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REVIEW ARTICLE

Synthesis and characterization of some new aromatic diamine monomers from oxidative coupling of anilines and substituted aniline with 4-amino-*N*,*N*-dimethyl aniline

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KEYWORDS

New aromatic diamine;
Monomer;
Oxidative coupling;
Aniline;
Nucleophilic substitution

Abstract New aromatic diamine monomers prepared from condensation reactions of aniline, *p*-chloroaniline, p-nitro aniline, *p*-chloro-*m*-nitro aniline with 4-amino-*N*,*N*-dimethylaniline (2:1) (aniline:reagent) in the presence of potassium dichromate in acidic media yielded new monomers of a highly colored violet and reddish-violet. Mechanism of the reaction of aniline with 4-amino-*N*,*N*-dimethylaniline in the presence of potassium dichromate as an oxidant is expected to proceed through nucleophilic substitution reaction, and the mechanism proceeds facilitated a nucleophilic attack of the substituted aniline ring on the –NH_2 group of the reagent; through partial protonation of their –NH_2 group, forming in diamine dye and their identification was confirmed by IR, ^1H NMR, and CHN analyses.

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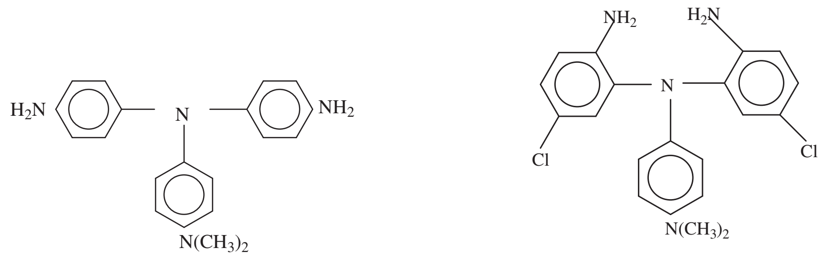
1. Introduction

Study of aromatic amines is important due to the presence of amines in natural products, sulpha drugs, dyes, vitamins, amino acids and nucleic acids (Hart and Schuetz, 1972; Harper, 1972; Casky, 1979). Aniline compounds are used in many industries, including dyes, agrochemicals by further reaction functionalization and pigments (Berry and Royd, 1984; John, 2005). Both amines and some of its salts are excellent bactericides, fungicides and algaecides. Aminophenol oxidized readily, so, it is widely used as photographic developers (Kirk-Othme, 1968). Aromatic amines are of growing significance in environmental chemistry due to their hazardous wastes and potential carcinogenic properties (Berry and Royd, 1984; Kasthuri et al., 2008; Al-Abachi et al., 1990).

4-Amino-*N*,*N*-dimethylaniline is used in microbiology as a test reagent for cytochromixidase and its derivatives are used in hair dye (Dalling et al., 1986). Aniline and *N*-methyl aniline reacted extensively in aprotic solution containing potassium superoxide in the case of aniline trans-azobenzene and 4-nitro-diphenylamine, which take the major products, but with *N* -methyl aniline both oxidation and dimethylation occurred (Stuehr and Marletta, 1985). *N,N* and 2,6-disubstituted anilines were oxidized by Ce (IV) per chlorate in aqueous perchloric acid medium and cerium(IV) ammonium nitrate as oxidant and water as solvent to the corresponding derivatives of 4,4′-diphenoquinone-diimine and *N*-phenyl-*p*-phenylenediimine in high yields (Chanjuan et al. 2005; Seliger et al., 1999).

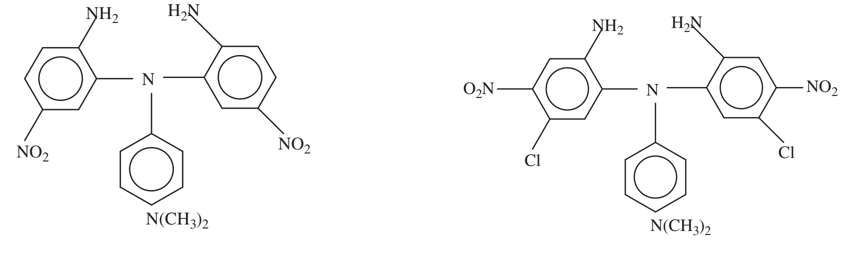
HCl-doped emeraldine formed from poly aniline (PANI-H) through synthesizing by oxidative polymerization of aniline in aqueous hydrochloric acid solution using potassium dichromate as an oxidant. The structure, doping, conductivity, and thermal stability of the reduced poly aniline (PANI-R) were studied by elemental analysis, FI-IR, solid state NMR and TGA (Salih, 2010; Zeng and Ko, 1998). Aniline is readily oxidized by tert-butyl hydro peroxide in the presence of molybdenum and vanadium compounds as a catalyst (Howe and Hiatt, 1970).

