

## Oligoaniline intermediates in the aniline-peroxydisulfate system

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### ABSTRACT

Chemical oxidative polymerization of aniline using peroxydisulfate oxidant in aqueous pH 2.5–10.0 buffers yields electrically insulating brown powders that are believed to be mixtures of Michael-type adducts of benzoquinone monoimine and aniline at various stages of hydrolysis. A spectroscopically similar product is formed when solid 1,4-benzoquinone is added to an aqueous solution of aniline at room temperature in the absence of peroxydisulfate. This suggests that the peroxydisulfate oxidant in the aniline/S<sub>2</sub>O<sub>8</sub><sup>2−</sup> system provides a pathway for the formation of benzoquinone monoimine as an intermediate. Benzoquinone monoimine intermediate could be formed as a result of a Boyland–Sims rearrangement of aniline proceeding via the intermediacy of *p*-aminophenyl sulfate. Benzoquinone monoimine undergoes a series of conjugate 1,4-Michael-type addition/reoxidation/coupling steps with aniline or *p*-aminophenyl sulfate yielding the oligoaniline product. The precipitate that is isolated is also in the midst of two simultaneous pH dependent hydrolysis reactions: (i) hydrolysis of the imine groups to quinone, and (ii) hydrolysis of arylsulfates to phenols. The ratio of hydrolysis in each case was determined by the C/N ratio and sulfur elemental analysis values yielding analytical data that is consistent with experimentally determined values and also with our proposed reaction scheme. These findings offer a rationale for the high C/N ratios (>6.0) frequently observed in these systems while tracing the genesis of the residual sulfur in the product to unhydrolyzed arylsulfate. The oligoaniline product has previously been reported to have a novel poly-aza structure consisting of continuously linked –N–N– bonds, and alternately also reported to consist of phenazine-type linkages. This study is consistent with the latter and describes a pathway to phenazine coupling through a second and third stage hydrolysis of the arylsulfate and reoxidation with peroxydisulfate. There is no pathway for the formation of linear –N–N– linkages in the aniline/benzoquinone adduct and the striking similarity between its spectroscopic properties and the aniline/S<sub>2</sub>O<sub>8</sub><sup>2−</sup> adduct suggests that it is not a preferred pathway under these experimental conditions.

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### 1. Introduction

Large-scale synthesis of doped conducting polymers like polyaniline, polypyrrole, polythiophene, etc., is typically carried out by chemical oxidative polymerization of the respective monomers resulting in electrically conducting powders having granular morphology [1–3]. For example, the conducting polymer, polyaniline, is synthesized by the chemical oxidative polymerization of aniline in dilute aqueous acids by ammonium peroxydisulfate oxidant [4–9]. The reaction is characterized by an induction period that is a function of temperature and reagent concentration, e.g., it can last for a few minutes for a reaction carried out at room temperature and high concentration, or for a few hours for a reaction carried out at 0–5 °C at high dilution [10]. The induction period is followed

by a darkening of the reaction mixture to a blue/green color followed by a rapid precipitation of a green powder, frequently called by its common name, emeraldine salt. The polyaniline obtained in this form is doped and electrically conducting having room temperature DC conductivity in the range 1–5 S/cm. The bulk morphology of the emeraldine salt obtained above is granular and lacking in any significant nanoscale features. To obtain conducting polymers having nanoscale morphology by chemical polymerization, a variety of template and non-template routes have been reported. Most of these involve initiating the reaction along the walls of nanostructured pores (hard template approach) [11–13] or within soft nanostructured templates such as surfactant or polymeric micelles (soft template approach) [14–18]. For example, several groups have altered the synthetic conditions during the induction period to affect a dramatic granule-fiber change in bulk morphology of the polyaniline precipitate, e.g., addition of small quantities of aniline oligomers [19,20], lengthening the induction period by diluting the reaction mixture [21,22], inducing the

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polymerization at an aqueous-organic interface [23–25], carrying out the reaction under UV or  $\gamma$  irradiation, etc. [26,27]. We have shown that adding small, seed quantities of organic, inorganic or biological nanofibers of known composition during the induction period also results in a granule to nanofiber change in the bulk morphology [20]. This method, called nanofiber seeding, is general and can be extended to all major classes of conducting polymers. While the precise mechanism underlying the phenomenon is still being investigated, the impact of early-stage intermediate species formed during the induction period on bulk polymer morphology has spurred renewed interest in this area.

For example, several groups have now reported that when oxidative polymerization of aniline using peroxydisulfate oxidant is carried out under alkaline, neutral or weakly acidic conditions, a product that is different from conventional polyaniline is obtained [7,28–33]. For example, the four-probe pressed pellet room temperature, DC conductivity of the polyaniline powder is 2–3 orders of magnitude lower than conventional polyaniline [7,28,29], and depending on the experimental conditions, polyaniline having different micro or nanoscale bulk morphologies, such as spheres, tubes and fibers, can be obtained [34]. It is to be noted that in most of these studies, the peroxydisulfate performs a dual role as an oxidant and as a dopant, i.e., following the redox reaction with aniline, peroxydisulfate is converted to sulfate which is incorporated in the polyaniline chains as dopant ions [7,35,36]. A study on the role of intermediate species formed in this system is complicated by the constantly falling pH during the course of the reaction resulting from proton release associated with the coupling of aniline monomers. Several groups have found that depending on the reaction conditions the pH can change significantly, e.g., from an initial value of pH  $\sim 10$  to a final value of pH  $\sim 1$  [29]. The polymerization has been shown to proceed via two pathways resulting in two types of polymerized aniline products, one at high pH resulting in a low molecular weight, electrically insulating oligomeric polyaniline, and the other at low pH, resulting in conducting polyaniline, i.e., having classical head to tail coupling of aniline chains [7,34].

The oligoaniline product formed during the early stage of the reaction, presumably when the pH was still high, has been isolated and characterized by several groups and shown to be structurally different from the polyaniline formed in the later stages of the reaction and also different from conventional polyaniline synthesized at low pH [7,29–31,34]. The spectroscopic and analytical properties of the oligoaniline are sensitive to experimental conditions that complicate accurate structure elucidation. Two elemental analysis findings pose a significant challenge to structure elucidation since they vary widely depending on the experimental conditions: (i) residual sulfur in the product, and (ii) the C/N ratio that is different from the theoretical value of 6 [29–31]. A firm understanding of these two issues should assist in the determination of the chemical structure of the oligoaniline intermediate and the mechanism of its formation. For example, Trchova et al. have shown that the reaction proceeds in two exothermic steps, one when the pH is high corresponding to the formation of oligoaniline, and the other at low pH leading to conducting polyaniline [34]. From spectroscopic data of the oligoaniline product corresponding to the first exothermic step, a phenazine-type structure was proposed (e.g., using the  $1414\text{ cm}^{-1}$  peak in the FT/IR), and analytical data showing significant residual sulfur in the product was rationalized as originating from aromatic ring sulfonation during the reaction. However, the analytical data also show the C/N ratio of the oligomeric and final products close to 5, compared to conventional polyaniline which has a C/N ratio close to the theoretical value of 6. This suggests that there is significant loss of carbon during the reaction, which is puzzling. Zujovic et al. have also recently highlighted the differences in the properties of the oligoaniline product obtained by different groups and have isolated and characterized a product from the early stages

of the polymerization of aniline in water using ammonium peroxydisulfate [30]. There are some spectroscopic similarities with the product obtained in the earlier study [34], and  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR data are consistent with the presence of phenazine-type groups, although there are also striking differences in the analytical composition, e.g., the C/N ratios are consistently above the theoretical value of 6 suggesting significant loss of nitrogen during the reaction which is also a challenge to rationalize mechanistically (see later section). Epstein et al. have isolated an early stage brown-colored intermediate product from the reaction of aniline with a large molar excess of peroxydisulfate using water as a solvent, and although no analytical data was provided, the product was believed to be consistent with aniline dimers obtained in previous studies based on spectroscopic data [7].

