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o-Benzoquinone photoreduction products in the presence of *N*,*N*-dimethylanilines

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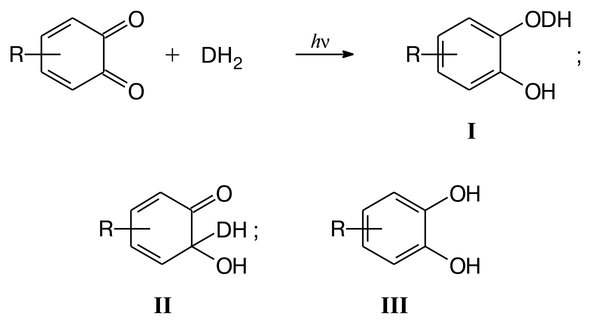
Photoreduction of *o*-benzoquinones in the presence of *para*-substituted *N*,*N*-dimethylanilines under irradiation at $\lambda \geq 500$ nm affords pyrocatechol monoethers of the 2-(aminomethoxy)phenol type. In the subsequent dark reaction, these monoethers undergo quantitative decomposition by a heterolytic mechanism to give the corresponding pyrocatechols and nitrogen-containing compounds. The rate of this decomposition decreases with decreasing size of the substituent at the position adjacent to the ether bond that is formed upon photoreduction. The redox characteristics of such pyrocatechol monoethers can serve as the criterion of their stability. A weakening of the electron-withdrawing properties of quinones and the electron-donating properties of amines leads to an increase in stability of their reaction products.

Key words: photoreduction, *o*-benzoquinones, *N*,*N*-dimethylanilines, pyrocatechol monoethers.

It is known that *o*-quinones are efficiently subjected to photoreduction in the presence of various hydrogen donors (DH_2).[1,2] Studies of photoreduction of 9,10-phenanthrenequinone[3,4] and 1,2-naphthoquinone[5] demonstrated that the reaction pathway is largely determined by the nature of the hydrogen donor. For example, photoreduction of 9,10-phenanthrenequinone in the presence of alcohols,[6,7] ethers (dialkyl[5] or alkylaryl[3]), or aldehydes[1] gives rise to compounds containing the 2-alkoxyphenol fragment (Scheme 1, product **I**). Photoreactions in the presence of hydrocarbons (alkanes,[8,9] alkenes,[2,10] alkylarenes,[8] or alkynes[2]) produce the corresponding ketols (products **II**). Prolonged sunlight irradiation of 9,10-phenanthrenequinone in a mixture with *o*- and *p*-xylenes and 1,2,4-trimethylbenzene affords 2-alkoxyphenols.[1] These reactions produce also pyrocatechol derivatives **III** identified as quinhydrones.[1,5] Photoreduction of camphoroquinone (1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione) in the presence of xylenes and lower alcohols affords 2,3-ketols,[11] whereas photoreduction in the presence of tertiary amines gives the corresponding 2,3-diol as the major product.[12] Photoreduction of *o*-benzoquinones has received much less attention. Under UV or visible light irradiation, these compounds undergo photoreduction in the presence of such hydrogen donors as tertiary amines.[13] The photoreaction of *o*-benzoquinone with 4-bromo-*N*,*N*-dimethylaniline produces a mixture of compounds **I** and **III**.[14]

Scheme 1



In the present study, we investigated the products, which were obtained by photoreduction of sterically hindered *o*-benzoquinones in the presence of *para*-substituted *N*,*N*-dimethylanilines, by NMR spectroscopy. We also examined the influence of the electronic and steric factors of substituents in the reagent molecules on the kinetics of dark decomposition of 2-alkoxyphenols **I**, which are the primary products of the process.

Results and Discussion

Visible light irradiation of benzene solutions of *o*-benzoquinones (**1**) and *para*-substituted *N*,*N*-dimethylanilines (**2**) is known[15] to lead to decoloration of the solutions due to photoreduction of *o*-benzoquinones.

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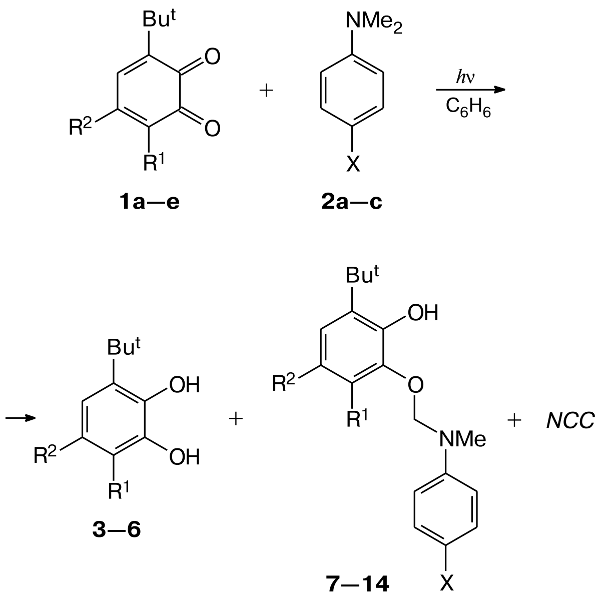
In the present study, we examined the reactions of sterically hindered *o*-benzoquinones **1a—e** with anilines **2a—c**. Photoreduction of these *o*-benzoquinones was found to give mixtures of pyrocatechols **3—6** and 2-(aminomethoxy)phenols **7—14** (Scheme 2).