Oxidation of *N*,*N*-dimethyl-aniline (DMA) by various oxidizing agents and formation of methyl violet is a well known process in the manufacturing of the dye (Vansant and Yariv, 1970). Oxidation coupling reactions of aromatic amines have got wide applications in the recent year. These reactions involved coupling between two or more aromatic amines in



monomer (1) : N^1,N^1_Bis(4_aminophenylene) _N^4,N^4_Dimethylbenzen-1,4-diamine.

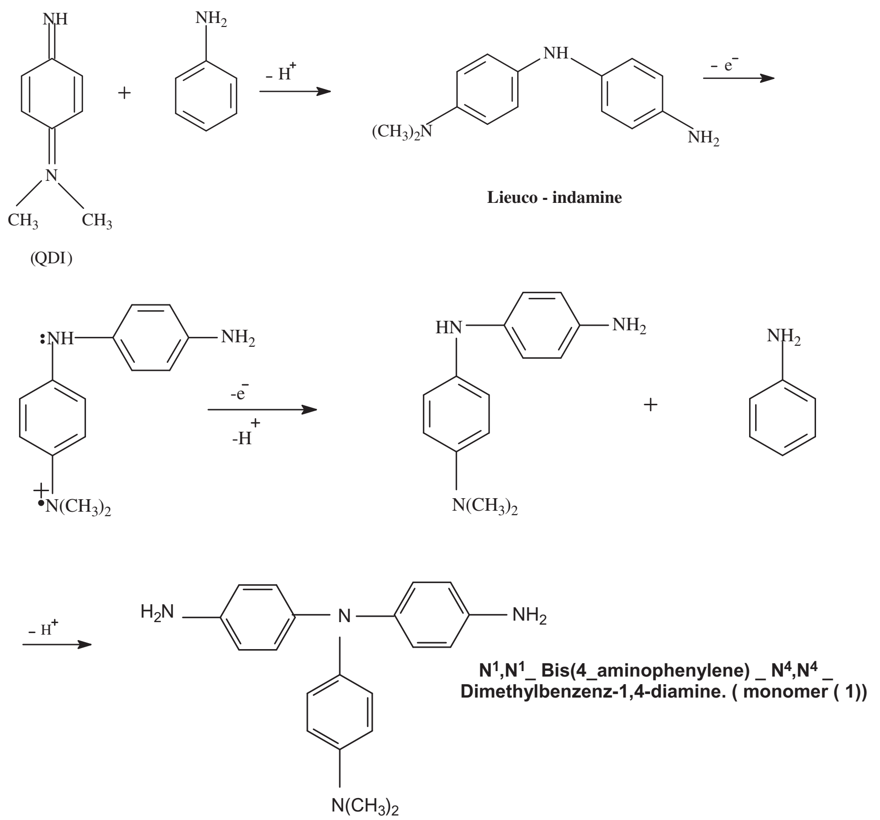
monomer (2) : N^1,N^1_Bis(5_chloro_2_aminophenylene) _N^4,N^4_Dimethylbenzene-1,4-diamine.



monomer (3) : N^1,N^1_Bis(5_nitro_2_aminophenylene) _N^4,N^4_Dimethylbenzene-1,4-diamine.

monomer (4) : N^1,N^1_Bis(5_chloro_4_ nitro_2_amino-phenylene) _N^4,N^4_Dimethylbenzene-1,4-diamine.

Scheme 1 The structure of prepared monomers **1**–**4**.



Scheme 2 Mechanism of the reaction of aniline with 4-amino-*N*,*N*-dimethylaniline in the presence oxidant.

the presence of a suitable oxidant. Throughout the literature cited it was found that little attention has been considered on studies of aromatic amines oxidative coupling (Kareem, 2000). Kinetics of oxidation of aniline and substituted anilines by sodium iodate in an aqueous acetic acid medium and in the presence of perchloric acid has been studied the reactions are catalyze by Ru (III) (Prasada Rao and Padmanabha, 1980).

