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A ONE-STEP METHOD TO SYNTHESIZE N,N'-BIS(4'-AMINOPHENYL)-1,4-QUINONENEDIIMINE AND ITS DERIVATIVES

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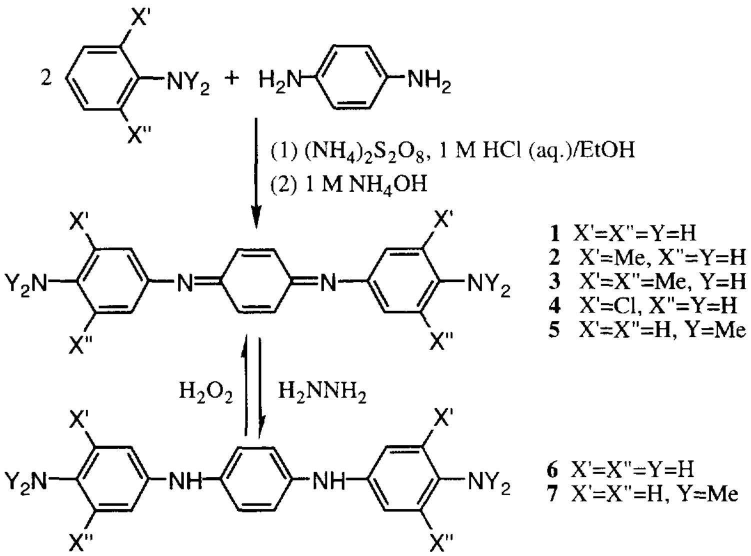
Summary: A convenient, one-step method has been developed for the synthesis of N,N'-bis(4'-aminophenyl)-1,4-quinonenediimine and its derivatives from the oxidation of *p*-phenyl-enediamine in the presence of aniline or substituted anilines in an acidic aqueous medium. These diimine compounds can be readily reduced to afford their corresponding diamine derivatives.

Oligomeric aromatic amines with amino groups at both ends are of great importance in polymer science and industries because of their applications as model compounds for electroactive polyanilines and as monomers to prepare polyamides, polyimides and epoxy polymers. N,N'-Bis(4'-aminophenyl)-1,4-phenylenediamine, a reduced form of N,N'-bis(4'-aminophenyl)-1,4-quinonenediimine, was synthesized in 1965 by catalytic hydrogenation of N,N'-bis(4'-nitrophenyl)-1,4-phenylenediamine[1] and was used as a trimer of aniline in elucidating the structure-semiconductivity relationship of the aniline oligomers.[2,3] In 1989, Gebert et al.[4] developed another method to prepare this oligomer in order to use it as a building block in their attempt to achieve a total unambiguous synthesis of polyaniline via Schiff base chemistry. Both methods involve multiple synthetic steps and reduction of the nitro groups in the precursors. Hence, it is difficult to generalize these methods in the synthesis of its derivatives and of, more importantly, higher oligomers. In our previous studies,[5] we found that a small amount of aromatic amine additives, such as *p*-phenylenediamine, could drastically accelerate the oxidative polymerization of aniline monomers. According to the mechanism we have proposed for the oxidative polymerization of aniline,[5] these additives function essentially as chain initiators in the polymerization and, therefore, the molecular weights of polyaniline can be tailored by varying the molar ratio of the additives to aniline in the system. At the molar ratio of 2 to 1, we should expect the trimeric species such as N,N'-bis(4'-aminophenyl)-1,4-quinonenediimine to form in an appreciable yield under favorable reactions conditions.

Indeed, as described in this paper, we have successfully prepared N,N'-bis(4'-aminophenyl)-1,4-quinonenediimine (**1**) and its derivatives (**2-5**) by oxidation of 2 eq. aniline and substituted anilines with ammonium persulfate as oxidant in the presence of 1 eq. *p*-phenylenediamine. The oxidation state of the products can be readily interconverted by simple redox reactions. The synthesis is depicted in Scheme 1 and the yields are summarized in Table 1. We have found that the stoichiometry of the amine reactants, adequate solvents, amount of oxidant and reaction temperature are important factors for obtaining the products in good yield and high purity. The conventional procedures for chemical oxidative polymerization of aniline in 1 M HCl in the absence of the additive usually favor the chain growth reactions to yield polyaniline products with molecular weights as high as 10^5 and with a bimodal type of molecular weight distribution.[6] As the amount of the additives is increased (e.g. 1 to 5 mol-% relative to the aniline monomer), the molecular weight of polyaniline decreases accompanying with narrower molecular weight distributions.[5] For the synthesis of the trimers, the amount of the additive *p*-phenylenediamine in the reaction was increased to 50 mol-%, so that the trimers formed in a relatively large quantity and precipitated out without further polymerization. Since the trimer products in the acidic medium should exist mainly in form of hydrogen chloride salt, addition of some organic solvents would facilitate the precipitation of the products. About 30% of ethanol or methanol in 1 M or 2 M HCl was found to be quite satisfactory for this purpose. The presence of the organic solvents also allows us to lower the reaction temperatures to -5 °C, which would further reduce the tendency of polymerization reactions.