Scheme 2



Compound	R^1	R^2	Compound	R^1	R^2
1a, **10**	Bu^t	MeO	**1d**, **5**, **9**	Me	H
1b, **3**, **7**, **12**	Bu^t	H	**1e**, **4**, **8**, **13**, **14**	H	Bu^t
1c, **6**, **11**	Bu^t	F			

X = MeO (**2a**, **13**), Br (**2b**, **7—11**), CN (**2c**, **12**, **14**)

NCC are nitrogen-containing compounds.

The typical dynamics of the changes in the ^{1}H NMR spectra of the reaction mixture during irradiation and in the course of the dark reaction is presented in Fig. 1. The spectrum of the starting solution of **1b** and **2b** in C_6D_6 shows signals for the protons of the methyl groups in compound **2b** (δ_H = 2.31) and two equivalent *tert*-butyl groups of **1b** (δ_H = 1.11) (see Fig. 1, *a*). Figure 1, *b* shows the spectrum of the reaction mixture recorded at 2 min after completion of irradiation (the irradiation time was 1 min). Irradiation of the solution leads to a decrease in the intensity of the signals for the protons of the *tert*-butyl groups of **1b** and the appearance of new signals for the protons of the *tert*-butyl groups of 3,6-di(*tert*-butyl)pyrocatechol **3** (δ_H = 1.37) and the protons of two *tert*-butyl groups, the methyl group, and methylene group of 2-[*N*-(4-bromophenyl)-*N*-methyl]aminomethoxy-3,6-di(*tert*-butyl)phenol (**7**) (δ_H = 1.40, 1.54, 2.34, and 4.48, respectively). The signal intensity ratio of the *tert*-butyl groups in compounds **3** and **7** is 3 : 1. In the course of the dark process, the intensities of the signals of pyrocatechol **3** increase, whereas the intensities of the signals of 2-(aminomethoxy)phenol **7** decrease (see Fig. 1, *c*). Toward the end of the fourth minute of the dark reaction, this ratio reaches 15 : 1. Analogous changes in the ^{1}H NMR spectra are characteristic of photoreduction of all tested *o*-benzoquinones in the presence of tertiary amines.

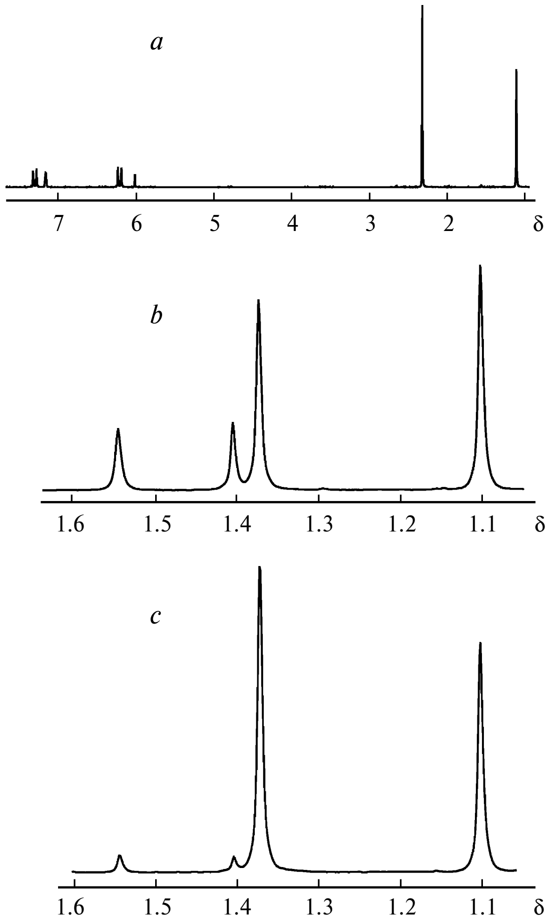


Fig. 1. ^{1}H NMR spectra recorded during photoreduction of 3,6-di(*tert*-butyl)-1,2-benzoquinone (**1b**) ($3 \cdot 10^{-2}$ mol L^{-1}) with 4-bromo-*N*,*N*-dimethylaniline (**2b**) ($1.5 \cdot 10^{-1}$ mol L^{-1}) in C_6D_6 before irradiation (*a*), within 2 min after irradiation (*b*), and within 6 min after irradiation (*c*). The irradiation time was 1 min.

Therefore, 2-(aminomethoxy)phenols **7—14** produced in photoreactions are unstable compounds and decompose in the dark reaction to give pyrocatechol and nitrogen-containing compounds. Earlier,[14] we have attempted to identify nitrogen-containing photoreaction products of compounds **1b** and **2b**. However, the ^{1}H and ^{13}C NMR and DEPT spectra revealed only that the reaction produced a mixture containing presumably $4\text{-}BrC_6H_4NHMe$, $[4\text{-}BrC_6H_4N(Me)]_2CH_2$, and $ArN(Me)CH_2Br$-type compounds.

Figure 2 shows the kinetic curves of the dark decomposition reaction of 2-(aminomethoxy)phenol **9** (curve *1*) and accumulation of pyrocatechol **5** (curve *2*) in the reac-

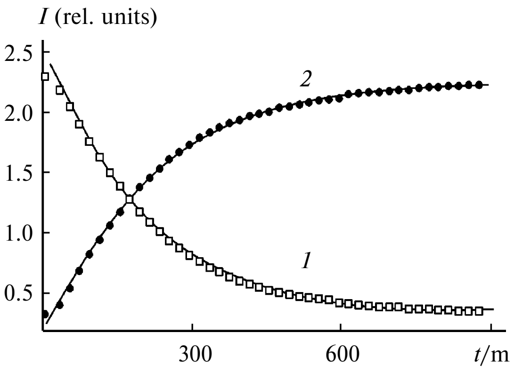


Fig. 2. Kinetic curves of decomposition of 2-(aminomethoxy)phenol **9** (*1*) and accumulation of pyrocatechol **5** (*2*) (the reaction medium, without irradiation, vacuum, $T = 298$ K).

tion mixture (photoreduction products of 3-methyl-6-*tert*-butyl-1,2-benzoquinone in the presence of 4-bromo-*N*,*N*-dimethylaniline). Analogous dependences were obtained in the study of the kinetics of decomposition of other 2-(aminomethoxy)phenols. As is evident from these data, compound **9** is transformed into pyrocatechol **5** in an equimolar amount in the course of the dark reaction.

