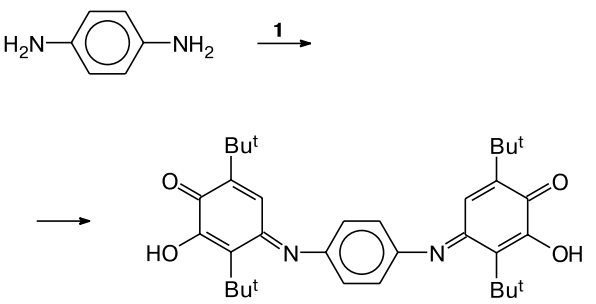
3

4

The IR spectrum of compound **3** contains bands characteristic of the O—H and N—H (3450, 3370, and 3220 cm^{-1}) and C=O stretching vibrations (1640 and 1625 cm^{-1}). The structures of *p*-quinonimines **3** and **4** were also confirmed by NMR data.

In a reaction of quinone **1** with *p*-phenylenediamine, both mono- and bisadducts formed together already at the initial step. Apparently, in contrast to the reaction with benzidine, here the rates of the first and second steps are comparable; because of this, only bis(*p*-quinonimine) **5** was isolated in the individual state (Scheme 3).

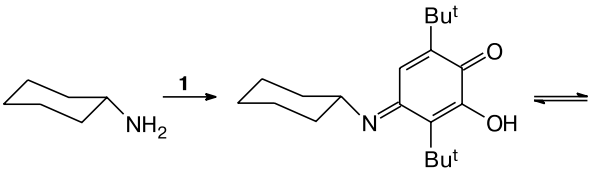
Scheme 3



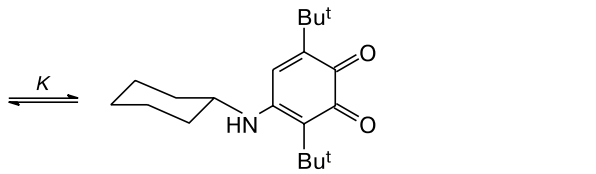
5

Quinone **1** reacted with cyclohexylamine more rapidly than with anilines, giving *N*-cyclohexyl derivative **6** (Scheme 4).

Scheme 4



6



6′

It is worth noting that quinonimine **6**, unlike aryl analogs **2**—**5**, exhibit a number of specific features. Its solutions in saturated and aromatic hydrocarbons are colored yellow, while those in chloroform and dichloromethane turn intensely violet. Its IR spectra substantially vary with solvents: in hexane, characteristic bands appear at 3340 (narrow, OH) and 1640 and 1625 cm^{-1} (C=O); in CH_2Cl_2, a new narrow peak appears at 3470 cm^{-1} (NH); in the carbonyl range, the band at 1680 cm^{-1} is characteristic of *o*-quinones. The existence of compound **6** as two tautomers, *viz.*, *p*-quinonimine (**6**) and *o*-quinone (**6′**), was unambiguously confirmed by NMR data (Scheme 4).

The ^1H NMR spectrum of compound **6** in C_6D_6 shows signals for the protons of two nonequivalent *tert*-butyl groups, multiplets for the protons of the cyclohexyl substituent, and narrow signals for the H(5) proton at δ 6.91 and for the OH proton at δ 7.66. The ^1H NMR spectrum of compound **6** in $CDCl_3$ shows strongly broadened signals for the H(5) and OH protons at δ 7.10 and 7.47, respectively. In addition, new signals observed at δ 6.85

and 5.68 are due to the H(5) proton of the quinone ring and to the NH proton, respectively. According to the intensities of these signals, the ratio of *p*-quinonimine **6** to *o*-quinone **6´** in $CDCl_3$ at 20 °C is 2 : 1.