1 X'=X''=Y=H
2 X'=Me, X''=Y=H
3 X'=X''=Me, Y=H
4 X'=Cl, X''=Y=H
5 X'=X''=H, Y=Me

6 X'=X''=Y=H
7 X'=X''=H, Y=Me

Scheme 1

Table 1. Yields and wavelengths of maximum absorption (λ_{max}) of N,N'-bis(4'-aminophenyl)-1,4-quinonenediimine (**1**) and its derivatives.

compound	yield (%) at [O]/[DA] ratio[a] of		λ_{max} (nm) in		
	1:1	2:1	DMF	THF	CH_2Cl_2
1	40	77	572	556	532
2	42	83	578	558	539
3	42	64	578	560	546
4	28	---	554	544	520
5	35	75	596	590	585
6			312	310	307
7			319	316	314

[a] [O]/[DA] is the molar ratio of ammonium persulfate to *p*-phenylenediamine that was employed in the synthesis.

In a typical procedure for the synthesis of compound **1**, 0.86 g (8 mmol) of *p*-phenylenediamine was dissolved in a solution of 100 mL aqueous 1 M HCl and 40 mL ethanol. The solution was then cooled to about -5 °C in a NaCl-crushed ice bath. To this solution was added 1.8 g (8 mmol) of ammonium persulfate in one portion with stirring under air atmosphere. After about 5 min, the reaction solution became dark brown and 1.5 mL (16 mmol) of doubly distilled aniline was added quickly. Several minutes later, a blue particle suspension was formed and the reaction mixture was stirred vigorously for additional 30 minutes. The solid product was collected by filtration through a Buchner funnel under a reduced pressure and was washed with 30 mL 1 M HCl followed by 80 mL distilled water. The product was then treated with 40 mL 1 M aqueous solution of ammonium hydroxide for 1 to 2 h. The mixture was filtered under a reduced pressure and the remaining solid was washed with distilled water until the filtrate became neutral in pH. Upon drying at 40 °C overnight under vacuum, 0.93 g of the product **1** was obtained as a blue powder in 40% yield. It is important to note that when the amount of the oxidant was increased to, e.g., two equivalents (16 mmol) in the reaction, the higher yields (e.g. > 80%, Table 1) were obtainable by otherwise identical procedure. However, the product needed to be purified by dissolution in THF followed by column chromatography over silica gel with a 1/3 (v/v) mixture of ethyl acetate/n-hexane or diethyl ether alone as eluant.

As shown in Scheme 1, the derivatives of the trimer **1** were also synthesized using the same procedure from *p*-phenylenediamine and various substituted anilines. Our attempt to use 2,6-dichloroaniline to get the corresponding compound has not been successful. This could be attributed to the low reactivity of 2,6-dichloroaniline because of the electron-withdrawing nature of the chloro groups. Such an electronic effect is supported by the observation that the yield of the reaction of 2-chloroaniline is lower than that of unsubstituted aniline. Reduction of compound **1** with hydrazine under nitrogen atmosphere afforded quantitatively a white solid, which was characterized as N,N'-bis(4'-aminophenyl)-1,4-phenylenediamine (**6**) with melting point 198 °C (exactly the same as reported in the literature[1]). Other derivatives could be reduced to the corresponding amine forms as well. All the compounds were characterized by means of infrared, electronic absorption, exact mass, ^{1}H- and/or ^{13}C-NMR spectroscopy and the results are consistent with the proposed structures.[7]

The wavelengths of maximum UV absorption (λ_{max}) were measured in various solvents as listed in Table 1. The electron-donating groups on the phenyl ring (e.g. **2** and **3**) or on the terminal nitrogen atom (e.g. **5**) tend to increase the λ_{max} value while the electron-withdrawing groups (e.g. **4**) to decrease the λ_{max} value. Such a tendency remains the same regardless of polarity of solvents. For the same compound, the increase in the polarity of the solvent apparently leads to a bathochromic shift of the λ_{max}. These tendencies might correlate with the electronic and electrochemical properties of these compounds which are currently under investigation. The reduced form of the compounds (e.g. **6** and **7**) was found to have much lower λ_{max} values than their corresponding oxidized counterparts (e.g. **1** and **5**, respectively). It should be noted that the reduced form undergoes oxidation by air or by other oxidants such as hydrogen peroxide to regenerate the oxidized form of the compounds.

