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Activated Sterically Strained C=N Bond in *N*-Substituted *p*-Quinonemono- and -diimines: XI.* Redox Potentials of 2,6- and 3,5-Dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimines

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Abstract—Due to steric effect of the methyl groups the lone electron pair on the nitrogen atom in 3,5-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine is forced out of the quinoid ring plane, so that the nitrogen atom adopts a near-*sp* hybridization. As a result, its electrophilicity and hence redox potential increase, leading to activation of the C=N bond to addition of nucleophiles, as compared to the corresponding 2,6-dimethyl isomer.

We previously [2] revealed a relation between the barriers to *Z*,*E* isomerization and structural parameters of various N-substituted 1,4-benzoquinonimines: The activation energy for the *Z*,*E* isomerization ($\Delta G^{\neq}$) was found to change in the opposite direction to the C=N–X bond angle. Increase of the C=N–X angle in the crystalline state leads to decrease of $\Delta G^{\neq}$, thus increasing the rate of *Z*,*E* isomerization in solution. Anomalously low barriers to *Z*,*E* isomerization were found for *N*-aroyl-1,4-benzoquinonimines [3] and *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines [4]; therefore, it was reasonable to presume that the C–N–X bond in such 1,4-benzoquinonimines in crystal is considerably greater than 120°. Our X-ray diffraction study showed that the C=N–S bond angle in 2,6-di-*tert*-butyl-*N*-4-chlorobenzoyl-1,4-benzoquinonimine and 2,6-dimethyl-*N*-(*N*-phenylsulfonylbenzimidoyl)-1,4-benzoquinonimine is 124.6 and 124.1°, respectively [4]. These values are clearly inconsistent with the low activation energies for *Z*,*E*-isomerization. According to the X-ray diffraction data, the reason is that the aroyl C=O group in *N*-aroyl-1,4-benzoquinonimines and the C=N group in the *N*-aroylsulfonylbenzimidoyl fragment of *N*-(*N*-arylsulfonylbenzimidoyl)-1,4-benzoquinonimines are arranged orthogonally to the quinoid ring plane. Therefore, the π^* orbital of the C=O or C=N bond is parallel to the nitrogen lone electron pair (LEP) orbital (n_N), which favors the n_N–$\pi^*_{C=O\,(C=N)}$ interaction and leads to reduction of the energy of n_N and the energy of linear transition state [4].

N,*N*′-Bis(trimethylsilyl)-1,4-benzoquinonediimine was assigned [5] a linear structure with *sp*-hybridized nitrogen atom, which is stabilized by the exchange interaction $n_N \rightarrow d_{Si}$, i.e., via electron transfer from the nitrogen LEP on the *d* orbital of silicon. The structure was established on the basis of spectral data, including ^{1}H NMR spectra (all four quinoid ring protons are magnetically equivalent).

We believe that in this case a very fast (on the NMR time scale) *Z*,*E* isomerization with respect to the C=N bond occurs, and we can speak about a considerable contribution of a linear structure with *sp*-hybridized nitrogen atom. Anomalously low energy barriers to *Z*,*E* isomerization were also found for N-substituted 1,4-benzoquinonemonoimines, including *N*-arylsulfonyl-1,4-benzoquinonemonoimines with two substituents (CH_3, Cl) in the quinoid ring in the *ortho* positions with respect to the imino group [2]. The latter are more reactive toward nucleophiles than their isomers containing the same substituents in the *ortho* positions with respect to the C=O group or analogs

* For communication X, see [1].