A study of the temperature dependence of the ^{1}H NMR spectrum of compound **6** in $CDCl_3$ from −50 to 50 °C confirmed the above assumption. With a decrease in the temperature, the signals for the H(5) (δ 7.08) and OH protons (δ 7.53) become narrower and less intense. This is accompanied by the appearance and growth of two new signals for the NH (δ 6.00, br.s) and H(5) protons in the *o*-quinone form (δ 6.87). At −50 °C, the presence of the two forms is also indicated by the signals for the *tert*-butyl groups: along with the signals of the Bu^t protons in the *p*-quinonimine form **6** (δ 1.26 and 1.44), more intense peaks of 4-amino-*o*-quinone (**6´**) become pronounced (δ 1.24 and 1.40). With an increase in the temperature, the ^{1}H NMR pattern returns to its original state, which suggests reversible tautomerism.

The temperature dependence of the ^{1}H NMR spectra was used to determine the thermodynamic parameters of the equilibrium **6** ⇄ **6´**. Because the signals corresponding to the HO and HN protons are broadened, we employed the signals for the H(5) proton of the quinone ring for both the forms (δ 7.08 and 6.87, respectively). The equilibrium constants for this temperature range were calculated from the integral intensity ratio of the signals (Table 1). The enthalpy and entropy of this process were determined from a plot of ln*k* *vs.* the reciprocal temperature: $\Delta H = -11.2\pm1$ kJ mol^{-1} and $\Delta S = -42.8\pm4$ J mol^{-1} K^{-1}.

Earlier,[4] a similar isomerism has been reported for 4-*N*-phenyl-1,2-naphthoquinone; however, in that case, the *o*-quinone form is stable in the solid state, while the quinonimine form exists in a solution in F_3CCO_2H.

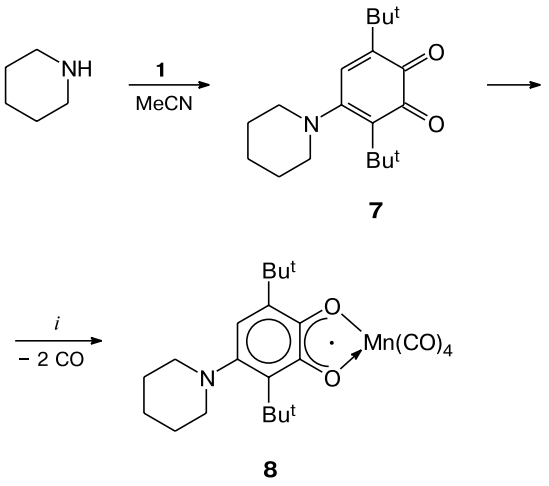
In the case of secondary aliphatic amines, the formation of an *o*-quinone product should be expected. Indeed, a reaction of quinone **1** with piperidine gave new 4-piperidino-*o*-benzoquinone derivative **7** (Scheme 5).

The structure of *o*-quinone **7** was confirmed by the ESR spectra of *o*-semiquinone derivatives (potassium *o*-semiquinonolate and tetracarbonylmanganese *o*-semiquinonolate **8**) obtained by its reduction.

Table 1. Temperature dependence of the equilibrium constant for the transition **6** ⇄ **6´**

T/K	*K*
223	2.56
243	1.27
263	0.90
283	0.60
303	0.58
323	0.33

Scheme 5



i. $Mn_2(CO)_{10}$, toluene, *h*ν.

The isotropic ESR spectrum of potassium semiquinonolate shows a doublet due to the HFC between the unpaired electron and the H(5) proton in the quinone ring (a = 0.35 mT, g_i = 2.0061). The ESR spectrum of manganese derivative **8** in toluene (g_i = 2.0033) (Fig. 1) reflects the HFC between the unpaired electron and the magnetic isotopes of one Mn atom (^{55}Mn, I = 5/2, 100% (see Ref. 5), a_i (1Mn) = 0.67 mT), the amino N atom (^{14}N, I = 1, a_i (1N) = 0.05 mT), and one H(5) proton in the quinone ring (a_i(1H) = 0.34 mT). In addition, this spectrum shows a weak coupling with two equivalent protons of the α-methylene groups of the piperidine fragment (a_i (2H) = 0.06 mT). The absence of such an additional splitting in the ESR spectrum of potassium semiquinonolate can be due to the fact that its HFC constants of the unpaired electron with the N atom and the protons of the piperidine fragment are comparable with the line width.