In an effort to decouple the primary oligoaniline formation reaction from those associated with a continuously falling pH, MacDiarmid et al. carried out the oxidative polymerization of aniline using ammonium peroxydisulfate oxidant under various weakly acidic buffers and isolated and characterized an oligoaniline product in the form of a powder and also as thin films on glass surfaces formed by *in situ* adsorption polymerization [31,32]. Once again, structure identification proved to be a challenge with elemental analysis yielding a C/N ratio always  $>6$  and closer to 7, suggesting loss of nitrogen (or increase in carbon). In order to rationalize the higher carbon content, a hexameric aniline unit having benzoquinone units as side groups was proposed as a possible structure. In addition, an unusual linearly linked hexa-aza linkage was proposed for the main oligomeric chain, i.e., one containing six nitrogen atoms linearly linked together with covalent bonds. The term “polyazane” was used to describe this potentially novel type of polymeric material.

Since these oligomeric intermediates could also be formed during the conventional synthesis of conducting emeraldine salt they could potentially be important in the evolution of bulk morphology of the emeraldine salt. We initiated this study to: (i) determine the chemical structure of the oligoaniline intermediate, (ii) propose a mechanism for its formation based on classical aromatic amine chemistry, and (iii) confirm the mechanism by independent synthesis using a non-oxidative route.

## 2. Experimental

### 2.1. Materials

Aniline (99.5+%), ammonium peroxydisulfate (98%), and were purchased from Sigma–Aldrich (Milwaukee, WI). Concentrated hydrochloric acid (37%), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99+%) and sodium bicarbonate ( $\text{NaHCO}_3$ , 99+%) were purchased from Mallinckrodt (Phillipsburg, NJ). Acetonitrile (HPLC grade), *N*-methyl-2-pyrrolidone (NMP, 99+%), concentrated ammonium hydroxide (35%), Citric acid ( $\text{H}_3\text{C}_3\text{H}_5\text{O}(\text{COO})_3$ , 99.5%) and trisodium citrate dihydrated ( $\text{Na}_3\text{C}_3\text{H}_5\text{O}(\text{COO})_3 \cdot 2\text{H}_2\text{O}$ , 99+%) were purchased from EMD Chemical Inc. (Gibbstown, NJ). Water (HPLC grade) was purchased from Fisher Chemical (Fairlawn, NJ). Sodium dihydrogen phosphate dehydrate ( $\text{NaH}_2\text{PO}_4$ , 99+%) and disodium hydrogen phosphate heptahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ , 99+%) and 1,4-benzoquinone were purchased from Acros Organics (Morris Plains, NJ). All Chemical were used without further purification with the exception of aniline which was distilled three times under vacuum prior to use.

### 2.2. Instruments

#### 2.2.1. Scanning electron microscopy (SEM)

The polymer morphologies were imaged using a JEOL 7401F field emission scanning electron microscope (FE-SEM) with a field

emission gun operated at 10 keV. 0.5–1.0 mg of the oligomer was placed into the carbon tab sample holder. To acquire scanning electron microscopy images, the sample was placed on the carbon tab sample holder and coated with Au using a Denton Vacuum Desk II sputter-coater.

### 2.2.2. Potential-time profiling

The open circuit voltage ( $V_{oc}$ ) was recorded at room temperature on an Arbin electrochemical workstation (Model # MSTAT4+, serial # DEMO-14). A platinum wire immersed in the reaction media was used as a working electrode. Another platinum wire was used as a counter electrode. Saturated calomel electrode (SCE) was used as the reference electrode.

### 2.2.3. Electronic absorption spectroscopy (UV–vis)

UV–vis absorbance spectra were measured by a UV-1601PC Shimadzu spectrometer. The samples were prepared by dissolving 0.1 mg in 5 mL of NMP.

### 2.2.4. Vibrational spectroscopy (FT-IR)

Attenuated total reflectance AT-FTIR spectra were recorded on an AVATAR 360 FTIR using a dried sample of the oligoaniline powder.

### 2.2.5. Gel permeation chromatography (GPC)

Size exclusion chromatography was carried out using a PerkinElmer Series 200 GPC set up (auto-sampler, pump, column oven and RI detector) using NMP as the mobile phase was used using narrow distribution polystyrene (Polymer Laboratories) as the standard for the calibration curve. A low molecular weight column was used.

### 2.2.6. Mass spectroscopy

The sample was diluted to a concentration of  $\sim 50$  ng/mL with 0.1% acetic acid in acetonitrile and analyzed by API 3000 Mass spectrometer using electrospray as ionization source, Applied Biosystems (Foster City, CA). The sample was introduced to the mass spectrometer by direct infusion using a syringe pump Harvard 11 plus. Harvard Apparatus Inc. (Holliston, MA) at a flow rate of 10  $\mu$ L/min.

## 2.3. Synthesis

### 2.3.1. Preparation of buffers

The citric acid/phosphate buffers were prepared by mixing approximately 500 mL of 0.20 M  $\text{Na}_2\text{HPO}_4$  and 200 mL of 0.10 M of citric acid as described by MacDiarmid et al. [31]. The acetic acid/sodium acetate buffer was prepared by combining equal volumes of aqueous 0.1 M  $\text{CH}_3\text{COOH}$  and 1.0 M  $\text{CH}_3\text{COONa}$ . The citric acid/sodium citrate, the phosphate buffer saline (PBS) and sodium carbonate/sodium bicarbonate buffers were prepared in the same manner as the citric acid/sodium citrate buffer by mixing equal volumes of the weak acid and its conjugated salt. The resulting pH was measured using a pH meter.

### 2.3.2. Reaction of aniline with peroxydisulfate

The synthesis was performed exactly as described by MacDiarmid et al. for all the buffer systems [31]. In a 1-L Erlenmeyer flask with a magnetic stirrer, aniline (0.55 g, 6.0 mmol) was dissolved in 300 mL of the buffer solution. After  $\sim 1$  min, 300 mL of a solution of ammonium peroxydisulfate (1.37 g, 6.0 mmol) was added. After 5 min, the stirring was stopped and the reaction vessel was left undisturbed. The solution turned light brown in color in  $\sim 30$  min followed by the formation of a brown precipitate over a period of 18 h. The reaction was quenched by addition of 100 mL of 1.0 M  $\text{NH}_4\text{OH}$  and the contents were suction filtered in air using a water

aspirator. The dark brown precipitate was washed with D.I. water ( $10 \times 100$  mL) followed by a 3:1 mixture of water and acetonitrile ( $4 \times 50$  mL) and dried in vacuum oven at  $35^\circ\text{C}$  for 12 h.

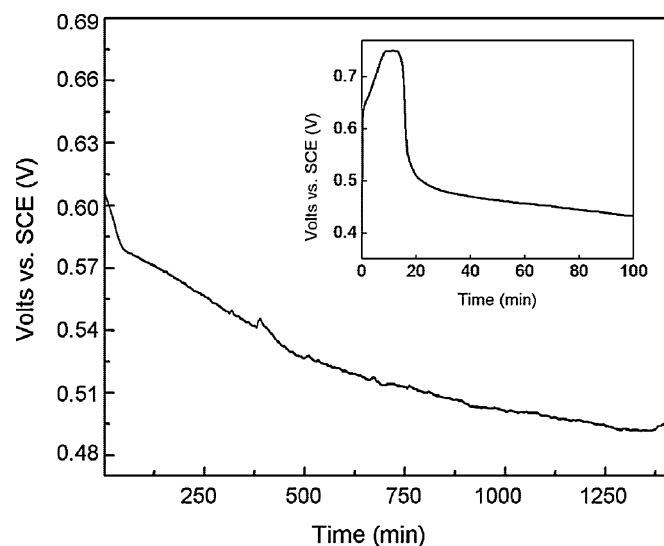
### 2.3.3. Reaction of aniline with 1,4-benzoquinone in aqueous 1 M HCl/satd. NaCl

Aniline (1.0 mL, 11.0 mmol) was dissolved in 100 mL of 1 M HCl/saturated NaCl solution in a 150-mL beaker followed by addition of 1,4-benzoquinone (0.05 g, 4.6 mmol). The 1,4-benzoquinone did not dissolve completely in the reaction mixture and remained in suspension as a light yellow powder. The reaction mixture turned brown over a period of 2 min followed by the formation of a dark brown precipitate. After 60 min, the reaction mixture was suction filtered in air using a water aspirator and the precipitate was washed with D.I. water ( $10 \times 100$  mL) and dried in vacuum oven at  $35^\circ\text{C}$  for 12 h.