Decomposition of 2-(aminomethoxy)phenols starts at the moment of their formation and occurs during irradiation and set-up of the NMR spectrometer (2 min, see the Experimental section). Correspondingly, based on the kinetic curves of decomposition of 2-(aminomethoxy)phenols and accumulation of pyrocatechols, it is impossible to determine whether photoreduction of quinones affords exclusively 2-(aminomethoxy)phenols, whereas pyrocatechols appear in the mixture only as decomposition products of the latter or, alternatively, 2-(aminomethoxy)phenols and pyrocatechols are generated simultaneously. Assuming that 2-(aminomethoxy)phenols are the only primary photoreduction products of quinones, the change in their concentration during irradiation and in the course of the dark reaction should obey the system of kinetic equations corresponding to the consecutive (1) and monomolecular (2) reactions.

$$\begin{cases} [\mathrm{PE}]_{\tau_1} = \dfrac{k_{\mathrm{acc}}[o\text{-Q}]_0}{k_{\mathrm{dec}} - k_{\mathrm{acc}}}\left(\mathrm{e}^{-k_{\mathrm{acc}}\tau_1} - \mathrm{e}^{-k_{\mathrm{dec}}\tau_1}\right), & (1) \\[2ex] [\mathrm{PE}]_{\tau_2} = [\mathrm{PE}]_{\tau_1} \cdot \mathrm{e}^{-k_{\mathrm{dec}}\tau_2}, & (2) \end{cases}$$

where $[\mathrm{PE}]_\tau$ is the current concentration of 2-(aminomethoxy)phenol, $[o\text{-Q}]_0$ is the initial concentration of *o*-benzoquinone, k_{acc} is the rate constant of accumulation of 2-(aminomethoxy)phenol, which is equal to the rate constant of photoreduction of *o*-benzoquinone, k_{dec} is the rate constant of decomposition of 2-(aminomethoxy)phenol, τ_1 is the irradiation time of the reaction solution, and τ_2 is the dark reaction time, including the time of set-up of the NMR spectrometer. Substituting the constants k_{acc} and k_{dec} determined under the same experimental conditions in Eqs (1) and (2), respectively, one can calculate the theoretical concentration of 2-(aminomethoxy)phenol at the reaction time $\tau = \tau_1 + \tau_2$ and compare this concentration with the experimental value. An agreement between the experimental and theoretical constants will imply that 2-(aminomethoxy)phenol is the only primary photoreduction product of *o*-benzoquinones in the presence of *N*,*N*-dimethylanilines. Table 1 gives the effective rate constants of accumulation and decomposition of 2-(aminomethoxy)phenols and their experimental (P_{exp}) and calculated (P_{calc}) normalized concentrations (which are equal to the ratio of the current concentration of 2-(aminomethoxy)phenol to the initial concentration of quinone), which were determined at the reaction time τ equal to the total time of irradiation (τ_1) and the dark reaction (τ_2).

Table 1. Effective rate constants of accumulation (k_{acc}) and decomposition (k_{dec}) of 2-(aminomethoxy)phenols and the experimental (P_{exp}) and theoretical (P_{calc}) normalized concentrations of 2-(aminomethoxy)phenols in the reaction mixture at the reaction time $\tau = \tau_1 + \tau_2$, where τ_1 is the irradiation time and τ_2 is the dark reaction time (C_6D_6, 298 K)

Compound	$k_{\mathrm{acc}} \cdot 10^4$	$k_{\mathrm{dec}} \cdot 10^4$	P_{exp}	P_{calc}	τ_1	τ_2
	s^{-1}		%		s	
7	54.7	33.0	25±3	19±7	60	90
8	40.7	0.26	53±5	52±4	180	120
9	46.3	0.22	62±6	56±4	180	120
10	13.6	0.14	14±1	61±5	700	120
11A,B	46.4	17.0	33±3	31±6	120	120
12	14.5	0.60	23±2	17±2	120	120
13	22.9	3.0	20±2	23±3	120	120
14	29.0	0.50	14±1	16±2	60	120

The rate constants of photoreduction of the quinones under study and, correspondingly, the rate constants of accumulation of 2-(aminomethoxy)phenols are similar to each other (see Table 1). At the same time, the constants k_{dec} vary by two orders of magnitude depending on the nature of quinone and amine. The calculated curves of the changes in the normalized concentrations of 2-(aminomethoxy)phenols **7** and **8** with time are shown in Fig. 3. The curve $P_{\mathrm{calc}} = f(\tau)$ for compound **11** is similar to that for **7** (see Fig. 3, *a*), and the curves for compounds **12—14** are similar to those for compound **8** (see Fig. 3, *b*).