Thus, 3,6-di(*tert*-butyl)-*o*-benzoquinone (**1**) is prone to add various amines at position 4. The resulting products can exist in the 2-hydroxy-*p*-quinonimine and/or 4-amino-*o*-quinone forms, depending on the structure of the amine.

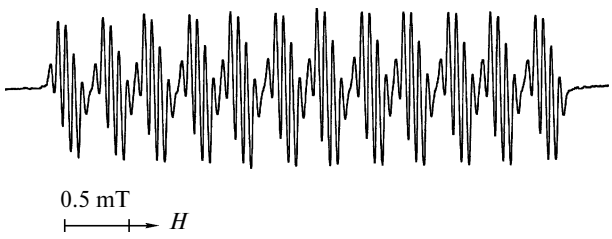


Fig. 1. Isotropic ESR spectrum of tetracarbonylmanganese *o*-semiquinonolate **8** in toluene at 290 K.

Experimental

NMR spectra were recorded on Tesla BS-567A (100 MHz (^{1}H)) and Bruker Avance DPX-200 spectrometers (200 (^{1}H) and 50 MHz (^{13}C)) with HMDS as the internal standard. ESR spectra were recorded on a Bruker ER 200 D-SRC spectrometer fitted with a ER 4105 DR double resonator (9.5 GHz). Spectra were simulated with the WinEPR SimFonia v1.25 program (Bruker). *g* Factor was determined with diphenylpicrylhydrazyl as a standard. IR spectra were recorded on a Specord M80 spectrometer.

Solvents were purified and dehydrated according to standard procedures.[6] 3,6-Di(*tert*-butyl)-*o*-benzoquinone (**1**) was prepared according to a known procedure.[7] Commercial aniline, *o*-toluidine, benzidine, *p*-phenylenediamine, piperidine (Reakhim), 2,6-dimethylaniline, cyclohexylamine (Fluka), and 2,6-diisopropylaniline (Aldrich) were used. Column chromatography was carried out on Silokhrom S-120 (Reakhim) with hexane—ethyl acetate (100 : 1) as an eluent.

***N*-Phenyl-3,6-di(*tert*-butyl)-2-hydroxy-*p*-benzoquinone 4-monoimine (2a).** Aniline (2 mL, 21.9 mmol) and HCOOH (2—3 drops) were added to a solution of quinone **1** (3 g, 13.6 mmol) in MeOH (50 mL). The reaction mixture was refluxed for 2 h and concentrated. The residue was dissolved in hexane and chromatographed to collect a red fraction. The yield of compound **2a** was 2.3 g (54%), red crystals, m.p. 79—80 °C. Found (%): C, 77.02; H, 8.31. $C_{20}H_{25}NO_2$. Calculated (%): C, 77.14; H, 8.09. IR (Nujol), ν/cm^{-1}: 3360, 3340 (OH); 1655 and 1640 (C=O, C=N). ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 1.16, 1.55 (s, 9 H, Bu^t); 6.74 (m, 2 H, H(2′), H(6′)); 6.77 (s, 1 H, H(5)); 7.13 (tt, 1 H, H(4′), ^3J = 7.4 Hz, ^4J = 1.2 Hz); 7.36 (m, 2 H, H(3′), H(5′)); 7.66 (s, 1 H, OH). ^{13}C DEPT NMR ($CDCl_3$, 50 MHz), δ: 28.7, 31.6 (C$\underline{Me}_3$); 34.7, 36.4 ($\underline{C}Me_3$); 119.9 (*o*-CH_{Ph}); 128.7 (*m*-CH_{Ph}); 124.4 (CH, *p*-CH_{Ph}); 126.8 (CH(5)); 127.1 (C(3)); 145.8, 148.5, 149.9 (C(2), C(6), C(Ph)); 157.7 (C=N); 183.3 (C=O).