A similar reaction takes place when carried out in the various buffers, D.I. water or aqueous 1.0 M HCl suggesting that the reaction is invariant of pH. In pH 7 and 10 buffers, the reaction is noticeably faster and the reaction is complete in  $< 2$  min, presumably due to the higher concentration of unprotonated free aniline in the system. There is no observable induction period in any of the aniline/benzoquinone systems, and the reaction is significantly faster than the corresponding aniline/peroxydisulfate buffer systems.

## 3. Results and discussion

We chose to evaluate the oxidative polymerization of aniline using peroxydisulfate under buffered conditions given that it is free from complications associated with a continuously falling pH. In pH 3 citrate/phosphate buffer we were able to reproduce the study by MacDiarmid et al., and isolated a yellow-brown colored product having similar analytical and spectroscopic properties [31]. We also monitored the reaction continuously with time using potential-time profiling (Fig. 1) and found significant differences from conventional polyaniline, e.g., immediately upon addition of ammonium peroxydisulfate to a solution of aniline in pH 3 buffer the potential rises from an initial value of 0.48 V (vs. SCE) to 0.62 V and gradually falls to 0.49 V over a period of 24 h [5,37]. In contrast, the corresponding potential-time profile of the conventional polyaniline system (Fig. 1, inset) shows the standard features: (i) a gradual rise in potential to 0.75 V during the induction period,



**Fig. 1.** Potential-time profile of the oxidation of aniline with peroxydisulfate in pH 3 buffer. Inset: potential-time profile of a conventional oxidative chemical polymerization of aniline using peroxydisulfate oxidant.



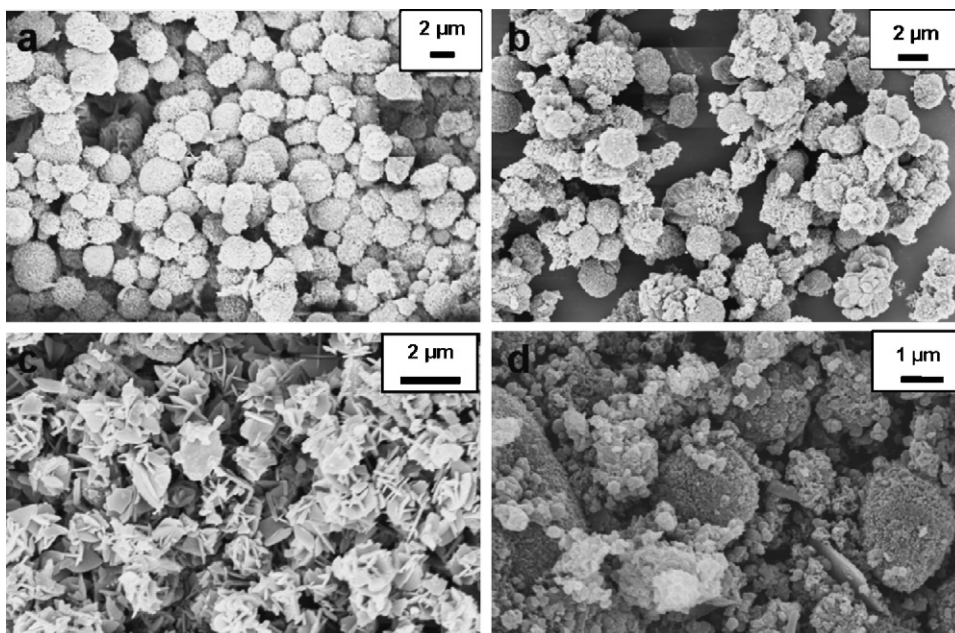


Fig. 2. SEM images of oligomeric aniline product obtained by oxidation of aniline with peroxydisulfate in pH buffer: (a) 2.5; (b) 4.5; (c) 7.0; (d) 10.0.

followed by a plateau region at 0.75 V when aniline is oxidized to pernigraniline, and (ii) a final rapid fall to 0.43 V when pernigraniline is reduced to emeraldine. In pH 3 buffer, the gradual fall in potential to 0.49 V over a long time period is consistent with the consumption of peroxydisulfate oxidant during the reaction and, to a lesser degree, indicative of the redox changes taking place on the yellow-colored *in situ* film of oligomeric aniline that is deposited on the electrode surface.

The reaction was also carried out in various buffers ranging from pH 2.5 to pH 10 and the products isolated after 24 h. In each case, the final product is a yellow brown colored powder having bulk morphology ranging consisting of micron size spheres at pH 2.5, 4.5 and 10.0 and flakes at pH 7 (Fig. 2). There is no observable pH dependent trend from spherical to tubular as has been observed previously in unbuffered systems when the reaction was allowed to proceed to the second stage yielding conducting polyaniline [28,29,34]. There is also no “bottle-and-stopper” morphology observed previously when the reaction was allowed to proceed all the way to conducting polyaniline which is consistent with the suggestion by Stejskal et al., that its genesis could be traced to heat of the reaction when the aniline trapped inside the spheres undergoes polymerization during the second stage when the pH drops [29]. The reaction rate, as determined visually by the darkening of the reaction mixture, is pH dependent with pH 10 being the fastest. The product yield is also higher at pH 10 for a 24 h reaction, suggesting that at higher pH either the formation of the oligoaniline intermediate is favored and/or its conversion to other products is slow. The oligoanilines all display similar spectroscopic properties, e.g., the electronic absorption spectrum in NMP shows 2 peaks at 269 and 379 nm (Fig. 3) which is similar to what was observed previously for “polyazane” and consistent with benzenoid and quinoid groups in the product. The vibrational spectra of the oligoanilines (Fig. 4) are similar not only to each other but also to the early intermediate product formed in unbuffered systems (see later section for differences). For example, in a recent report, Stejskal et al. show that when aniline is oxidatively polymerized in unbuffered systems, the oligoaniline intermediate had vibrational spectra that are invariant of starting pH [29], and phenazine linkages were proposed based on the  $1414\text{ cm}^{-1}$  peak in the FT/IR. A complete elemental analysis of the products obtained in the various buffer systems provides

important clues about the chemical structure of the oligoaniline intermediate (Table 1). Unlike previous studies where oxygen composition was assumed, i.e., calculated as difference from 100%, in this study oxygen content was experimentally determined. We also find a significant amount of residual sulfur in the product which is fairly persistent and varies depending on the experimental conditions with lower amounts observed at high pH. In previous studies its genesis was attributed to the presence of sulfonic acid groups attached to the aromatic ring formed by electrophilic aromatic sulfonation during the course of the reaction [34]. We believe this would not be favored under the mild, aqueous and oxidizing environment in the reaction. Aromatic ring sulfonation typically requires harsh reaction conditions, and polyaniline sulfonation under aqueous conditions has only been observed in the case of pernigraniline when the quinoid group undergoes nucleophilic

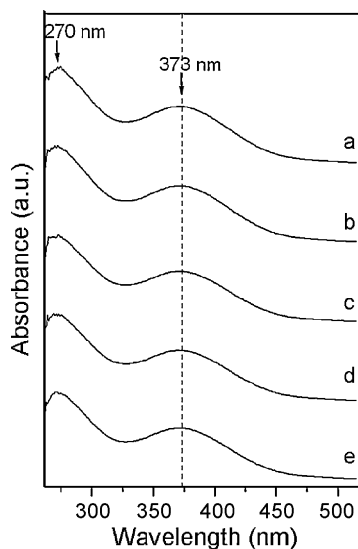
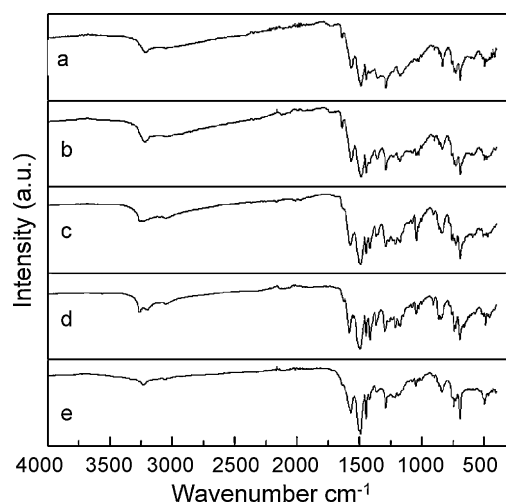


Fig. 3. Electronic absorption spectra (solution in NMP) of the oligomeric aniline product obtained by oxidation of aniline with peroxydisulfate in pH buffer: (a) 2.5; (b) 3.0; (c) 4.5; (d) 7.0; (e) 10.0.



