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SHORT COMMUNICATIONS

New Syntheses of *N*,*N*′-Diaryl-Substituted Quinone Diimines: I. Synthesis of *N*,*N*′-Bis(4-aminophenyl)-1,4-benzoquinone Diimine

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Abstract—Oxidative condensation of *p*-phenylenediamine by the action of $K_2S_2O_8$ in acetic acid afforded *N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinone diimine which underwent self-condensation on heating. Acetylation of the title compound with acetic anhydride in acetic acid gave more stable diacetyl derivative.

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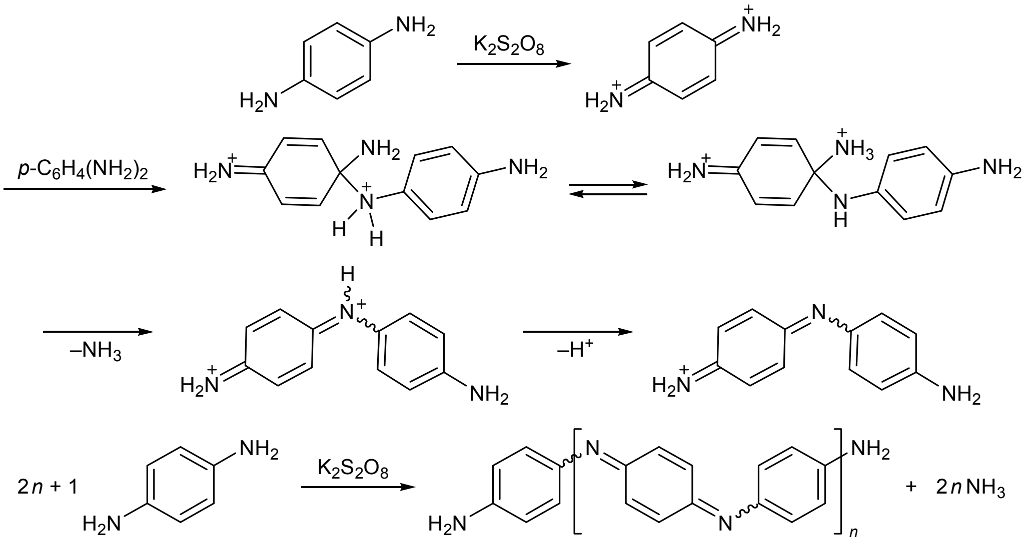
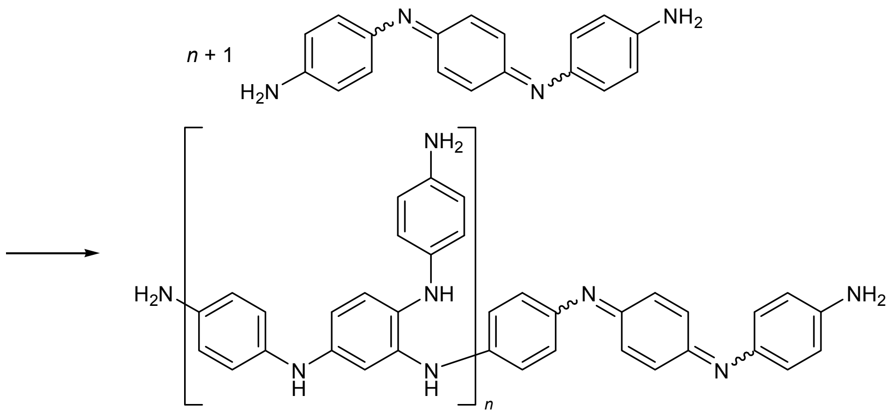
The emeraldine base form of polyaniline contains benzoquinone diimine fragments and is one of the most important conducting polymers [1, 2]. Polymers and oligomers containing quinone diimine fragments structurally similar to polyaniline (also known as pernigraniline) were synthesized by condensation of aromatic amines only with those quinones which cannot be involved in Michael reaction [3–5], as well as by reaction of *N*,*N*′-dichloro-1,4-benzoquinone diimine with organometallic compounds [6]. Oxidative condensation of *N*-phenyl-*p*-phenylenediamine by the action of $FeCl_3 \cdot 6H_2O$ gave aniline tetramer with a quinone diimine fragment [7]. *N*,*N*′-Diaryl-1,4-benzoquinone diimines were obtained in 28–42% yield by oxidation of *p*-phenylenediamine in the presence of aniline and substituted anilines in aqueous ethanol in the presence of an acid [8]. Aniline oligomers including three to eight rings were prepared by reaction of *N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinone diimine with substituted diphenylamines on exposure to air [9]. Enzymatic oxidation of *p*-phenylenediamine with hydrogen peroxide was reported [10] to produce 2,5-diamino-*N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinone diimine; however neither procedure for the isolation of

Scheme 1.