***N*-(2-Methylphenyl)-3,6-di(*tert*-butyl)-2-hydroxy-*p*-benzoquinone 4-monoimine (2b).** *o*-Toluidine (1.6 mL, 15 mmol) and HCOOH (2—3 drops) were added to a solution of quinone **1** (3 g, 13.6 mmol) in MeOH (50 mL). The reaction mixture was refluxed for 3 h and concentrated. The residue was dissolved in hexane and chromatographed to collect a dark red fraction. The yield of compound **2b** was 2.2 g (50%), cherry-colored crystals, m.p. 59—60 °C. Found (%): C, 77.31; H, 8.52. $C_{21}H_{27}NO_2$. Calculated (%): C, 77.50; H, 8.36. IR (Nujol), ν/cm^{-1}: 3350 (OH); 1645, 1630 (C=O). ^{1}H NMR ($CDCl_3$, 100 MHz), δ: 1.13 (s, 9 H, $\underline{Bu}^tC(6)$); 1.56 (s, 9 H, $\underline{Bu}^tC(3)$); 2.12 (s, 3 H, Me); 6.44 (m, 1 H, H(6′)); 6.67 (s, 1 H, H(5)); 7.00—7.30 (m, 3 H, H(3′), H(4′), H(5′)); 7.68 (s, 1 H, OH).

***N*-(2,6-Dimethylphenyl)-3,6-di(*tert*-butyl)-2-hydroxy-*p*-benzoquinone 4-monoimine (2c).** 2,6-Dimethylaniline (2 mL, 16.2 mmol) and HCOOH (2—3 drops) were added to a solution of quinone **1** (3 g, 13.6 mmol) in MeOH (50 mL). The reaction mixture was refluxed for 8 h and concentrated. The residue was dissolved in hexane and chromatographed to collect a cherry-colored fraction. The yield of compound **2c** was 2.1 g (47%), cherry-colored crystals, m.p. 94—95 °C. Found (%): C, 77.52; H, 8.78. $C_{22}H_{29}NO_2$. Calculated (%): C, 77.83; H, 8.61. IR (Nujol), ν/cm^{-1}: 3350 (OH); 1645, 1625 (C=O, C=N). ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 1.10, 1.60 (both s, 9 H each, Bu^t); 1.96 (s, 6 H, CH_3); 6.46 (s, 1 H, H(5)); 6.96 (m, 1 H, H(4′)); 7.08 (d, 2 H, H(3′) + H(5′), J = 7.4 Hz); 7.66 (s, 1 H, OH). ^{13}C DEPT NMR ($CDCl_3$, 50 MHz), δ: 18.5 (CH$\underline{Me}_2$); 28.7, 29.2 (C$\underline{Me}_3$ (Bu^t)); 34.4, 36.5 ($\underline{C}Me_3$); 123.5 (*p*-CH_{arom}); 124.7 (*o*-C_{arom}); 126.2 (C(5)H); 126.6 (C—N); 127.8 (*m*-CH_{arom}); 146.0, 148.5, 148.7 (C(2), C(3), C(6)); 159.0 (C=N); 183.0 (C=O).