**Fig. 4.** Vibrational spectra (ATR/FTIR) of the oligomeric aniline product obtained by oxidation of aniline with peroxydisulfate in pH buffer: (a) 2.5; (b) 3.0; (c) 4.5; (d) 7.0; (e) 10.0.

1,4-Michael-type addition by the highly reducing bisulfite ion [38]. The residual sulfur has also been attributed to sulfate ion adhering to the product due to incomplete/inefficient washing [30] as is sometimes observed in the emeraldine base form of conventional polyaniline synthesized in highly acidic sulfuric acid (sulfur levels <0.5%). This too is unlikely since values as high as 3% sulfur is observed in some cases, even after thoroughly washing with water. Importantly, our various buffer solutions contain ions other than sulfate in much higher concentrations and one might have expected incomplete washing to result in a significant amount of these ions to be present alongside sulfate ion (e.g., phosphate buffer). We also attempted to remove any residual sulfate ion by subjecting the pH 7 buffer product to membrane dialysis for 48 h and found that the sulfur values decreased by less than 4%. This suggests that sulfur could be covalently bound to the product but unlike the sulfur present in aromatic ring sulfonation, it is present in a form that is capable of being chemically removed under both acidic and basic conditions, e.g., by hydrolysis (see section below).

Our working hypothesis is that residual sulfur in the product could originate from incomplete hydrolysis of nitrogen or ring-substituted sulfates of the type shown in Schemes 1 and 2. These intermediate sulfates could be formed as result of a Boyland–Sims

type reaction/rearrangement [39–46]. In this classical organic “name reaction”, aniline and its ring/nitrogen-substituted analogs react with peroxydisulfate ion under aqueous alkaline conditions yielding *ortho*- and *para*-hydroxy anilines. Extensively investigated in the past, the reaction is believed to take place along the following sequence of steps (Scheme 1): (i) nucleophilic attack by the nitrogen atom of aniline on peroxydisulfate resulting in the zwitterionic phenylhydroxylamine-*O*-sulfate intermediate, (ii) rearrangement of this intermediate to *ortho* and *para* aminophenyl sulfates, and (iii) hydrolysis of the sulfates to the corresponding phenols. In the presence of excess peroxydisulfate these phenylaminophenols would be further oxidized to the corresponding benzoquinone imines.

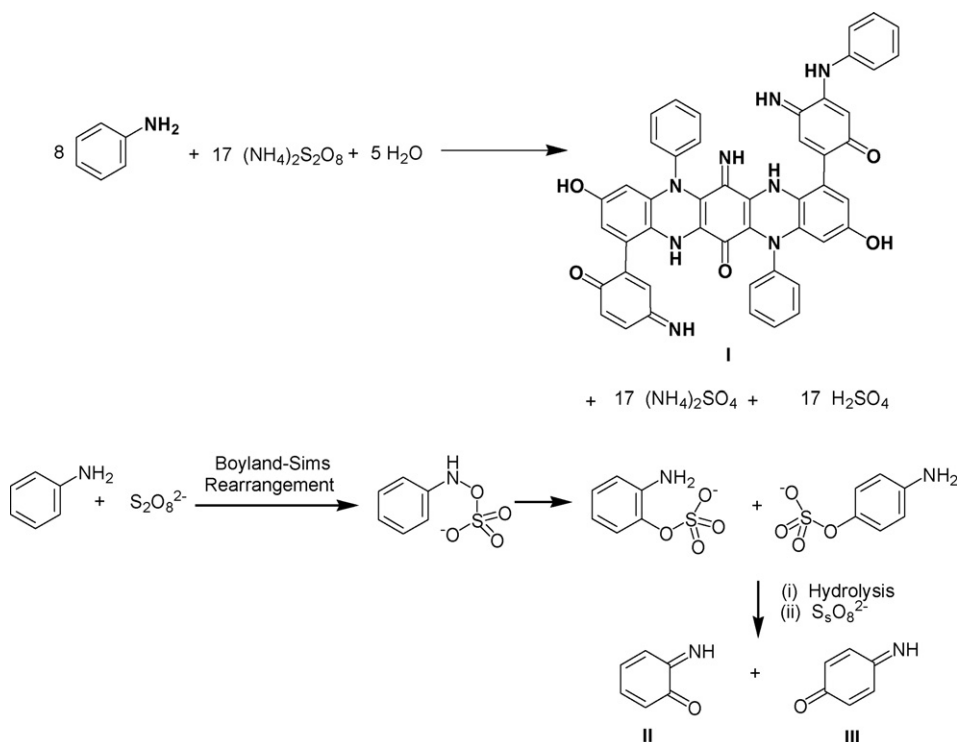
This sequence of steps could also be taking place in our system, e.g., the 1,2- or 1,4-benzoquinone monoimine intermediate could couple with aniline and/or *p*-aminophenyl sulfate by a series of 1,4-Michael-type addition reactions as shown in Scheme 2. These types of Michael-type adducts have been isolated as by-products in the conventional synthesis of aniline and its ring-substituted analogs [47,48]. In our buffered system, these early adducts containing aniline and/or *p*-aminophenyl sulfate units attached to a central 1,2- or 1,4-benzoquinone monoimine moiety could react further to yield the corresponding benzoquinone imines that can extend the chain.

We propose that the reaction proceeds along the following sequence of steps: (i) a Boyland–Sims reaction/rearrangement of aniline yielding the corresponding *ortho* and *para* arylaminosulfates. *For the sake of clarity, only the para isomer is shown in Scheme 2*, (ii) hydrolysis of the sulfates to the corresponding phenols and reoxidation by excess peroxydisulfate to the benzoquinone monoimine, (iii) 1,4-Michael-type addition of four aniline and/or *p*-aminophenyl sulfate by the nitrogen lone pairs (N-terminal attack) to benzoquinone monoimine which is accompanied by reoxidation of the resulting aminophenol by excess peroxydisulfate, (iv) attack by the *ortho*-carbon of the electron rich *para*-hydroxyl-*N*-phenylaniline units (C-terminal attack) to benzoquinone monoimine by 1,4-Michael-type addition. This type of C-attack has been previously reported in the reaction of aromatic amines to quinones, and in our case, would be favored over N-attack in view of steric hindrance to approach at the nitrogen atom [49,50], (v) addition of an aniline unit at the end followed by reoxidation by peroxydisulfate. This provides a pathway to progressively increase the chain length, (vi) addition of *p*-aminophenyl sulfate (or a Boyland–Sims reaction/rearrangement of the *N*-phenyl segment) on one or both sides of the central ring to the corresponding *p*-aminophenyl sulfate followed by hydrolysis and reoxidation to the quinone, (vii) phenazine coupling of the central aniline unit on

**Table 1**

Elemental analysis of the oligoaniline product obtained by oxidation of aniline with peroxydisulfate in various pH buffers. The calculated values were obtained on the basis of products being mixtures containing various amounts of intermediate species depicted in Scheme 2 and in Supporting Information. Their relative proportions are derived from the experimentally observed value for sulfur and the C/N ratio.

	C	H	N	O	S	Total	C/N	Sulfate (%)	# Imines hydrolyzed
pH 2.5									
Found	69.27	4.87	10.93	11.88	1.86	98.81	7.39	51.24	1.50
Calc.	70.24	4.24	11.09	12.54	1.89	100	7.39	–	–
pH 3.0									
Found	70.25	4.69	11.54	11.32	1.47	99.27	7.10	40.5	1.23
Calc.	70.36	4.14	11.57	12.44	1.49	100	7.10	–	–
pH 4.5									
Found	67.49	4.82	11.94	12.46	2.83	99.54	6.59	78.0	0.69
Calc.	67.82	4.13	12.04	13.14	2.87	100	6.57	–	–
pH 7.0									
Found	69.50	4.81	13.11	10.62	1.49	99.53	6.18	41.04	0.24
Calc.	69.97	4.14	13.19	11.21	1.49	100	6.19	–	–
pH 10.0									
Found	70.04	4.38	10.58	13.27	0.64	98.91	7.72	17.63	1.78
Calc.	70.65	3.78	10.68	14.25	0.64	100	7.72	–	–



**Scheme 1.** Balanced chemical equation of the reaction of aniline with peroxydisulfate in various buffers (top) and the Boyland–Sims rearrangement of aniline and peroxydisulfate ion resulting in *ortho*- and *para*-substituted products (bottom).