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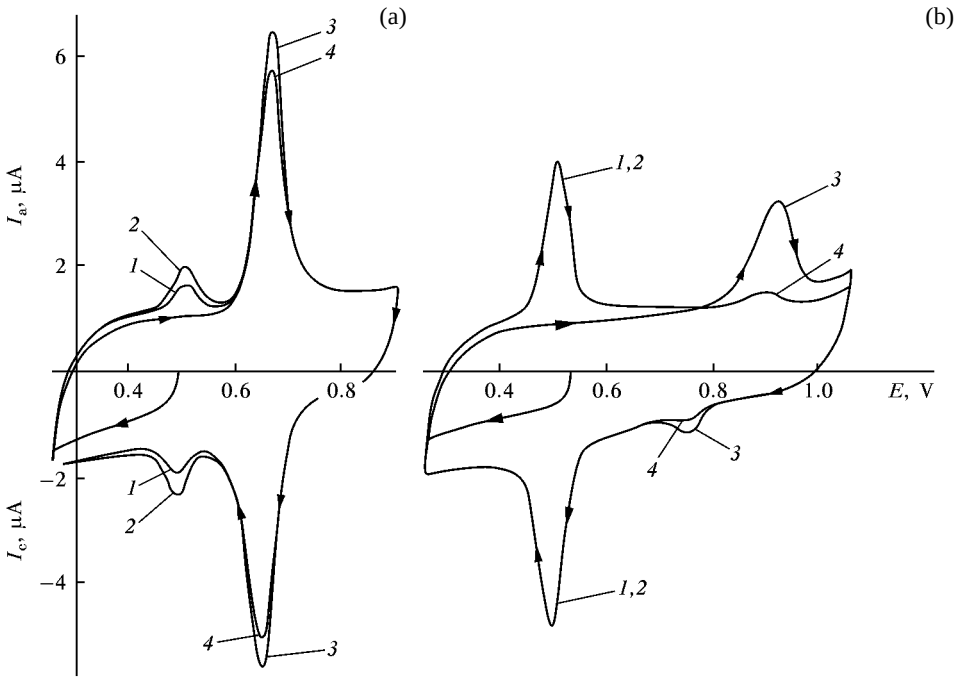
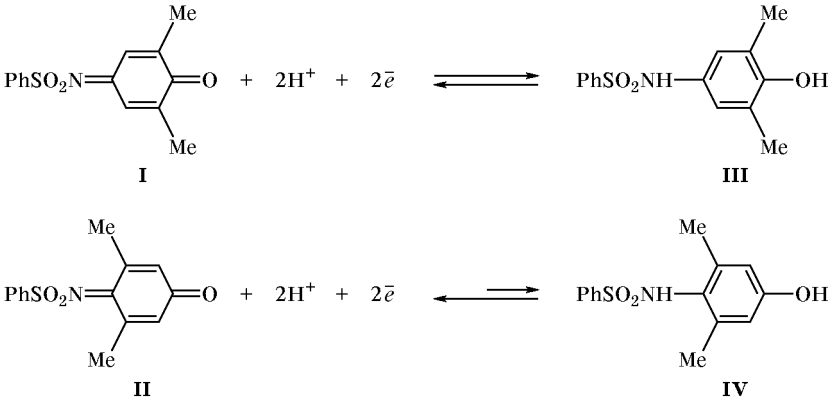


Fig. 1. Cyclic voltammograms of (a) 2,6-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine (**I**) (pH 1.50, $c = 2.2 \times 10^{-9}$ mol/cm^2, r = 1 mV/s) and (b) 3,5-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine (**II**) (pH 1.49, $c = 2.2 \times 10^{-9}$ mol/cm^2, r = 1 mV/s); peaks corresponding to redox transformations of quinonimines **I** and **II**: (*3*) first cycle and (*4*) second cycle; peaks corresponding to redox transformations of 2,6-dimethyl-1,4-benzoquinone: (*1*) first cycle and (*2*) second cycle.

having no substituents at all. Here, the most characteristic are 1,2-addition or 1,2-addition–elimination reactions, i.e., those involving the C=N bond. 1,2-Addition reactions give rise to 4-hydroxy-2,5-cyclohexadienone structures [1, 2, 6–9]. Thus the C=N bond in N-substituted 1,4-quinonemonoimines having two substituents in the *ortho* positions with respect to that bond is activated and sterically strained. As follows from the X-ray diffraction data [8] and also from the results of studying analogous structures with both donor and acceptor substituents in the quinoid ring [1], activation of the C=N bond is induced by steric rather than electronic effect of the substituents, which leads to increase of the C=N–S bond angle. It is known [2] that the larger the C=N–X angle, the lower the barrier to *Z*,*E* isomerization and hence the higher the isomerization rate. Taking into account fast *Z*,*E* isomerization in solution of *N*-arylsulfonyl-1,4-benzoquinonimines with activated C=N bond, we can assume (as well as for the other quinonimines considered above) a significant contribution of a linear structure with *sp*-hybridized nitrogen atom.