***N*-(2,6-Diisopropylphenyl)-3,6-di(*tert*-butyl)-2-hydroxy-*p*-benzoquinone 4-monoimine (2d).** 2,6-Diisopropylaniline (5 mL, 26.5 mmol) and HCOOH (2—3 drops) were added to a solution of quinone **1** (3 g, 13.6 mmol) in MeOH (50 mL). The reaction mixture was refluxed for ~72 h and concentrated. The residue was dissolved in hexane and chromatographed to collect a dark cherry fraction. The yield of compound **2d** was 1.7 g (31%), dark cherry crystals, m.p. 120—121 °C. Found (%): C, 78.70; H, 9.38. $C_{26}H_{37}NO_2$. Calculated (%): C, 78.94; H, 9.43. IR (Nujol), ν/cm^{-1}: 3350 (OH); 1650, 1635 (C=O). ^{1}H NMR ($CDCl_3$, 100 MHz), δ: 1.04 (d, 6 H, $CH_3CH\underline{CH}_3$, J = 6.6 Hz); 1.07 (s, 9 H, $\underline{Bu}^tC(6)$); 1.13 (d, 6 H, $\underline{CH}_3CHCH_3$, J = 6.6 Hz); 1.58 (s, 9 H, $\underline{Bu}^tC(3)$); 2.58 (sept, 2 H, $\underline{CH}Me_2$, J = 6.6 Hz); 6.48 (s, 1 H, H(5)); 7.17 (m, 3 H, H(3′), H(4′), H(5′)); 7.68 (s, 1 H, OH).

***N*-[4-(4-Aminophenyl)phenyl]-3,6-di(*tert*-butyl)-2-hydroxy-*p*-benzoquinone 4-monoimine (3).** Quinone **1** (3 g, 13.6 mmol) and benzidine (2.5 g, 13.6 mmol) were dissolved in MeOH (30 mL) and HCOOH (2 drops) were added. The reaction mixture was stirred with a magnetic stirring bar at room temperature for 6 h. The precipitate that formed was recrystallized from toluene. The yield of compound **3** was 2.96 g (54%), dark lilac needle-like crystals, m.p. 197—199 °C. Found (%): C, 77.84; H, 7.31. $C_{26}H_{30}N_2O_2$. Calculated (%): C, 77.58; H, 7.51. IR (Nujol), ν/cm^{-1}: 3450, 3370, 3220 (OH, NH); 1640, 1625 (C=O). ^{1}H NMR ($CDCl_3$, 100 MHz), δ: 1.17 (s, 9 H, $\underline{Bu}^tC(6)$); 1.55 (s, 9 H, $\underline{Bu}^tC(3)$); 3.60 (br.s, 2 H, NH_2); 6.86 (s, 1 H, H(5)); 6.70—7.60 (m, 8 H, C_6H_4—C_6H_4); 7.7 (br.s, 1 H, OH).

4,4′-Bis[2,5-di(*tert*-butyl)-3-hydroxy-4-oxocyclohexa-2,5-dien-1-ylideneamino]-1,1′-biphenyl (4). Quinone **1** (1 g, 4.55 mmol) and compound **3** (1.5 g, 3.74 mmol) were dissolved in MeOH (30 mL). The reaction mixture was stirred with a magnetic stirring bar at room temperature for 8 h. The precipitate that formed was recrystallized from heptane—diethyl ether (3 : 1). The yield of compound **4** was 1.13 g (49%), lilac crystals, m.p. 243—244 °C. Found (%): C, 77.60; H, 8.03. $C_{40}H_{48}N_2O_4$. Calculated (%): C, 77.39; H, 7.79. IR (Nujol), ν/cm^{-1}: 3350 (OH); 1650, 1630 (C=O). ^{1}H NMR ($CDCl_3$, 100 MHz), δ: 1.19 (s, 18 H, $\underline{Bu}^tC(6)$); 1.56 (s, 18 H, $\underline{Bu}^tC(3)$); 6.87 (s, 2 H, H(5)); 6.85 (m, 4 H, *o*-CH_{arom}); 7.62 (m, 4 H, *m*-CH_{arom}); 7.66 (s, 2 H, OH).