The kinetic studies of oxidation of aniline with a fresh solution of per borate in acetic acid showed that the oxidation is sluggish at room temperature but is smooth at 45–65 °C; the product formation confirms pseudo-first order kinetics (Karunakaran and Kamalam, 2002). Aromatic diamine such as (4,4-diaminodiphenyl sulfone (DDS)) in the polymeric lithium salt matrix curing with poly (ethylene glycol) diglycidyl ether (PEGDGE) used to prepare a novel single ion conducting solid polymer electrolyte (SPE). The ionic conductivity, thermal stability and tensile properties were investigated as a function of degree of sulfonation and PEGDGE concentration (Soma, 2010).

Aniline reacts with the catalytic amount of di acetyl monoxime cobalt(II) chloride complex along with hydrogen peroxide to give C–N-bonded oligomer having M_n and M_w of 1256 and 1892, respectively. Mass spectra determined by MALDI suggest the poly aniline. The oligomer thus formed has semi conducting properties (Puzari and Baruah, 2000).

Poly dihalo anilines have been synthesized from dihalo anilines in protic and aprotic solvent media with different oxidizing agents such as copper per chlorate, potassium dichromate and potassium permanganate (Diaz et al., 1998). Aromatic polyimide was synthesized from bis (4-amino-2-biphenyl) ether, which had phenyl groups at the 2- and 2′-positions of the biphenyl ether moiety, and various tetra carboxylic dianhydrides by the conventional two-step procedure that included ring-opening polymerization in NMP and subsequent thermal cyclic dehydration, and the properties compared with those of the corresponding polyimide without phenyl groups (Morikawa et al., 2005).

Substituted benzyl amines readily undergo self-coupling reactions to produce benzylidene–benzylamines, while aliphatic amines and anilines cannot produce self-coupled products. A mixture of a benzyl amine and an aniline or aliphatic amine effectively and selectively can produce mixed imine such as benzylidene–aniline and benzylidene–alkyl amine (Landge et al., 2007). In the clay-mediated reaction of N,N-disubstituted anilines using microwave radiation as an energy source in the absence of solvent, crystal violet and derivatives, diphenylmethanes, and biphenyls were isolated along with intermediates supporting an oxidative coupling-type mechanism (López-Cortés et al., 2000).

Polyamide and polyimide have got a wide application in the world. A series of rod–coil–rod triblock copolymers were synthesized by two-step poly condensation with polycaprolactam (PA6) as the flexible block, while poly (*p*-benzamide) (PBA) as the rod (Junjun et al., 2010). Novel macro and mesoporous polysulfone materials were prepared from miscible blend of polysulfone with a phenylindane containing polyimide by selective chemical decomposition of the polyimide phase using a dilute hydrazine or tetra ammonium hydroxide solution in methanol (Yong and Benjamin, 2010).

2. Experimental

2.1. Instruments

Melting points were determined using the Gallen Kamp melting point apparatus. Room temperature Fourier transform infrared spectra were taken using a pye – unicam Sp3-300 IR spectrometer with pressing potassium bromide troche (KBr).

Proton nuclear magnetic resonance (^{1}H NMR) spectra of each monomers sample in DMSO-d_6 were obtained with a 400 MHz Super Conducting NMR Spectrometer (NMR-Untersuchungsauftrag AVS-400). As well as, an elemental analysis (C, H and N) was recorded on Carlo Erba type 1106.