Redox potential E^0 which characterizes the equilibrium between the quinoid and benzoid structures is an important parameter for estimation of the reactivity of quinoid compounds [10]. We could expect a considerable difference in E^0 for *N*-arylsulfonyl-1,4-benzoquinonimines with activated and nonactivated C=N bond, as well as in their behavior in electrode processes. As subjects for study we chose 2,6-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine (**I**) and 3,5-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine (**II**). Their redox potentials were determined by studying systems **I**–**III** and **II**–**IV** (Scheme 1), i.e., those containing both oxidized and reduced forms of the corresponding quinonimines. Strong differences were observed in the electrochemical behavior of the above systems in the pH range from 0 to 5.74. Figure 1 shows voltammograms obtained for **I** and **II**. Each curve contains two pairs of conjugate oxidation–reduction peaks on variation of the potential over a fairly wide range. One pair corresponds to electrochemical transformations of the quinonimine, and the other, to transformations of its hydrolysis product, dimethyl-1,4-benzoquinone. As follows from Fig. 1a, transformations in system **I**–**III** are reversible. The peaks of quinonimime **I** in the anode and cathode processes are symmetric, and they have approximately equal areas. The irreversibility (the difference between the peak potentials for the anode and cathode processes) does not exceed 15–45 mV throughout the examined range. At pH 0, the standard redox potential

Scheme 1.



is 7.748±0.003 V. This value lies within the expected range (E^0 = 0.875 V for benzoquinonimine having no substituents in positions *2* and *6*, and E^0 = 0.817 V for 2-methyl-1,4-benzoquinonimine [11]). Quinonimine **I** undergoes hydrolysis during electrochemical experiment; as a result, a couple of peaks appears, which correspond to reversible oxidation–reduction of the hydrolysis product, 2,6-dimethyl-1,4-benzoquinone, E^0 = 0.587 V [12]. Appreciable hydrolysis of **I** occurs in strongly acidic medium; it is relatively stable at pH 1.5 to 5.74.

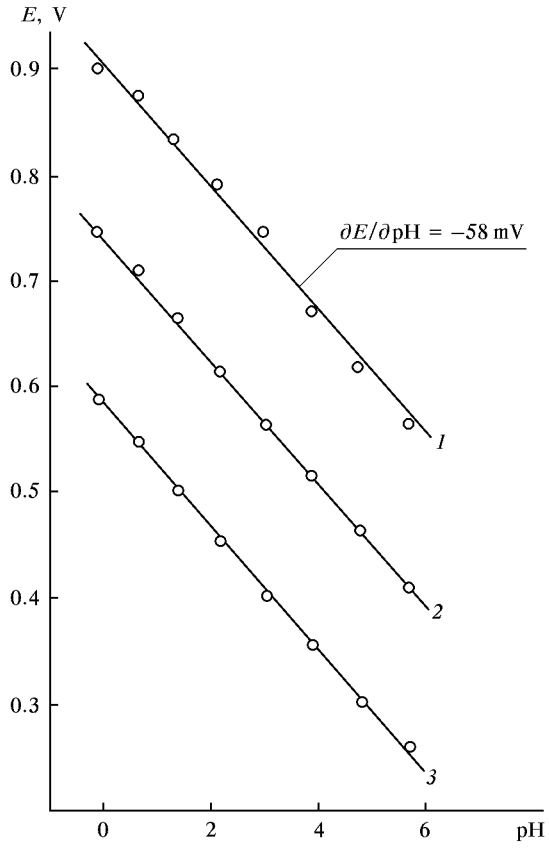


Fig. 2. Plots of the redox potentials *E* of (*1*) 3,5-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine (**II**), (*2*) 2,6-dimethyl-*N*-phenylsulfonyl-1,4-benzoquinonimine (**I**), and (*3*) 2,6-dimethyl-1,4-benzoquinone (hydrolysis product) versus pH of the medium.

A quite different pattern is observed for system **II**⇄**IV**. Figure 1b shows that electrochemical transformations of quinonimine **II** are largely irreversible. The oxidation and reduction peaks are asymmetric, and they appear at appreciably different potentials. The irreversibility is 140–180 mV at pH < 3.5; it decreases to 43 mV at pH 5.74. The oxidized form (aminophenol **II**) undergoes almost complete hydrolysis to 2,6-dimethyl-1,4-benzoquinone even in the first cycle. Therefore, the cathode peak of **II** is small and poorly resolved. The same pattern was observed throughout the examined range of pH. As a result, the standard redox potential was determined with a relatively low accuracy, E^0 = 0.912±0.011 V. At pH 0, the oxidation potential is 0.971 V, and the reduction potential, 0.829 V. Figure 2 shows the dependences $E^0 = f(\text{pH})$ for systems **I**⇄**III** and **II**⇄**IV** and for the hydrolysis product, 2,6-dimethyl-1,4-benzoquinone. These dependences are straight lines with a slope of –58 mV per unit pH, indicating that the redox process involves two protons and two electrons, in keeping with Scheme 1.