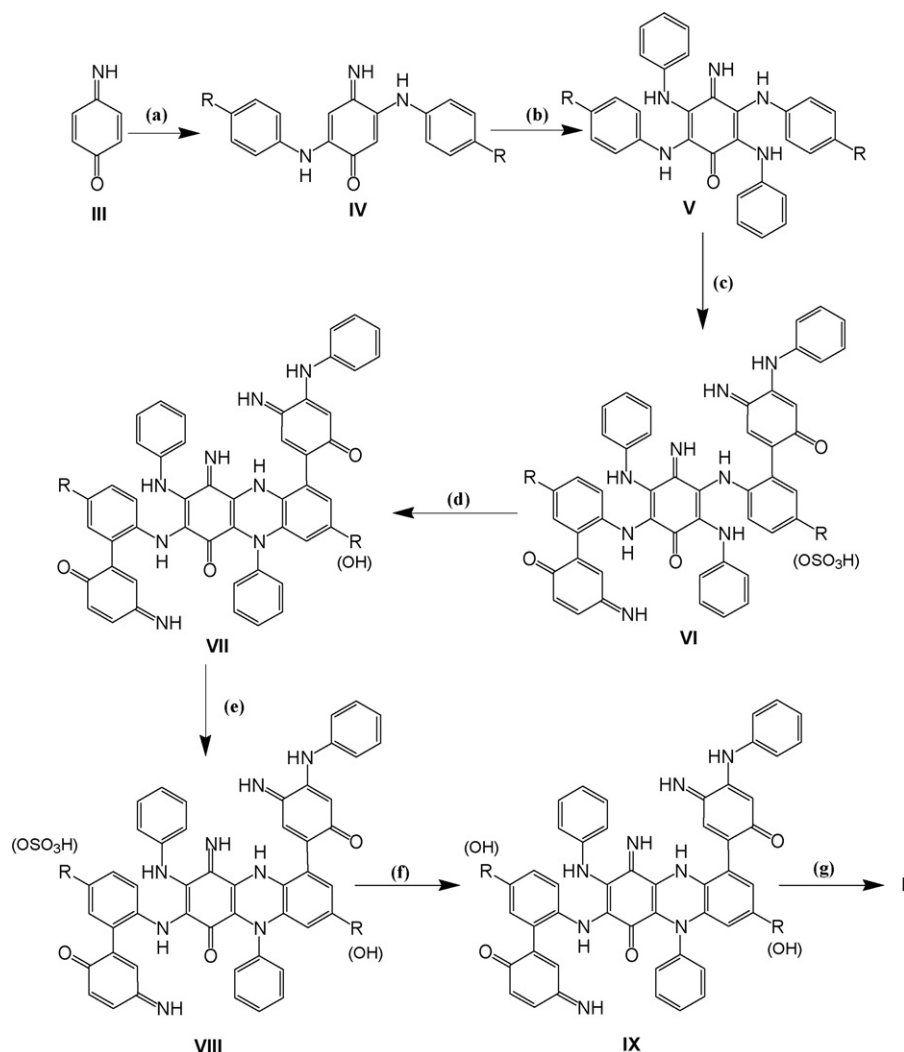
one or both sides of the central ring followed by reoxidation to the quinone. Structure (I) shown in Scheme 1 is a late stage in the reaction and we believe it stops short of this stage and what we isolate are mixtures of intermediates that are formed prior to its formation (see discussion below).

The molecular weight of the products by gel permeation in buffered systems is in the range 800–1200 Da, consistent with Zujovic et al. who reported values in the range 970–1660 Da [30]. The molecular weight of the products obtained in our buffer systems are in the range 750–950 Da depending on the reaction conditions. It is to be noted that structure (I) is consistent with the following experimental data: (i) the presence of phenazine-type linkages, (ii) hydroxy groups providing a rationale for sulfur present in the product (from incomplete hydrolysis of the corresponding sulfate). For example, in step (vii) above, the attack of aniline between the two oxidized rings yielding phenazine type linkages is consistent with vibrational and NMR data reported previously [30,34]. The mechanism requires the addition of one or two *p*-aminophenyl sulfate on the central ring that could account for the residual sulfur in the product. Alternately, should the reaction proceed via addition of aniline, sulfur could be introduced as a result of a second Boyland–Sims rearrangement on these rings. For example, diphenylamine has been shown to react with peroxydisulfate in mildly acidic buffers yielding *N*-phenyl-1,4-benzoquinone monoimine (the *para* isomer only) that was also believed to proceed via the intermediacy of diphenylhydroxylamine-*O*-sulfate [51]. In either case one expects to find, as does experimentally, residual sulfur in the product as a result of incomplete hydrolysis of the *p*-arylamino-sulfate intermediates. From the experimentally determined elemental analysis values for sulfur the percentage of unhydrolyzed sulfated product is calculated (Table 1).

Importantly, the presence of imine groups also helps explain why the C/N ratios are consistently above the theoretical value of 6. For example, if all three imine groups remain intact as depicted in structure (I), the C/N ratio would be exactly 6 (Table 2). This ratio would increase to 6.86 if one of the imine groups is fully hydrolyzed

to quinone, and to 8.0 if two of the imine groups are hydrolyzed. Experimentally, our C/N ratios range from 6.18 to 7.56 suggesting that two of the three imine units are susceptible to hydrolysis and the product is a mixture containing different proportions of hydrolyzed and unhydrolyzed imine units. Recent NMR studies by Zujovic et al., showed that their oligoaniline intermediate product when reduced with hydrazine still contained peaks corresponding to intact imine groups implying that some of these groups are resistant to reduction. These results are consistent with the proposed structure for the oligoaniline product shown in Scheme 2 where access to the imine group in the central ring is sterically hindered by the flanking phenazine groups.

The combination of C/N ratio and sulfur elemental analysis values provides a rationale that supports our proposed reaction sequence and also offers clues consistent with the product being a mixture of different intermediate species. For example, the calculated elemental analysis values for (I) which has no sulfate groups and has all three imine groups intact has an elemental composition that is not consistent with the experimental elemental analysis values for any of the products isolated. For example, for the pH 7 buffer product, there is too much oxygen in structure (I) even after taking into account contributions from imine hydrolysis (from the C/N ratio) and unhydrolyzed arylsulfate groups (from sulfur values). This suggests strongly that the product should have only one phenazine unit flanking the central ring since the other side is required to account for (i) the low oxygen levels, and (ii) sulfur in the product. The former requires that the ring to be unsubstituted and the latter for the ring to be sulfated. This leads to four possible structures that are intermediates in our proposed scheme whose relative proportions are governed by the experimentally determined C/N ratio and sulfur values (see Supporting Information). We also observe a trend when we calculated the corresponding theoretical elemental analysis values for pH 10, 4.5, 3.0 and 2.5 and we were led to use different combinations of a set of four structures that were intermediates further along in our proposed reaction scheme. Importantly, for pH 2.5 buffer, our calculated theoretical



**Scheme 2.** Reaction showing the various oligoaniline species formed in the reaction of aniline with peroxydisulfate proceeding via the intermediacy of 1,4-benzoquinone monoimine (III). R=H or OSO<sub>3</sub>H: (a) 2 (R)C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>/2 S<sub>2</sub>O<sub>8</sub><sup>2-</sup>; (b) 2 (R)C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>/2 S<sub>2</sub>O<sub>8</sub><sup>2-</sup>; (c) 2 HN=C<sub>6</sub>H<sub>4</sub>=O/2 S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, (R)C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, or if R=H Boyland–Sims rearrangement to intermediate arylsulfate (IV); (d) Hydrolysis of arylsulfate/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/phenazine coupling (VII); (e) If R=H, Boyland–Sims rearrangement to intermediate arylsulfate (VIII); (f) hydrolysis of arylsulfate (IX); (g) S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/phenazine coupling to yield (I).