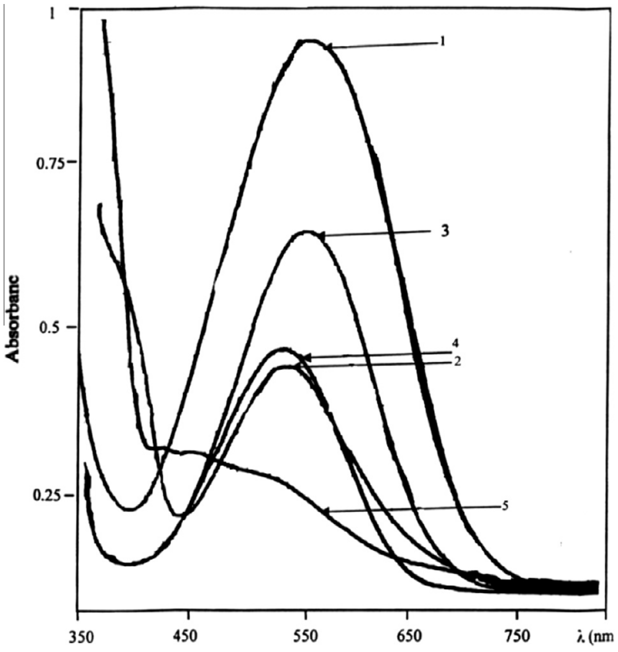


Figure 1 Absorption spectra of the product obtained by the reaction of 4-amino-*N*,*N*-dimethyl aniline with 10 μg/ml of: (1) aniline, (2) *p*-chloroaniline, (3) *p*-nitro aniline, (4) *p*-chloro-*m*-nitro-aniline, all versus reagent blank. Absorption spectrum of blank versus distilled water.

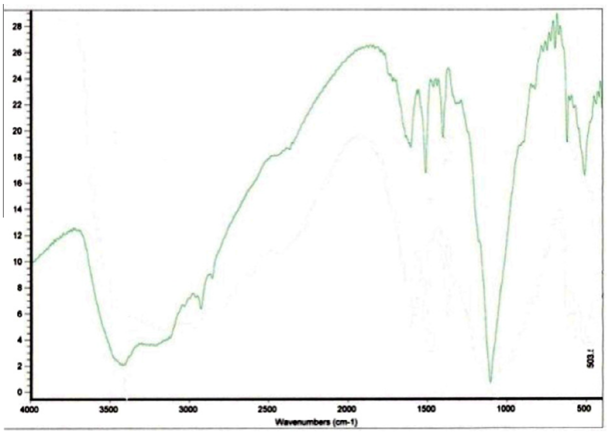


Figure 2 IR spectrum of reagent (4-amino *N*,*N*-dimethylaniline).

2.2. Materials

Aniline (BDH) was redistilled under vacuum before using and stored in a dark bottle in a refrigerator. *p*-Chloroaniline (BDH), *p*-nitro aniline (BDH), *p*-chloro-*m*-nitro aniline (Fluka), 4-amino-*N*,*N*-dimethylaniline sulfate (Fluka), potassium dichromate (Fluka) and phosphoric acid (98%) (BDH) were used as received without any purification.

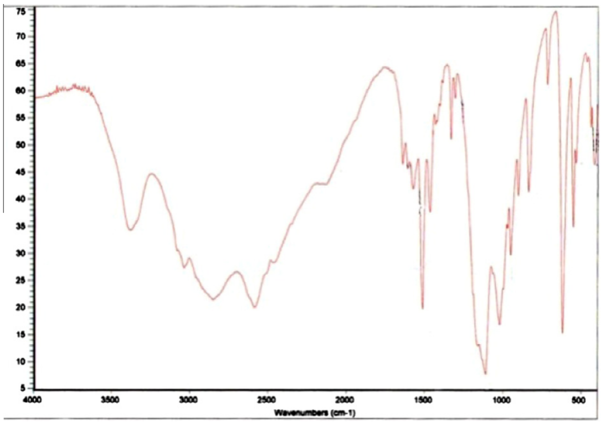


Figure 3 IR spectrum of monomer No. 1.

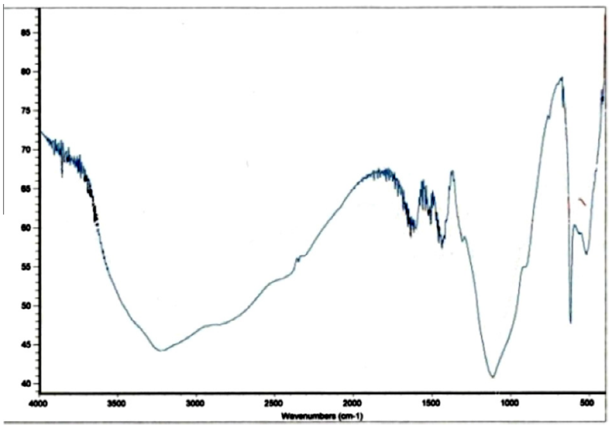


Figure 4 IR spectrum of monomer No. 3.