According to the X-ray diffraction data for 3,5-dimethyl-*N*-4-chlorophenylsulfonyl-1,4-benzoquinonimine, which is a structural analog of **II**, the C=N bond length is 1.290 Å [8]; this value is similar to that found for 2,6-di-*tert*-butyl-*N*-4-bromophenyl-1,4-benzoquinonimine [13] but appreciably smaller than the C=N bond length in *N*,*N*′-bis(2-naphthyl)-1,4-benzoquinonediimine (1.296 Å) [14], *N*,*N*′-bis(phenylthio)-1,4-benzoquinonediimine (1.317 Å) [15], *N*,*N*′-

bis(methylsulfonyl)-1,4-benzoquinonediimine [16], and the 2,6-dichloro-*N*-4-tolylsulfonyl-1,4-benzoquinonimine–pyrene complex [17]. The S–N bond (1.638 Å) is considerably shorter than the S–N bond in the 2,6-dichloro-*N*-4-tolylsulfonyl-1,4-benzoquinonimine–pyrene complex (1.655 Å) [17]. The C=N–S and N–S–C angles are 132.7 and 98.9°, respectively. These data indicate a significant conjugation between the nitrogen and sulfur atoms (n_N–d_S interaction). A plausible explanation is that closely arranged methyl groups in **II** force the nitrogen LEP out of the quinoid ring plane; as a result, the nitrogen atom acquires near-*sp* hybridization. Quinonimine **II** in solution gives rise to fast (on the NMR time scale) *Z*,*E* isomerization through a linear transition state with *sp*-hybridized nitrogen atom, so that both methyl and quinoid ring protons (2-H and 6-H) become magnetically equivalent.

The result is enhanced electrophilicity of the nitrogen atom, increased redox potential, and higher reactivity toward addition of nucleophiles, since the reactive species is protonated quinonimine. The irreversible character of oxidation of quinonimine **II** is explained by the presence (over a wide range of pH) of a considerable fraction of its protonated form which undergoes attack by nucleophilic species, directed orthogonally to the quinoid ring. As usually, nucleophile adds to the C^2 atom of the quinoid ring in the *ortho* position with respect to the carbonyl group (1,4-addition) or to the C^4 atom (C=N group) (1,2-addition or 1,2-addition–elimination). The attack on C^4 gives rise to a tetrahedral transition state in which steric hindrances are reduced (at the sp^3-hybridized carbon atom), and 1,2-addition or 1,2-addition–elimination becomes the predominant reaction path (e.g., hydrolysis of the oxidized form to the corresponding benzoquinone). The irreversibility of redox processes in system **II** $\rightleftarrows$ **IV** may be explained on the assumption that the electrophilic center in the oxidation is oxygen atom of the hydroxy group (OH acid), whereas in system **I** $\rightleftarrows$ **III** such center is nitrogen atom of the sulfonylamino group (NH acid). In all cases, the nucleophilic center in the reduction process is the nitrogen atom. Thus the oxidation and reduction processes in system **II** $\rightleftarrows$ **IV** involve different transition states, and this fact is responsible for the observed difference in the peak potentials.

EXPERIMENTAL

The study was performed by thin-layer voltammetry [18]. Experiments were carried out in a cell with two plane–parallel electrodes made of pyrolytic graphite with a total area of 2.26 cm^2. The effective gap was 18 μm. EVL-1M1 silver chloride electrodes were used as auxiliary and reference electrodes. The potentials are given relative to the standard hydrogen electrode at 22±1°C.

The reduced forms of quinonimines (compounds **III** and **IV**) were introduced into the cell as thin films deposited onto the surface of pyrolytic graphite electrodes from solution in DMF. The film thickness was several molecular layers. The density of **III** and **IV** in the film was 2.2×10^{-9} mol/cm^2. A 0.6 N solution of Na_2SO_4 was used as supporting electrolyte. The required pH values were maintained by addition of glycine–HCl (pH 1.1–3.5) or acetate buffer (pH 3.6–5.8). The pH values were measured using an EV-74 universal ionometer. The ionic strength was 1.0. The supporting solution was prepared from doubly distilled water and reactants of at least chemically pure grade. Cyclic voltammograms were recorded with the aid of an N307/1 two-coordinate recorder. The rate of potential sweep (1 mV/s) was set by a PU-1 universal polarograph. The potentials were measured with a Shch132 digital voltmeter. The redox potentials at a given pH value were determined from the position of the corresponding peak on the curve.

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