A comparison of P_{exp} and P_{calc} shows that P_{exp} are lower than P_{calc} only for 2-(aminomethoxy)phenol **10**. For the other compounds of this series, P_{exp} and P_{calc} are equal within experimental error. These results indicate that 2-(aminomethoxy)phenols **7—9** and **11—14** are the major photoreduction products of *o*-quinones. However, since the experimental accuracy is low, we cannot state with assurance that photoreduction of *o*-benzoquinones

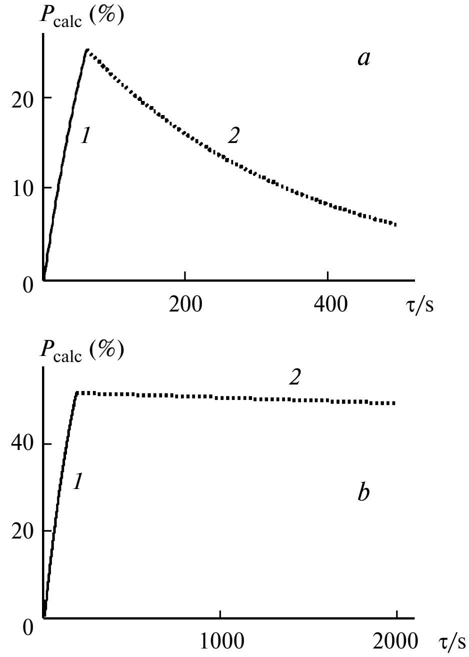
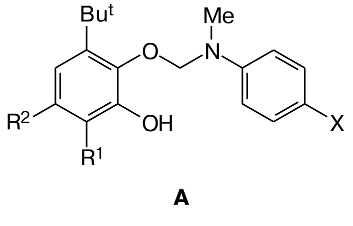


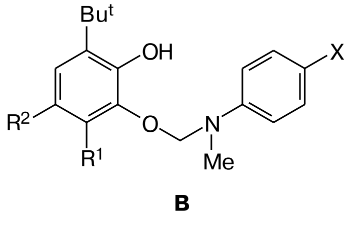
Fig. 3. Calculated curves of the changes in the normalized concentrations of 2-(aminomethoxy)phenols **7** (*a*) and **8** (*b*) during irradiation (*1*) and in the course of the dark process (*2*).

under study occurs only through the intermediate formation of the corresponding 2-(aminomethoxy)phenols.

The rates of formation and decomposition of 2-(aminomethoxy)phenols are substantially different (see Fig. 3 and Table 1). Depending on the nature of quinone and amine, the constants k_{dec} vary by two orders of magnitude. The structure is one of the factors responsible for stability of these compounds. Theoretically, photoreduction of *o*-benzoquinones under study (except for **1b**) can afford two isomeric forms of 2-(aminomethoxy)phenol (**A** and **B**). However, two isomers **11A,B** were experimentally detected only upon photoreduction of 3,6-di(*tert*-butyl)-4-fluoro-1,2-benzoquinone (**1c**) in the presence of 4-bromo-*N*,*N*-dimethylaniline (**2b**). These isomers were generated in equal amounts and decompose at an equal rate ($k_{dec} = 17.0 \cdot 10^{-4}$ s^{-1}). In the other cases, the formation of only one isomer was observed, and the constants k_{dec} in Table 1 correspond to the process of decomposition of this isomer. Presumably, the substantial difference between P_{exp} and P_{calc} for 2-(aminomethoxy)phenol **10** is attributed to the fact that the constant k_{acc} corresponds to the rate constant of accumulation of both isomers of compound **10**, whereas k_{dec} corresponds to only one of the isomers. The ^{1}H NMR spectra of the reaction products of **1a** and **2b** show signals in the regions characteristic of methylene and methyl groups; however, these signals cannot be unambiguously identified and assigned.



A



B

Based on the overall ^{1}H NMR spectrum, it is impossible to determine which regioisomer of 2-(aminomethoxy)phenol is produced in the reaction. Only photoreduction of benzoquinone **1b** in the presence of compound **2b** afforded individual stable 2-[*N*-(4-bromophenyl)-*N*-methyl]aminomethoxy-4,6-di(*tert*-butyl)phenol (**8**), which was characterized by elemental analysis, NMR and IR spectroscopy, and X-ray diffraction study. X-ray diffraction data demonstrated that compound **8** was formed as regioisomer **B** (Fig. 4).

Molecule **8** consists of the 2-[*N*-(4-bromophenyl)-*N*-methyl]aminomethoxy and 4,6-di(*tert*-butyl)phenol fragments. The Br(1), N(1), C(15) and O(1), O(2), C(11), C(7) atoms lie in the planes of the phenyl rings C(17)—C(22) and C(1)—C(6), respectively. The average deviation of these atoms from the planes of the phenyl rings is 0.06 Å. The dihedral angle between the planes of the Ph rings is 59.8(3)°. The C(16) atom deviates from the plane of the Ph ring C(17)—C(22) by 0.210(9) Å. In molecule **8**, the intramolecular O(1)...H(2´) distance is shortened (2.31(5) Å; O(1)...H(2´)—O(2), 116.8(9)°), and this distance is substantially smaller than the sum of the van der Waals radii of the O and H atoms (2.45 Å)[16] but is larger than the specific O...H distance characteristic of hydrogen bonding (2.15 Å).[16] It should be noted that the IR spectrum of compound **8** in solution shows an OH stretching band at 3490 cm^{-1} (see Ref. 14), which is

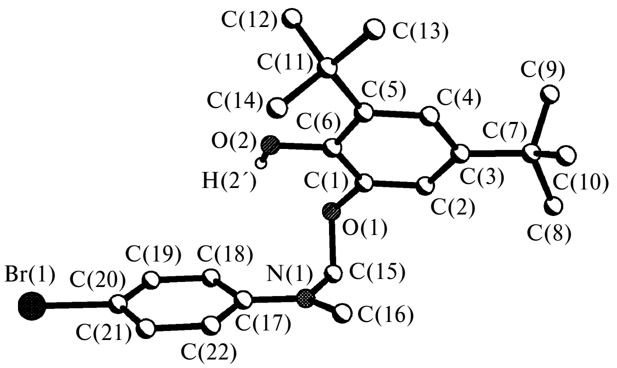


Fig. 4. Molecular structure of 2-[*N*-(4-bromophenyl)-*N*-methyl]aminomethoxy-4,6-di(*tert*-butyl)phenol (**8**).