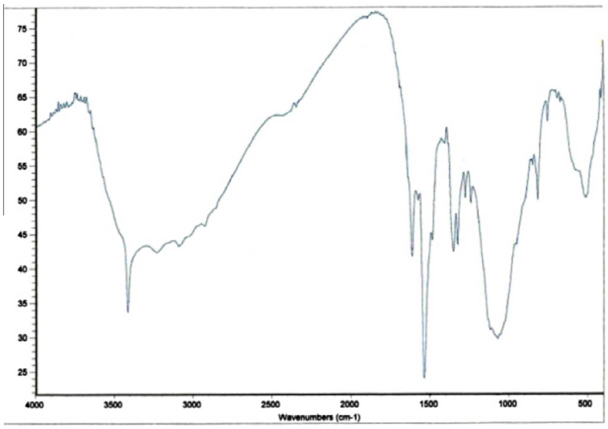


Figure 5 IR spectrum of monomer No. 2.

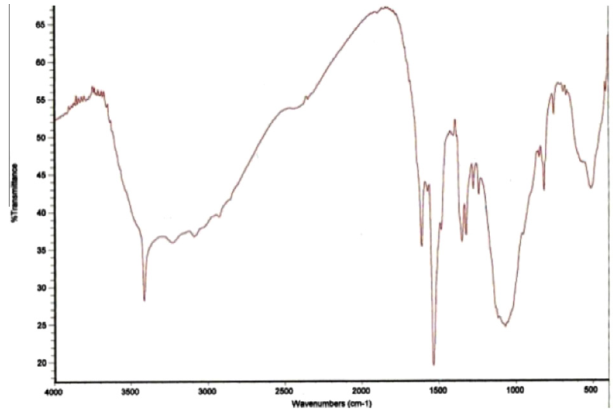


Figure 6 IR spectrum of monomer No. 4.

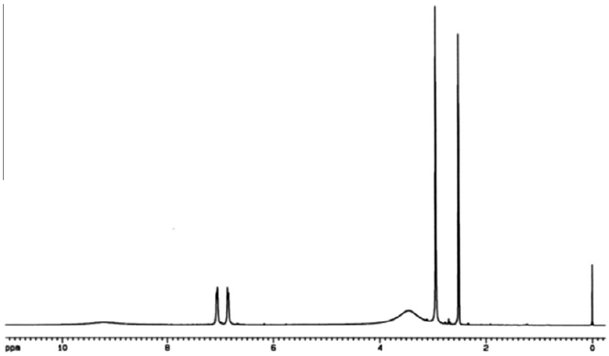


Figure 7 NMR spectrum of reagent (4-amino-*N*,*N*-dimethylaniline).

2.3. Procedure

0.186 g (2 mmol) aniline (in 6 ml ethanol) or substituted aniline was mixed with 0.234 g (1 mmol) reagent (in 6 ml distilled water), 7.4 ml (1 M) H_3PO_4 was added and followed by 0.187 g (0.636 mmol) $K_2Cr_2O_7$ (in 6 ml distilled water). The solution was mixed well, left aside for 1 h and then evaporated on water bath to avoid any possible decomposition by excess heating. The dry product was recrystallized in tetrahydrofuran (THF) giving the aromatic diamine monomers (**1**–**4**). The composition of monomers is shown in Scheme 1 (Kareem, 2000).

3. Results and discussion

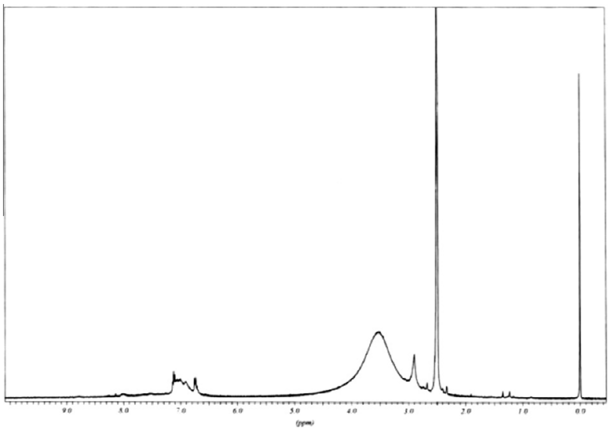


Figure 8 NMR spectrum of monomer No. 1.