values led us to oxygen levels that suggested that the product should not contain phenazine linkages at all. This is because each phenazine coupling forces the ring to have an oxygen atom that raises oxygen levels. A close observation of the vibrational spectra of all buffer products show that only the product obtained at pH 2.5 buffer shows no phenazine signature peak at 1414 cm<sup>-1</sup>. This suggests that the product formed in pH 2.5 buffer is a mixture of intermediates species formed earlier along the reaction continuum, i.e., before phenazine coupling takes place. The experimentally observed C/N ratio and sulfur values for the product obtained in pH 3.0 and 4.5 also leads one to the use of intermediate species that are present between the pH 7 and pH 2.5 systems which further supports our proposed reaction sequence. The pH 10 buffer product has 0.64% for sulfur which is the lowest among the group

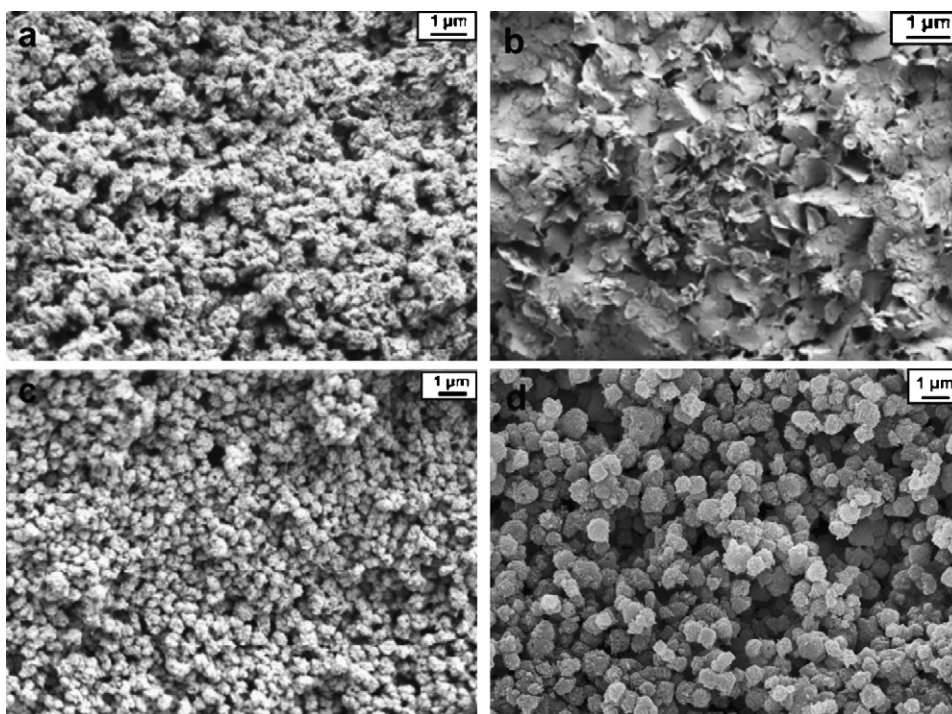
corresponding to ~17% unhydrolyzed sulfate in the product. This value and the oxygen values suggest that it should be furthest along the reaction scheme outlined in Scheme 1 and yet we see that the phenazine signature peak is smaller than the corresponding pH 7 system. The reason for this is not clear although we believe this could be because there is insufficient peroxydisulfate in the reaction mixture to oxidize the aminophenol ring. Indeed when we carried out the pH 10 buffer reaction at 1:3 aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ratio we observe a strong 1414 cm<sup>-1</sup> peak in the FT/IR spectrum (see Supporting Information). Higher C/N ratio values are obtained at pH 10 and 2.5 suggesting that imine hydrolysis is favored under both acidic and basic conditions, which is consistent with the aqueous chemistry of imines. There is no corresponding pH dependent trend in the hydrolysis of sulfate other than the lowest sulfur

**Table 2**

The calculated values based on hydrolysis of imine groups in structure (I).

	C	H	N	O	Total	C/N
No imine hydrolysis	71.99	4.03	13.99	9.99	100.00	6.00
Hydrolysis of one imine group	71.90	3.90	12.23	11.97	100.00	6.86
Hydrolysis of two imine groups	71.81	3.77	10.47	13.95	100.00	8.01
Hydrolysis of three imine groups	71.73	3.64	8.71	15.92	100.00	10.51





**Fig. 5.** SEM images of the product obtained in the reaction of aniline with 1,4-benzoquinone in: (a) aq. 1 M HCl/satd. NaCl; (b) aq. 1.0 M HCl; (c) D.I. water; (d) pH 7.0 buffer.

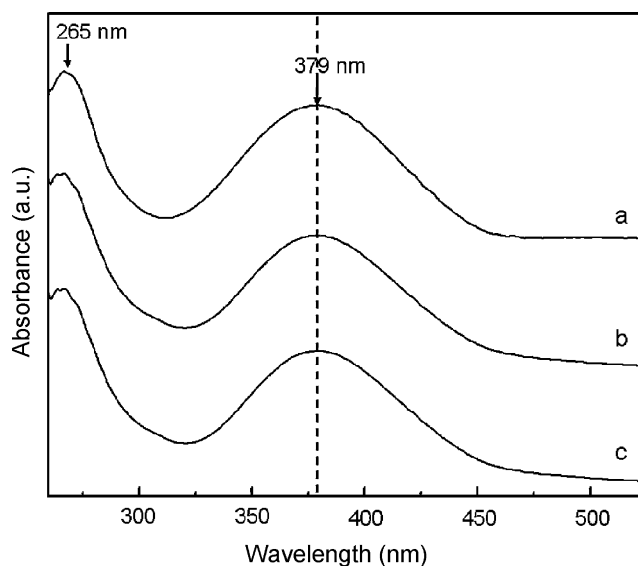
values obtained in pH 10 buffer. It is to be noted that although the above rationale is based solely on elemental analysis, that part of the difficulty in structure elucidation of the oligoaniline product in the past can be traced to the product being a mixture and confirmatory analytical and spectroscopic data is required.

Evidence supporting the intermediacy of benzoquinone monoimine can be elicited from a further analysis of the C/N and N/O ratios as a function of hydrolysis of the three imine groups in the proposed structure. If all the three imine groups are fully hydrolyzed to quinone, the C/N ratio would be 10.51 and the N/O ratio should be <1. In this idealized structure, the central ring is a functionalized 1,4-benzoquinone (vs. 1,4-benzoquinone monoimine) and the product could hypothetically be viewed as proceeding via the intermediacy of 1,4-benzoquinone.

We tested this hypothesis by mixing aniline and 1,4-benzoquinone in water (no peroxydisulfate) and were surprised to find that almost immediately the reaction mixture turned yellow brown yielding a powder having spectroscopic properties similar to the oligoaniline products obtained in the aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system. The reaction also takes place in aqueous 1.0 M HCl, 1.0 M HCl/saturated NaCl and in the various pH buffers. SEM images shown in Fig. 5 show that the product has bulk morphology consisting of well-defined spheres (pH 7 buffer), granules (1.0 M HCl/NaCl), and flakes (1.0 M HCl). Similar to the aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, no pH dependent trend is observed in changes in bulk morphology. The electronic absorption spectra in NMP (Fig. 6), vibrational spectra (Fig. 7) and aqueous electrochemistry (not shown) are very similar to the oligoaniline product obtained in the aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system (see below for differences). For example, the electronic absorption spectrum in NMP shows two peaks at 265 and 379 nm (Fig. 6) that are close to the oligoaniline product obtained in the aniline/peroxydisulfate/buffer system ( $\lambda_{\text{max}}$  270 and 373 nm). The vibrational spectra are also similar (Fig. 7). Elemental analysis is consistent with the structures (X) and (XI) proposed in Scheme 3. Importantly, the C/N ratio is 10.78 and the N/O ratio is >1 (Table 3).