Table 2. Selected bond lengths (d) and bond angles (ω) in 2-[N-(4-bromophenyl)-N-methyl]aminomethoxy-4,6-di(*tert*-butyl)phenol (**8**)

Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d/Å
Br(1)—C(20)	1.902(5)	C(7)—C(10)	1.524(6)
O(1)—C(1)	1.397(5)	C(11)—C(12)	1.539(6)
O(1)—C(15)	1.457(5)	C(11)—C(13)	1.528(6)
O(2)—C(6)	1.375(5)	C(11)—C(14)	1.534(6)
N(1)—C(15)	1.411(6)	C(17)—C(18)	1.410(6)
N(1)—C(16)	1.453(6)	C(17)—C(22)	1.388(6)
N(1)—C(17)	1.400(6)	C(18)—C(19)	1.384(6)
C(1)—C(2)	1.386(6)	C(19)—C(20)	1.371(7)
C(1)—C(6)	1.393(6)	C(20)—C(21)	1.381(7)
C(2)—C(3)	1.380(6)	C(21)—C(22)	1.389(7)
C(3)—C(4)	1.403(6)		
C(3)—C(7)	1.539(6)	Angle	ω/deg
C(4)—C(5)	1.396(6)	C(1)—O(1)—C(15)	112.5(3)
C(5)—C(6)	1.404(6)	C(15)—N(1)—C(16)	119.2(4)
C(5)—C(11)	1.536(6)	C(17)—N(1)—C(15)	120.8(4)
C(7)—C(8)	1.526(8)	C(17)—N(1)—C(16)	119.0(4)
C(7)—C(9)	1.536(8)	N(1)—C(15)—O(1)	114.4(4)

indicative of the presence of an intramolecular hydrogen bond and agrees well with the published data.[17] Therefore, 2-(aminomethoxy)phenol **8** contains two planar fragments linked to each other by the O(1)—C(15) bond. Selected bond lengths and bond angles are typical of pyrocatechols (Table 2). In the crystalline state, molecules **8** are linked to each other to form chains through the normal van der Waals interactions H(2′)...O(1) (2.47(6) Å) and Br(1)...H(13) (2.93(5) Å) between the terminal molecules (Fig. 5).

The ^{1}H NMR spectrum of individual compound **8** is identical to the spectrum of this compound in the reaction mixture. This is evidence that only sterically less hindered isomer **B** of 2-(aminomethoxy)phenols rather than two regioisomers is generated upon photoreduction. In turn, stability of 2-(aminomethoxy)phenols is determined also by steric hindrance resulting from the ether bond formation. For example, compound **7** prepared by the photoreaction of **1e** with **2b** is much less stable than isomer **8** (the constant k_{dec} changes from $33.0 \cdot 10^{-4}$ s^{-1} for **7** to $0.26 \cdot 10^{-4}$ s^{-1} for **8**). Consequently, a decrease in the size of the substituents at the position adjacent to the new ether bond leads to an increase in stability of 2-(aminomethoxy)phenols. This is also confirmed by stability of compound **9** containing the methyl group at position 3 of the quinoid ring ($k_{\text{dec}} = 0.22 \cdot 10^{-4}$ s^{-1}).

Analysis of the data in Table 1 also shows that the electron-withdrawing and electron-donating properties of quinones and amines, respectively, can serve as the second criterion responsible for stability of 2-(aminomethoxy)phenols. For example, stability of the products