In summary, we have developed a very convenient, one-step method to synthesize N,N'-bis(4'-aminophenyl)-1,4-quinonenediimine and its derivatives from the oxidative reactions of *p*-phenylenediamine with aniline and various substituted anilines in an acidic aqueous medium. These 1,4-quinonenediimine compounds can be readily reduced to afford their corresponding 1,4-phenylenediamine derivatives. Many of the products could be employed as monomers in preparing new step-growth polymers such as polyamides, polyimides and epoxy plastics. This method could also be further extended to synthesize some higher oligomers of aniline. The exploration of the both possibilities is in progress in our laboratory.

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7. Characterization: Melting points were determined with a Mel Temp apparatus and were uncorrected. IR spectra of KBr powder-pressed pellets were recorded on a Perkin-Elmer Model 1600 FTIR spectrometer. The ^{1}H- and ^{13}C-NMR spectra were measured on an IBM Bruker AM 250 FTNMR spectrometer with DMSO-d_6 as solvent. Exact mass spectra were determined on a VG ZAB-HF high resolution mass spectrometer. UV-Vis spectra were recorded on a Perkin-Elmer HP8451 spectrophotometer. Compound **1:** m.p. 172 °C; IR (in cm^{-1}) 3338, 3208, 1560, 1501, 1294, 1166, 836; ^{1}H-NMR δ (in ppm) 6.94 (s, 4H), 6.77 (d, 4H), 6.60 (d, 4H), 5.44 (s, 4H); Exact MS (M$^+$+2H) 290.1519 (calc. 290.1531); Compound **2:** m.p. 105-107 °C; IR (in cm^{-1}) 3347, 3224, 1597, 1498, 1308, 1135, 813; ^{1}H-NMR δ (in ppm) 6.91 (s, 4H), 6.67 (s, 2H), 6.63 (d, 4H), 2.05 (s, 6H); Exact MS (M$^+$+2H) 318.1838 (calc. 318.1844); Compound **3:** m.p. 102-104 °C; IR (in cm^{-1}) 3372, 1605, 1481, 1300, 854; ^{1}H-NMR δ (in ppm) 6.91 (s, 4H), 6.70 (s, 4H), 4.85 (b, 4H), 2.08 (s, 12H); Exact MS (M$^+$+2H) 346.2147 (calc. 346.2157); Compound **4:** m.p. 129-130 °C; ^{1}H-NMR δ (in ppm) 6.97 (s, 4H), 6.91 (s, 2H), 6.84 (d, 2H), 6.67 (d, 2H); Exact MS (M$^+$+2H) 358.0729 (calc. 358.0752); Compound **5:** m.p. 182-184 °C; IR cm^{-1}, 1597, 1515, 1366, 1176, 829; ^{1}H-NMR δ (in ppm) 7.01 (s, 4H), 6.98 (d, 4H), 6.74 (d, 4H), 3.00 (s, 12H); Exact MS (M$^+$+2H) 346.2153 (calc. 346.2157); Compound **6:** m.p. 198 °C (lit. 198 °C)[1]; IR (in cm^{-1}) 3355, 2960, 1596, 1503, 1366, 1262, 1164, 1030, 809; ^{1}H-NMR δ (in ppm) 7.00 (s, 2H), 6.70 (s, 2H), 6.70 (d, 2H), 6.47 (d, 2H), 4.60 (b, 4H); ^{13}C-NMR δ (in ppm) 142.1, 138.0, 134.5, 119.7, 117.1, 115.1; Compound **7:** m.p. 178-179 °C (lit. 173 °C)[1]; IR (in cm^{-1}) 3401, 3368, 2933, 2863, 2778, 1530, 1512, 1448, 1312, 1225, 1135, 1057, 817; ^{1}H-NMR δ (in ppm) 7.17 (s, 2H), 6.79 (d, 4H), 6.72 (s, 2H), 6.59 (d, 4H), 2.70 (s, 12H); ^{13}C-NMR δ (in ppm) 145, 137.6, 135.4, 118.6, 117.6, 114.4, 41.2.

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