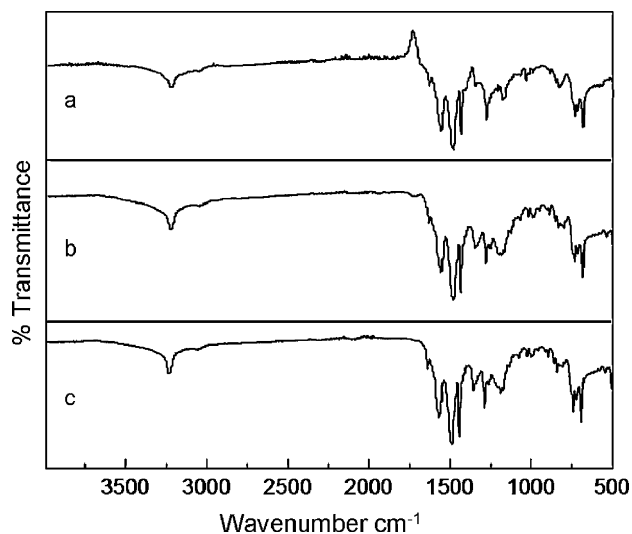
We propose that the reaction proceeds by the sequence of steps shown in Scheme 3: (i) 1,4-Michael-type addition of four neutral aniline units (N-terminal attack) to benzoquinone each taking place

in two steps where each addition step is followed by reoxidation by excess benzoquinone, (ii) coupling of two 1,4-benzoquinone units by attack by the *ortho*-carbon (C-terminal attack). Based on the molecular weight data (MW ~650) we believe the reaction stops at step (ii) yielding a product containing seven rings comprised of three benzoquinone units and four aniline units. It is to be noted from Table 2 that the C/N ratio of the product obtained in D.I. water and aqueous 1.0 M HCl is ~9.6 which is consistent with a mixture of compounds (X) and (XI) depicted in Scheme 3. In contrast, the product obtained in aqueous 1.0 M HCl/saturated NaCl has a C/N ratio of 10.78 which is higher than the theoretical value of 10.51 for structure (XI) which is consistent with a mixture of (XI) and its adduct with 1,4-benzoquinone. In pH 7 buffer even higher benzoquinone



**Fig. 6.** Electronic absorption spectra (solution in NMP) of the product obtained in the reaction of aniline with 1,4-benzoquinone in: (a) aq. 1 M HCl/satd. NaCl; (b) aq. 1.0 M HCl; (c) D.I. water.

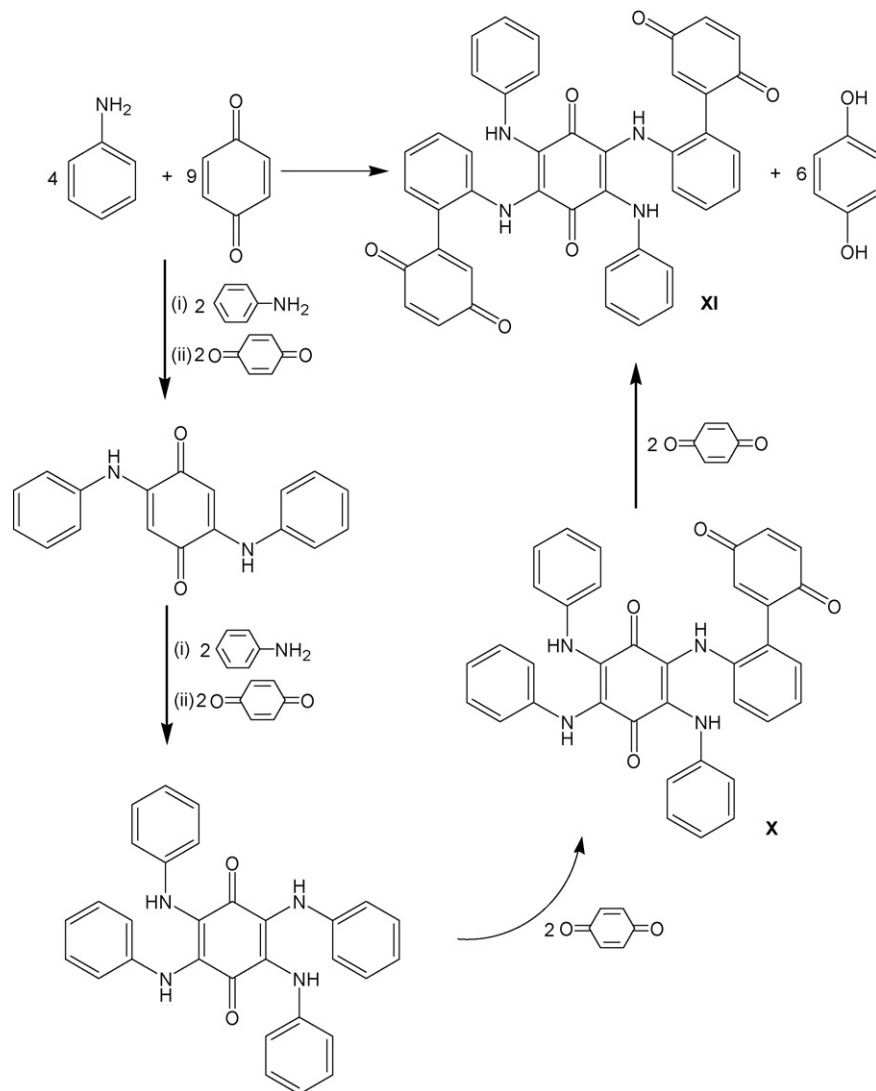




**Fig. 7.** Vibrational spectra (ATR/FTIR) of the product obtained in the reaction of aniline with 1,4-benzoquinone in: (a) aq. 1 M HCl/satd. NaCl; (b) aq. 1.0 M HCl; (c) D.I. water.

adducts are obtained, e.g., the product has a C/N ratio of 12.3 consistent with a mixture of (XI) containing one and two additional benzoquinone groups (see [Supporting Information](#)).

Our proposed structure for the aniline/benzoquinone product differs from the aniline/peroxydisulfate oligoaniline product in pH 3–10 buffer by not having any phenazine linkages and is similar to the product obtained in pH 2.5. This could be because there is no mechanistic pathway to introduce an oxygen atom at the *para* position after steps (i) and (ii) described above, i.e., no peroxydisulfate that can yield *p*-aminophenyl sulfate or initiate a Boyland–Sims rearrangement to a benzoquinone monoimine unit that can couple to yield phenazine linkages. Vibrational spectra provide evidence consistent with the absence of phenazine linkages in the product, e.g., the  $1414\text{ cm}^{-1}$  signature peak that has previously been assigned to phenazine linkage [34] is absent and aniline/benzoquinone product. Importantly, the  $1040\text{ cm}^{-1}$  peak assigned to sulfate present in aniline/peroxydisulfate oligoaniline product is also absent in the aniline/benzoquinone product which is consistent with the proposed mechanism. There is also debate in the literature about the assignment of the  $1414\text{ cm}^{-1}$  peak to phenazine linkages [30]. The absence of this peak in our aniline/benzoquinone product (no phenazine linkages), argues in favor of a correct assignment, although additional evidence is necessary to confirm this, e.g.,  $^{13}\text{C}$  NMR and  $^{15}\text{N}$  NMR spectroscopy.



**Scheme 3.** Balanced chemical equation of the reaction of aniline with 1,4-benzoquinone (no peroxydisulfate) showing the various intermediate species that are formed. The product formed is a mixture of (X) and (XI) and higher benzoquinone adducts.

**Table 3**

Elemental analysis of the oligoaniline 1,4-Michael-type adducts obtained in the reaction of aniline and 1,4-benzoquinone. The calculated elemental analysis values for the 1 M HCl/satd. NaCl system were obtained for the structure depicted as product (XI) in Scheme 3. For the 1 M HCl and D.I. water systems, the products are believed to be mixtures of (X) and (XI) whose relative proportions are derived from experimentally observed C/N ratios. For the pH 7 buffer system higher order benzoquinone adducts were used (see Supporting Information).

	C	H	N	O	Total	C/N
1 M HCl Satd. NaCl <sup>a</sup>						
Found	73.18	4.55	7.92	14.19	99.84	10.78
Calc.	73.68	4.12	8.18	14.02	100.00	10.51
1 M HCl <sup>a</sup>						
Found	73.37	4.68	8.95	12.70	99.70	9.56
Calc.	74.29	4.36	9.05	12.30	100.00	9.57
D.I. water <sup>a</sup>						
Found	73.27	4.71	8.92	12.70	99.60	9.58
Calc.	74.29	4.36	9.05	12.30	100.00	9.57
pH 7 buffer <sup>a</sup>						
Found	72.10	4.24	6.84	15.89	99.07	12.30
Calc.	72.78	3.78	6.92	16.52	100	12.27

<sup>a</sup> Solvent.