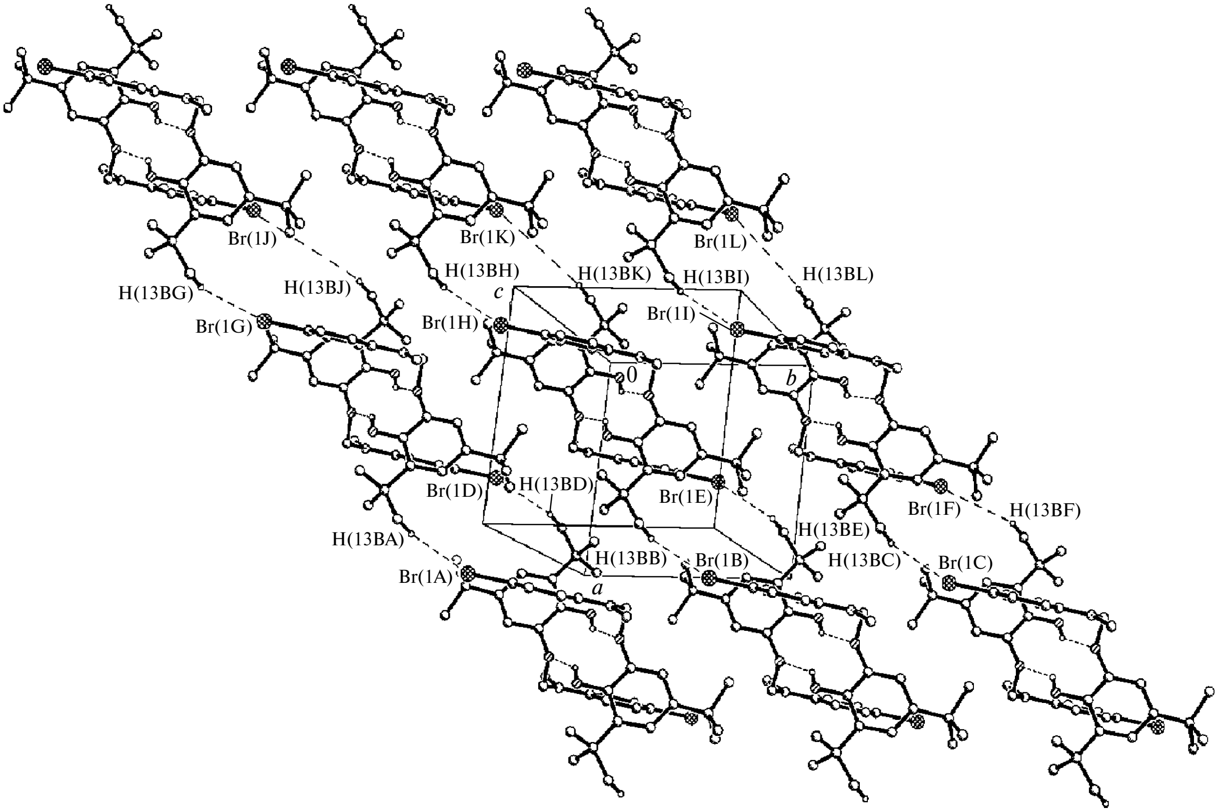
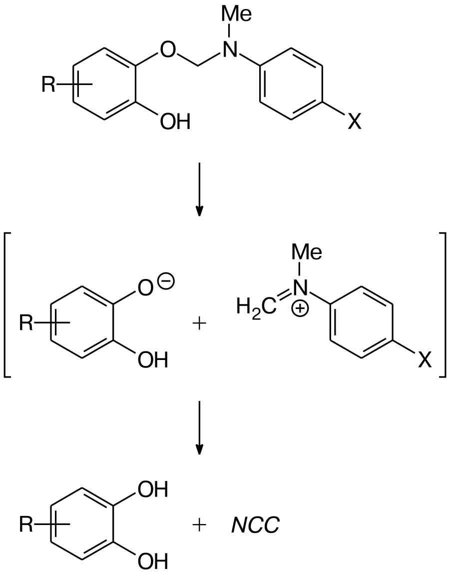


Fig. 5. Fragment of the crystal packing of 2-[N-(4-bromophenyl)-N-methyl]aminomethoxy-4,6-di(*tert*-butyl)phenol (**8**).

Scheme 3



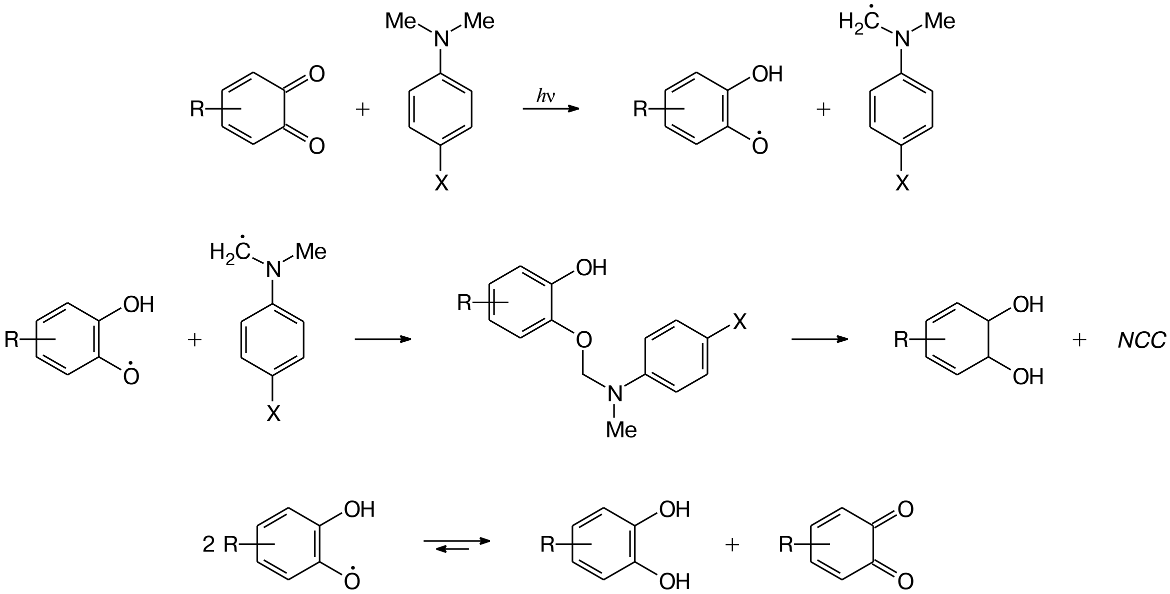
NCC are nitrogen-containing compounds.