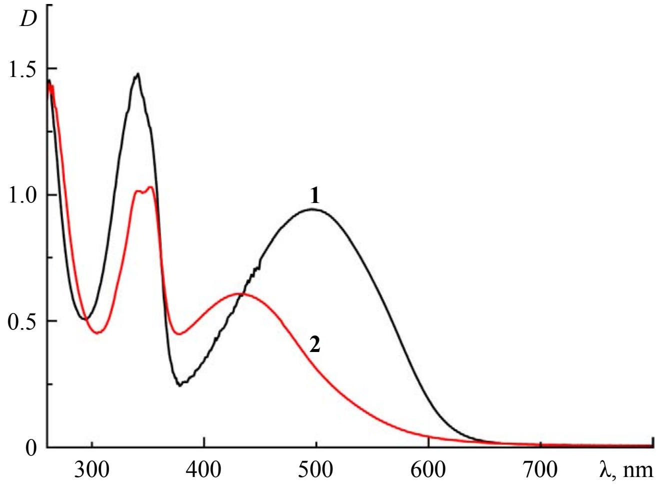


Scheme 2.



the pure compound nor its spectral parameters were given. The same compound in the salt form was formed in the oxidation of *p*-phenylenediamine with silver(I) ions [11]. Aniline oligomers containing benzoquinone diimine fragments were also obtained by oxidation of the corresponding amines that are difficultly accessible [12–17].

Cataldo [18] reported that the oxidation of *p*-phenylenediamine with potassium peroxodisulfate in aqueous HCl gives polyquinoxaline. However, we previously showed that the oxidative polymerization of *p*-phenylenediamine in aqueous HCl follows mainly Scheme 1 and yields poly(1,4-benzoquinone diimine-*N*,*N*′-diyl-1,4-phenylene) [19–21]. Under these conditions (22–25°C, aqueous HCl), the product undergoes further transformations, in particular bisulfate ion adds to the quinone diimine units [19, 20]. It is also known that treatment of pernigraniline with 1 N HCl leads to addition of hydrogen chloride to 50% of the quinoid rings [22]. According to our data, *N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinone diimine takes up water by ~90% under the action of 0.5 N H_2SO_4.



UV spectra of *N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinone diimine (**1**) and its acetyl derivative **2** in DMSO.

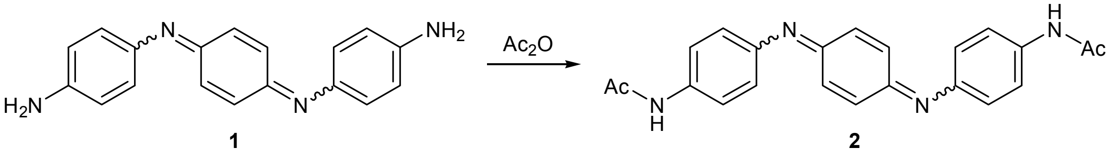
With the goal of minimizing side reactions promoted by strong acids, we have developed a new procedure for the synthesis of low- and high-molecular-weight quinone diimines via oxidation of *p*-phenylenediamines with potassium peroxodisulfate in acetic acid [23]. The reaction of *p*-phenylenediamine with $K_2S_2O_8$ at a molar ratio of 4 : 1 in acetic acid at 15°C afforded two fractions, one of which was soluble in methanol while the other was not.

Recrystallization of the first fraction from ethanol gave compound **1** (Scheme 1, *n* = 1) with mp 257–258°C. The melting point may change depending on the rate of heating due to thermal self-condensation (mp 172°C [8]).

The UV spectrum of **1** in DMSO displayed two absorption maxima at λ 341 and 496 nm (see figure). A solution of **1** in methanol showed the third maximum at λ 250 nm. According to published data, compound **1** absorbs at λ_{max} 572 nm in DMF, at 556 nm in THF, and at 532 nm in methylene chloride [8]. It should be noted for comparison that the UV spectrum of 2,5-dimethyl-*N*,*N*′-bis(4-methylphenyl)-1,4-benzoquinone diimine in DMF contains absorption maxima at λ 310 and 457 nm and that the absorption maximum of *N*,*N*′-bis(4-methylbenzenesulfonyl)-1,4-benzoquinone diimine is located at λ 484 nm [6]. In the ^{1}H NMR spectrum of **1** we observed signals from protons of the amino groups and quinone and benzene rings with the expected intensity ratio.

When compound **1** was extracted from the reaction mixture with hot ethanol, the amounts of the soluble and insoluble fractions were irreproducible, presumably because of self-condensation of **1** (Scheme 2). This assumption was checked as follows. A solution of

Scheme 3.



1 in ethanol was heated under reflux. As a result, a compound insoluble in methanol was formed. The same product was obtained when compound **1** was heated at 260°C. Obviously, the reaction involves 1,4-addition of primary amino group to the quinone diimine fragment (Scheme 2) with formation of oligomers and a polymer. The IR spectrum of the product obtained by heating, assumingly poly[imino-1,4-phenyleneimino-4-(4-aminoanilino)-1,3-phenylene], differed from the spectrum of initial compound **1**. Instead of absorption bands at 3337, 3418, and 3462 cm^{-1} typical of **1**, a broadened band appeared at 3448 cm^{-1} due to NH_2 and NH stretching vibrations. The NH_2 bending vibration band of **1** is observed at 1544 cm^{-1} against 1630 cm^{-1} in the spectrum of the product, presumably due to coordination of NH_2 groups to quinone diimine fragments; in addition, the bands at 1237 and 1275 cm^{-1} in the spectrum of **1** strongly decrease in intensity. This reaction will be studied in detail in future works.