Indirect evidence supporting the proposed mechanism comes from our finding that we could not deliberately introduce phenazine units in the aniline/benzoquinone system by treatment with peroxydisulfate (using the 1414 cm<sup>-1</sup> peak as a guide). This was attempted in two ways: (i) adding peroxydisulfate to an aqueous suspension of a powder of the aniline/benzoquinone product, and (ii) adding aniline to an aqueous solution of a mixture of benzoquinone and peroxydisulfate. In either instance, there is no significant change in the vibrational spectrum and no new phenazine signature peak appears at 1414 cm<sup>-1</sup>. In the first reaction when peroxydisulfate was added to aniline/benzoquinone product, the absence of the phenazine signature peak is consistent with the Boyland–Sims reaction being disfavored in this system. This could be because the *ortho* positions in the intermediates shown (III) cannot undergo the Boyland–Sims rearrangement, i.e., one side is substitutionally blocked by benzoquinone, and the other side could be sterically hindered. In the second reaction where aniline monomer was added to an aqueous solution of a mixture containing 1,4-benzoquinone and peroxydisulfate in D.I. water, a reaction immediately ensued that was visually similar to what was observed in the absence of peroxydisulfate. The absence of phenazine signatures suggests that under our experimental conditions, aniline reacts with benzoquinone much more rapidly than with peroxydisulfate. This is surprising in view of several reports describing a facile reaction between aniline and peroxydisulfate in various aqueous systems yielding the intermediate oligoaniline species having the phenazine signature at 1414 cm<sup>-1</sup>.

For example, we carried out a reaction by adding excess peroxydisulfate to aniline in water (no added benzoquinone) analogous to the system reported by Epstein et al. [7], and the vibrational spectra of intermediate isolated at 2 min and 4 min showed strong phenazine signatures at 1414 cm<sup>-1</sup>. Clearly, in the aniline/benzoquinone/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, the reaction between aniline and peroxydisulfate is suppressed presumably because of the high concentration of benzoquinone which is able to effectively intercept the aniline monomer yielding a product having no phenazine signatures. This is to be contrasted to our buffered system (aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) where the benzoquinone monoimine intermediate would be present in low concentration and would intercept only a small amount of aniline. This allows the unreacted *p*-aminophenyl sulfate to add to the central ring, or for the peroxydisulfate to react along the Boyland–Sims route to yield the oligoaniline product having phenazine signatures.

In the classical Boyland–Sims rearrangement only the *ortho* isomer (aminophenol) has been isolated and the *para* isomer is formed only if the *ortho* positions are substitutionally blocked [39–41]. However, the reaction is also accompanied by the formation of substantial quantities of colored oligomeric products that were filtered and not analyzed. In one study this product was isolated and classified as belonging to a family of synthetic humic acids whose FT/IR spectrum is similar to the oligoaniline product obtained in this study [46]. Our hypothesis is that the *para* isomer could indeed be formed in the Boyland–Sims rearrangement but could not be isolated because it would react rapidly with excess aniline to yield these synthetic humic acids. Although there is no *a-priori* reason to believe that the *ortho* intermediates would not couple in a similar fashion, the striking similarity in the spectroscopic properties between the oligoaniline products obtained in the aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and aniline/*p*-benzoquinone systems also argues in favor of the *p*-benzoquinone monoimine as being an intermediate. It is possible that the *para* isomer could also be formed by a Bamberger rearrangement where *N*-phenylhydroxyl amine rearranges to *para* aminophenol in aqueous acids [52,53]. This would require the aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> to proceed via the intermediacy of *N*-phenylhydroxyl amine which although unlikely, cannot be ruled out. The Bamberger rearrangement proceeds via phenylnitrene intermediate that reacts rapidly with water to yield *para* aminophenol [54]. Importantly in the classical synthesis of polyaniline [55] yielding conducting emeraldine, phenylnitrene has also been shown to be a key intermediate that rapidly couples with unreacted aniline monomer at the *para* position to yield the dimer 4-aminodiphenylamine. However, under the aqueous reaction conditions one would expect phenylnitrene to also react with water at the *para* position providing a route to 1,4-benzoquinone monoimine. If this should be the case, it would rapidly react with aniline yielding oligoaniline intermediates that could act as initiation sites for linear chain growth. The possibility that oligoaniline containing phenazine linkages could act as nucleating sites has been suggested before by Stejskal et al. [29], and from available experimental data it appears that this frequently results in polyaniline having very different properties compared to conventional emeraldine, e.g., having conductivity that is 1–2 orders of magnitude lower than conventional emeraldine salt. The theoretical conductivity of emeraldine salt ( $\sigma \sim 10^5$  S/cm) [56] is several orders of magnitude higher than the experimentally obtained value ( $\sigma \sim 1$ –5 S/cm) that has been attributed, in part, to defect sites present along the polymer chain acting as barriers to intrachain charge transport. Should the reaction proceed via the intermediacy of even small amounts of 1,4-benzoquinone monoimine, the oligoaniline segments that would be present along the polymer chain would also lower the conductivity significantly. Clearly, additional experimental evidence is needed to support this hypothesis.

Based on the analytical and spectroscopic data obtained so far, the oligoaniline product appears to be a classical Michael-type adduct and not the novel poly aza structure that was previously proposed [31,32]. The bond strength of –N–N– single bonds in a linear chain is expected to be too low to survive the harsh oxidizing conditions in our systems, and many aza structures synthesized to date like the hexazenes, are photo or shock sensitive as well [57–60]. At least in the case of the aniline/benzoquinone system there is no pathway for the formation of linearly linked –N–N– bonds, and in light of the spectroscopic similarities between the products in the two systems it appears unlikely in the aniline/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system as well. It is to be noted however, that evidence so far does not rule out the formation of these highly reactive species as intermediates in the reaction, and additional data is required to rule this option out as being part of the product (e.g., <sup>15</sup>NNMR).

In summary, we propose a new mechanism for the formation of oligoanilines formed in the reaction of aniline and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> in weakly

acidic, neutral or basic aqueous conditions. The reaction appears to be governed not by the classical two-electron oxidation chemistry of peroxydisulfate normally associated with the formation of linearly coupled emeraldine type products, but by nucleophilic attack by the nitrogen lone pairs of aniline. Both analytical and spectroscopic data are consistent with an initial nucleophilic attack by the nitrogen lone pairs of aniline on  $S_2O_8^{2-}$  triggering a Boyland–Sims rearrangement yielding benzoquinone monoimine as an intermediate. This is followed by nucleophilic attack by the nitrogen lone pairs of aniline and/or aminophenyl sulfate on benzoquinone imine by conjugate 1,4 Michael-type addition. Phenazine coupling takes place as a consequence of further oxidation on the oligoaniline intermediate. A detailed elemental analysis of the products obtained in various pH buffers show that they are mixtures of intermediates species at various stages of coupling and hydrolysis. These findings could also help explain why structure elucidation based on spectroscopic data alone had remained a challenge so far (and still is). When we tested our hypothesis about the intermediacy of benzoquinone type intermediates in the aniline/ $S_2O_8^{2-}$  system by adding aniline to 1,4-benzoquinone, we observed the rapid formation of an oligoaniline product that was spectroscopically and structurally similar (and expectedly, not identical) to the product obtained in the aniline/ $S_2O_8^{2-}$  system. The aniline/benzoquinone system also supports our hypothesis that the reaction is governed by classical nucleophilic addition chemistry and the role of a peroxydisulfate oxidant in the aniline/ $S_2O_8^{2-}$  system is mainly to provide a pathway for the formation of benzoquinone-type intermediates and subsequent phenazine coupling. We would like to add that the structural analysis and the chemical structure proposed for oligoanilines described in this study are not meant to be definitive in any way since they are based on a singular (our) interpretation of the experimental observations. This does not rule out other structures, e.g., based on *ortho*-benzoquinone monoimine intermediates, and/or completely new interpretations as more definitive experimental data (like XRD) becomes available.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.synthmet.2008.11.002.

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