prepared by the reaction of quinone **1a** ($E_{1/2}$ = –0.48 V)[18] with amine **2b** is substantially higher than that of compounds prepared by the corresponding reaction with more electron-withdrawing quinone **1c** ($E_{1/2}$ = –0.34 V)[18] (the constant k_{dec} increases from $0.14 \cdot 10^{-4}$ s^{-1} for **10** to $17.0 \cdot 10^{-4}$ s^{-1} for **11**). At the same time, an increase in the electron-donating properties of amine in bromo derivative **2b** ($E_{1/2}$ = 0.71 V)[15] compared to those in cyano derivative **2c** ($E_{1/2}$ = 1.12 V)[15] also leads to a substantial decrease in stability of 2-(aminomethoxy)phenols prepared by photoreactions of these compounds with quinone **1b**. The constant k_{dec} increases by more than two orders of magnitude from $0.6 \cdot 10^{-4}$ s^{-1} for **12** to $33.0 \cdot 10^{-4}$ s^{-1} for **7**. An analogous effect was observed for the photoreactions of **1e** with **2a** ($E_{1/2}$ = 0.49 V),[15] **2b** ($E_{1/2}$ = 0.71 V), and **2c** ($E_{1/2}$ = 1.12 V). The constants k_{dec} of the resulting 2-(aminomethoxy)phenols are $3.0 \cdot 10^{-4}$ s^{-1} for **13**, $0.26 \cdot 10^{-4}$ s^{1} for **8**, and $0.5 \cdot 10^{-4}$ s^{-1} for **14**. Therefore, it can be stated that an increase in the electron-withdrawing properties of quinone and the electron-donating properties of amine leads to a decrease in stability of 2-(aminomethoxy)phenols.

The influence of the redox properties of quinones and amines on stability of their photoreaction products suggests that decomposition of these products occurs by a heterolytic mechanism shown in Scheme 3. The introduction of the fluorine atom at position 4 of the quinone ring (R = F) stabilizes the anion in the intermediate ion pair due to which compound **11** decomposes much faster than **10**. The replacement of electron-withdrawing substituents X (Br or CN) in the *para* position of *N*,*N*-dimethylaniline with the electron-donating substituent (MeO) increases stability of the intermediate iminium cation due to which decomposition of compound **13** occurs more rapidly compared to compounds **8** and **14**.

The heterolytic mechanism of decomposition of 2-(aminomethoxy)phenols is confirmed by the fact that the decomposition rate of these compounds is sensitive to

Scheme 4



NCC are nitrogen-containing compounds.

the solvent polarity. The influence of the solvent polarity was examined using compound **8** as an example. Measurements demonstrated that the rate constant of decomposition in deuterochloroform ($\varepsilon = 4.39$)[19] is an order of magnitude higher than that in deuterobenzene ($\varepsilon = 2.12$)[19] ($0.41 \cdot 10^{-7}$ and $3.13 \cdot 10^{-7}$ s^{-1}, respectively).* Based on the above facts, photoreduction of *o*-benzoquinones in the presence of *N*,*N*-disubstituted anilines can be described by Scheme 4.

The proton abstraction from the methyl group of amine by the photoexcited *o*-quinone molecule gives rise to radical products, *viz*., the oxyphenoxy and aminomethyl radicals. Recombination of the oxyphenoxy and aminomethyl radicals affords aminoformal, *viz*., 2-(aminomethoxy)phenol, which is the major primary photoreduction product of *o*-benzoquinone. Disproportionation of the hydroxyphenoxy radicals giving rise to pyrocatechol and *o*-quinone cannot be ruled out as well. In the subsequent dark reaction, 2-(aminomethoxy)phenols (vacuum, room temperature) undergo quantitative decomposition to form pyrocatechols.

Experimental

The electronic absorption spectra were recorded on a SF-14 spectrometer. The NMR spectra were measured on a Bruker DPX-200 spectrometer. Photochemical reactions were carried out with the use of an illuminator equipped with a focusing system and a KGM-24-150 lamp. Radiation at $\lambda > 500$ nm was separated from the light flux of the lamp using a ZhS-16 light filter. All studies were performed in NMR tubes. A deaerated benzene solution (2 mL) containing *o*-benzoquinone ($3 \cdot 10^{-2}$ mol L^{-1}) and amine ($1.5 \cdot 10^{-1}$ mol L^{-1}) was placed in a tube, which was sealed and then exposed at a distance of 7 cm from the lens of the illuminator. The solvents (benzene and hexane) were purified according to a standard procedure.[19] 4-Methoxy-*N*,*N*-dimethylaniline was synthesized according to a known procedure.[20] 4-Bromo-*N*,*N*-dimethylaniline (Aldrich) and 4-cyano-*N*,*N*-dimethylaniline (Aldrich) were twice sublimed. The synthesis of *o*-benzoquinone and pyrocatechol derivatives has been described earlier.[21] 3,6-Di(*tert*-butyl)-4-fluoropyrocatechol was prepared by reduction of 3,6-di(*tert*-butyl)-4-fluoro-1,2-benzoquinone with hydrazine hydrate. ^{1}H NMR (C_6D_6), δ: 1.23 (s, 9 H, Bu^t); 1.54 (d, 9 H, Bu^t, $J = 2.5$ Hz); 3.95 and 4.12 (both s, 1 H each, OH); 6.23 (s, 1 H, C(5)H).

The compositions of the products prepared by photoreduction of *o*-benzoquinones in the presence of *para*-substituted *N*,*N*-dimethylanilines were monitored based on the changes in the ^{1}H NMR spectra. All 2-(aminomethoxy)phenols are unstable and were characterized by NMR spectroscopy in the reaction mixture.* The spectra show only one isomeric form, except for the products prepared by photoreduction of 3,6-di(*tert*-butyl)-4-fluoro-1,2-benzoquinone in the presence of 4-bromo-*N*,*N*-dimethylaniline. The ^{1}H NMR spectroscopic data for 2-(aminomethoxy)phenols are given below and were reported in the earlier publication.[14]

2-[*N*-(4-Bromophenyl)-*N*-methylamino]methoxy-3,6-di(*tert*-butyl)-4-methoxyphenol (10). ^{1}H NMR (C_6D_6), δ: 1.66 and 1.81 (both s, 9 H each, Bu^t); 3.00 (s, 3 H, MeO); 4.58 (s, 2 H, OCH_2N).