In order to obtain a more stable compound, the amino groups of **1** were acylated with acetic anhydride; as a result, we isolated and identified diacetyl derivative **2** (Scheme 3), which provided an additional support to the structure of **1**. Compound **2** is insoluble in methanol, ethanol, and chloroform and soluble in DMSO, DMF, and ethylene glycol at room temperature.

4,4′-[Cyclohexa-2,5-diene-1,4-diylidenediazanylylidene]dianiline (1). Potassium peroxodisulfate, 0.62 g (2.3 mmol), was added to a solution of 0.75 g (7 mmol) of *p*-phenylenediamine and 0.476 g (2.3 mmol) of *p*-phenylenediammonium sulfate in 6 mL of glacial acetic acid at 15–16°C, and the mixture was stirred for 21 h. The mixture was kept in a refrigerator at 6°C each time when the stirring was interrupted. It was then treated with 10% aqueous sodium carbonate to pH 9, and stirred for 4 h at 2°C. The precipitate was filtered off, washed on a filter with cold water until neutral washings and the absence of sulfate ions therein, dried in air, treated first with methanol at 15–16°C and then with diethyl ether, and dried under reduced pressure over P_2O_5 (0.2 kPa). Yield of the insoluble (in methanol) fraction 0.11 g (20%); yield of soluble fraction 0.50 g (75%), mp 257–258°C. IR spectrum, ν, cm^{-1}: 3462, 3418, 3337 (NH_2), 3034 (C–H), 1605 (C=C$_{\text{arom}}$), 1544 (NH_2), 1502 (C=C, quinone), 1384 and 1237 (=N–C), 1275 (N–C), 1166 (C–H), 833 (δC–H$_{\text{arom}}$). ^{1}H NMR spectrum, δ, ppm: 5.00 s and 5.75 s (4H, NH_2), 6.20 s (4H, quinone), 6.65 d (8H, H$_{\text{arom}}$, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 90.6, 114.2, 122.1, 140.0, 144.8, 148.2, 153.2. Found, %: C 74.81; H 5.71; N 19.35. $C_{18}H_{16}N_4$. Calculated, %: C 75.0; H 5.59; N 19.44.

Polycondensation of compound (1). A 0.04965-g sample of **1** was heated for ~1.5 h at 250–260°C in a test tube. After cooling, the product was treated with 20 mL of methanol, the mixture was kept for 24 h and stirred for 3 h, and the precipitate was filtered off and dried in a vacuum desiccator over P_2O_5 (0.2 kPa). Yield 0.04 g (80%). The isolated compound was insoluble in ethylene glycol, DMSO, DMF, acetic acid, and *N*-methylpyrrolidin-2-one and poorly soluble in formic acid.

***N,N′*-[Cyclohexa-2,5-diene-1,4-diylidenebis(azanylylidenebenzene-4,1-diyl)]diacetamide (2).** A solution of 0.05005 g (0.174 mmol) of compound **1** in a mixture of 2 mL of acetic acid and 0.08 mL (0.787 mmol) of 93% acetic anhydride was stirred for 7 h at 15°C. The mixture was treated with 10% aqueous sodium carbonate to pH 9 and stirred for 4 h at 2°C. The precipitate was filtered off, washed on a filter with ice water until neutral washings, dried in air, treated with methanol at 15°C, and dried in a vacuum desiccator over P_2O_5 (0.2 kPa). Yield 0.05 g (77%), mp >290°C. IR spectrum, ν, cm^{-1}: 3431, 3249 (N–H), 3034 (C–H$_{\text{arom}}$), 2925, 2848 (C–H$_{\text{aliph}}$), 1631 (C=O), 1605 (C=C$_{\text{arom}}$), 1564 (C=N), 1500 (C=C, quinone), 1384, 1306 (=N–C), 1213 (N–C), 1096, 1024 (C–H$_{\text{arom}}$), 815 (δC–H$_{\text{arom}}$). ^{1}H NMR spectrum, δ, ppm: 2.00 s (6H, CH_3), 5.40 s, 6.15 s (4H, quinone), 6.65 d and 7.50 d (4H each, H$_{\text{arom}}$), 9.80 s (2H, NH). Found, %: C 70.85; H 5.50; N 14.93. $C_{22}H_{20}N_4O_2$. Calculated, %: C 70.97; H 5.38; N 15.05.

The IR spectra were recorded in KBr on a Nicolet Nexus spectrometer with Fourier transform. The UV spectra were measured on a Specord 50 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury 300 spectrometer (300 MHz for ^1H) using DMSO-d_6 as solvent.

p-Phenylenediamine was purified by sublimation (mp 143–145°C), *p*-phenylenediammonium sulfate was recrystallized from water. Potassium peroxodisulfate and acetic acid were analytical grade chemicals.

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