4,4′-(1,4-Phenylenedinitrilo)bis[3,6-di(*tert*-butyl)-2-hydroxycyclohexa-2,5-dien-1-one] (5). Quinone **1** (5.5 g, 25 mmol) and *p*-phenylenediamine (1.5 g, 13.9 mmol) were dissolved in MeOH (30 mL). The reaction mixture was stirred with a magnetic stirring bar at room temperature for 12 h. The precipitate that formed was recrystallized from heptane—ether (3 : 1). The yield of compound **5** was 5.12 g (67%), dark lilac crystals, m.p. 229—231 °C. Found (%): C, 75.21; H, 8.17. $C_{34}H_{44}N_2O_4$. Calculated (%): C, 74.97; H, 8.14. IR (Nujol), ν/cm^{-1}: 3340 (OH); 1645, 1630 (C=O). ^{1}H NMR ($CDCl_3$, 100 MHz), δ: 1.19 (s, 18 H, $\underline{Bu}^tC(6)$); 1.56 (s, 18 H, $\underline{Bu}^tC(3)$); 6.80 (s, 4 H, C_6H_4); 6.85 (s, 2 H, H(5)); 7.86 (s, 2 H, OH).

***N*-Cyclohexyl-3,6-di(*tert*-butyl)-2-hydroxy-*p*-benzoquinone 4-monoimine (6).** Cyclohexylamine (1.65 mL, 16.6 mmol) and

HCOOH (2—3 drops) were added to a solution of quinone **1** (3 g, 13.6 mmol) in THF (50 mL). The reaction mixture was refluxed for ~48 h. The product was extracted with ether, the extract was concentrated, and the residue was dissolved in hexane and chromatographed to collect a yellow fraction. The yield of compound **6** was 1.8 g (42%), yellow crystals, m.p. 88—89 °C. Found (%): C, 75.73; H, 9.76. $C_{20}H_{31}NO_2$. Calculated (%): C, 75.67; H, 9.84. IR (Nujol), ν/cm^{-1}: 3360 (OH); 1645, 1635 (C=O). IR (hexane), ν/cm^{-1}: 3340 nar. (OH); 1640; 1625 (C=O). IR (CH_2Cl_2), ν/cm^{-1}: 3470; 3340 br (OH), (NH); 1680; 1640; 1625; 1550 (C=O). ^{1}H NMR (C_6D_6, 200 MHz), δ: 1.11 (s, 9 H, Bu^{t}C(6)); 1.77 (s, 9 H, Bu^{t}C(3)); 1.34—1.73 (m, 10 H, $(CH_2)_5$); 3.78 (m, 1 H, CHN); 6.98 (s, 1 H, H(5)); 7.72 (s, 1 H, OH). ^{13}C DEPT NMR (C_6D_6, 50 MHz), δ: 24.4, 26.0 (C(3′)H$_2$, C(4′)H$_2$, C(5′)H$_2$); 28.9, 32.4 (C$\underline{\text{Me}}_3$); 34.8, 37.0 ($\underline{\text{C}}$Me$_3$, C(2′)H$_2$, C(6′)H$_2$); 34.9 (C(2′)H, C(6′)H); 60.2 (C(1′)H); 122.0 (C(5)H); 128.4, 145.1 and 148.2 (C(2), C(3) and C(6)); 156.6 (C=N); 183.6 (C=O).

Form **6**. ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 1.27, 1.46 (both s, 9 H each, Bu^t(3)); 1.48—1.69 (m, 10 H, $(CH_2)_5$); 3.92 (sept, 1 H, CHN, J = 4.3 Hz); 7.09 (br.s, 1 H, H(5)); 7.47 (br.s, 1 H, OH). ^{13}C DEPT NMR ($CDCl_3$, 50 MHz), δ: 24.2, 25.7 (C(3′)H$_2$, C(4′)H$_2$, C(5′)H$_2$); 28.9, 31.9 ($\underline{\text{Me}}_3$C); 34.6 (C(2′)H, C(6′)H$_2$); 34.7, 36.6 ($\underline{\text{C}}$Me$_3$); 60.0 (C(1′)H); 121.8 (C(5)H); 128.5, 144.8, 147.4 (C(2), C(3), C(6)); 155.9 (C=N); 183.5 (C=O).