2-[*N*-(4-Bromophenyl)-*N*-methylamino]methoxy-3,6-di(*tert*-butyl)-4-fluorophenols (two isomers 11A,B). ^{1}H NMR (C_6D_6), δ: 1.26, 1.36, and 1.54 (all s, 9 H each, Bu^t); 1.69 (d, 9 H, Bu^t, $J = 3$ Hz); 4.42 and 4.48 (both s, 2 H each, OCH_2N).

3,6-Di(*tert*-butyl)-2-[*N*-(4-cyanophenyl)-*N*-methylamino]methoxyphenol (12). ^{1}H NMR (C_6D_6), δ: 1.37 and 1.47 (both s, 9 H each, Bu^t); 2.31 (s, 3 H, MeN); 4.49 (s, 2 H, OCH_2N).

4,6-Di(*tert*-butyl)-2-[*N*-(4-methoxyphenyl)-*N*-methylamino]methoxyphenol (13). ^{1}H NMR (C_6D_6), δ: 1.33 and 1.59 (both s, 9 H each, Bu^t); 2.61 (s, 3 H, MeN); 3.36 (s, 2 H, OCH_2N).

4,6-Di(*tert*-butyl)-2-[*N*-(4-cyanophenyl)-*N*-methylamino]methoxyphenol (14). ^{1}H NMR (C_6D_6), δ: 1.32 and 1.56 (both s, 9 H each, Bu^t); 2.34 (s, 3 H, MeN); 4.64 (s, 2 H, OCH_2N); 4.92 (s, 1 H, OH).

2-[*N*-(4-Bromophenyl)-*N*-methylamino]methoxy-4,6-di(*tert*-butyl)phenol (8), which was prepared by photoreduction of 3,5-di(*tert*-butyl)-1,2-benzoquinone in the presence of 4-bromo-*N*,*N*-dimethylaniline, was isolated in individual state[14] and studied by X-ray diffraction. Single crystals of **8** were grown from an *n*-hexane solution in an evacuated tube by slow cooling. At 100(2) K, crystals of **8** are triclinic: $C_{22}H_{30}BrNO_2$, $M = 420.38$, $a = 10.026(1)$, $b = 10.131(2)$, $c = 11.317(2)$ Å, $V = 1053.5(3)$ Å^3, space group $P\bar{1}$, $Z = 2$, $\mu = 1.966$ mm^{-1}, $d_{\text{calc}} = 1.325$ g cm^{-3}, 5783 reflections were measured, of which 3680 independent reflections ($R_{\text{int}} = 0.0261$) were used in calculations; R_1 ($I > 2\sigma(I)$) = 0.0572, wR_1 (based on complete data) was 0.1630, GOOF (F^2) = 1.055. The structure was solved by direct methods and refined against F^2 using the SHELXTL program package.[18] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference electron density maps, except for the hydrogen atoms at C(10), which were placed in geometrically calculated positions and refined using a riding model. Selected bond angles and bond lengths are given in Table 1.

The effective rate constants of photoreduction (k_{acc}) of *o*-benzoquinones in the presence of *para*-substituted *N*,*N*-dimethylanilines were determined spectrophotometrically based on a decrease in the intensity of the S-π—π^* absorption band of quinone. The solution was placed in an NMR tube and irradiated under standard conditions. Under experimental conditions, photoreduction initially obeys the first-order kinetic equation until the conversion of quinone reached ~30%. The effective rate constants of quinones were calculated from the slope of the linear region of the $\ln(C_0/C_\tau)$—τ plot, where C_0 and C_τ are the concentrations of *o*-benzoquinone before irradiation and at the

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* The fact that k_{dec} in C_6D_6 determined in this experiment differs from k_{dec} in Table 1 ($k_{\text{dec}} = 0.26 \cdot 10^{-4}$ s^{-1}) is, evidently, attributed to the difference in the experimental conditions. The solvent effect on k_{dec} was estimated with the use of solutions of individual compound **8**, whereas the data in Table 1 correspond to decomposition of 2-(aminomethoxy)phenols in the reaction mixture.

* The signals for the protons of the aromatic system of 2-(aminomethoxy)phenols are not reported because they overlap with the signals of the starting reagents.

time τ, respectively, where τ is the total time of irradiation of the solution. The numerical values of the effective rate constants were averaged based on three measurements with the convergence of the results within 10%.

The effective rate constants of decomposition of 2-(aminomethoxy)phenols (k_{dec}) were determined from the changes in the intensity of the characteristic signals in the ^{1}H NMR spectra. A solution of *o*-benzoquinone ($3 \cdot 10^{-2}$ mol L^{-1}) and *para*-substituted *N*,*N*-dimethylaniline ($1.5 \cdot 10^{-12}$ mol L^{-1}) in C_6D_6 was placed in an NMR tube and deaerated. The tube was exposed with a constant geometry. The irradiation time was varied taking into account the efficiency of photoreduction of the reaction pair. The changes in the intensity of the characteristic signals of the components of the mixture were recorded at intervals. Under experimental conditions, decomposition of 2-(aminomethoxy)phenols obeys the first-order kinetic equation. The constants k_{dec} were calculated from the slope of the linear region of the $\ln(I_0/I_\tau)$—τ plot (I_0 and I_τ are the intensities of the typical signals of 2-(aminomethoxy)phenols before irradiation and at the time τ, respectively, where τ is the dark reaction time). The numerical values of k_{dec} were averaged based on three measurements with the convergence of the results within 15—20%.

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