Form **6′**. ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 1.24, 1.40 (both s, 9 H each, Bu^{t}C(3)); 1.48—1.69 (m, $(CH_2)_5$); 3.51—3.66 (m, 1 H, CHN); 5.68 (d, 1 H, NH, J = 7.0 Hz); 6.85 (br.s, 1 H, H(5)). ^{13}C DEPT NMR ($CDCl_3$, 50 MHz), δ: 24.4, 25.2 (C(3′)H$_2$, C(4′)H$_2$, C(5′)H$_2$); 29.0, 30.9 (Me$_3$C); 34.2, 35.0 ($\underline{\text{C}}$Me$_3$); 34.8 (C(2′)H, C(6′)H); 52.5 (C(1′)H); 115.9, 150.2, 151.6 (C(2), C(3), C(6)); 128.8 (C(5)H); 177.2, 183.1 (C=O).

3,6-Di(*tert*-butyl)-4-piperidino-1,2-benzoquinone (7). Piperidine (0.8 mL, 8.1 mmol) and HCOOH (2—3 drops) were added to a solution of quinone **1** (1 g, 4.55 mmol) in MeCN (30 mL). The reaction mixture was stirred at ~20 °C until quinone **1** was completely consumed (TLC monitoring) and then concentrated. The brown crystals that formed were filtered off. The yield of compound **7** was 1.15 g (83%), m.p. 109—110 °C. Found (%): C, 75.55; H, 9.40. $C_{19}H_{29}NO_2$. Calculated (%): C, 75.19; H, 9.63. IR (Nujol), ν/cm^{-1}: 1675, 1665 (C=O). ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 1.23 (s, 9 H, Bu^t); 1.31 (s, 9 H, Bu^t); 1.66 (br.m, 6 H, *m*-, *p*-CH$_2$); 3.14 (br.m, 4 H, N(CH$_2$)$_2$); 6.90 (s, 1 H, H(5)). ^{13}C NMR ($CDCI_3$, 50 MHz), δ: 24.0 (*p*-CH$_2$); 26.7 (*m*-CH$_2$); 29.1, 30.3 ($\underline{\text{Me}}_3$C)); 34.8, 35.7 ($\underline{\text{C}}$Me$_3$); 53.5 (*o*-CH$_2$); 132.2 (N—C(4)); 133.5 (C(5)H); 146.6, 157.8 (C(3), C(6)); 182.0, 182.3 (C=O).

Potassium and tetracarbonylmanganese *o*-quinone **7** semiquinolates were obtained according to known procedures.[8,9]

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References

1. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2206 [*Russ. Chem. Bull.*, 1997, **46**, 2093 (Engl. Transl.)].
2. G. A. Abakumov, V. I. Nevodchikov, N. V. Zaitova, N. O. Druzhkov, L. G. Abakumova, Yu. A. Kurskii, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 351 [*Russ. Chem. Bull.*, 1997, **46**, 337 (Engl. Transl.)].
3. V. B. Vol′eva, T. I. Prokof′eva, A. I. Prokof′ev, I. S. Belostotskaya, N. L. Komissarov, and V. V. Ershov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1789 [*Russ. Chem. Bull.*, 1995, **44**, 1720 (Engl. Transl.)].
4. I. D. Biggs and J. M. Tedder, *Tetrahedron*, 1978, **34**, 1377.
5. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, p. 584.
6. A. Gordon and R. Ford, *Chemist′s Companion*, Wiley Interscience, New York, 1972.
7. E. G. Rozantsev and V. D. Sholle, *Organicheskaya khimiya svobodnykh radikalov* [*Organic Chemistry of Free Radicals*], Khimiya, Moscow, 1973, 344 pp. (in Russian).
8. E. Müller, F. Günter, K. Scheffler, and A. Reiker, *Liebigs Ann. Chem.*, 1965, **688**, 134.
9. B. L. Tumanskii, K. A. Sarbasov, S. P. Solodovnikov, N. N. Bubnov, A. I. Prokof′ev, and M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, 1981 [*Dokl. Chem.*, 1981 (Engl. Transl.)].

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