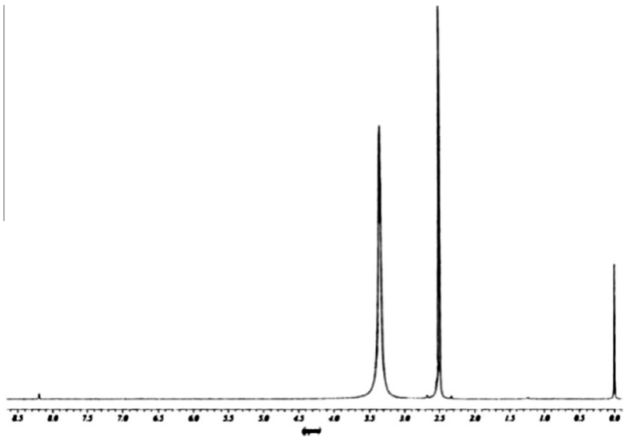


Figure 9 NMR spectrum of monomer No. 2.

Highly colored violet and reddish-violet condensation products were prepared from the reaction between 4-amino-*N*,*N*-dimethylaniline in the presence of potassium dichromate and acidic media with aniline or substituted aniline such as *p*-chloroaniline, *p*-nitro aniline, *p*-chloro-*m*-nitro-aniline.

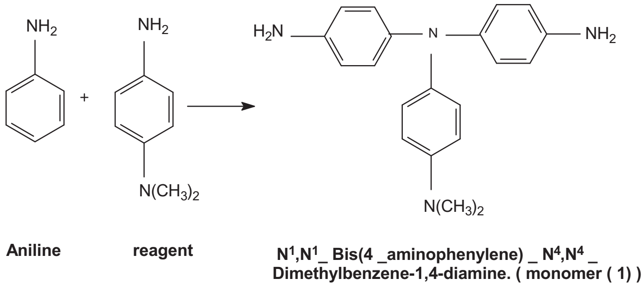


Table 1 The IR and ^{1}H NMR data of the reagent and monomers (**1**–**4**).

	IR vibration			Chemical shifts of compounds		
	ν NH_2 (cm^{-1})	ν C–N (cm^{-1})	ν C=C-ring (cm^{-1})	H-ring	$(–CH_3)_2$	$–NH_2$
Reagent	3378	1109	1510–1638	7.2–6.7	4.4	3
Aniline	3419	1099	1509–1604	7.1–6.7	3.6	2.9
p-NO_2-aniline	3229	1110	1507–1653	6.6–7.0	3.4	2.5
p-Cl-aniline	3413	1098	1517–1617	6.9–7.2	3.3	2.5
Cl-NO_2-aniline	3421	1066	1533–1610	6.8–7.4	3.4	2.5

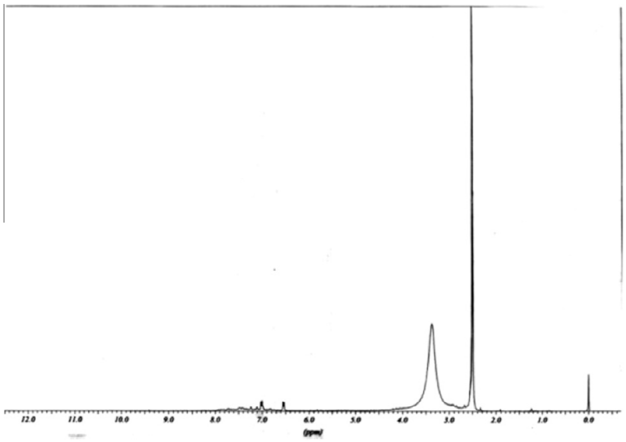


Figure 10 NMR spectrum of monomer No. 3.

Table 2 Elemental analysis of the reagent and monomers (**1**–**4**).

Compound	Theoretical (%)			Practical (%)		
	C	H	N	C	H	N
Reagent	40.97	5.97	11.95	40.79	5.81	11.7
Aniline	33.815	3.121	7.89	33.59	5.01	7.63
p-NO_2-aniline	30.15	3.52	10.6	29.89	4.24	10.32
p-Cl-aniline	30.88	3.6	7.21	30.67	4.24	6.89
Cl-NO_2-aniline	27.72	3.01	9.71	27.43	3.64	9.43

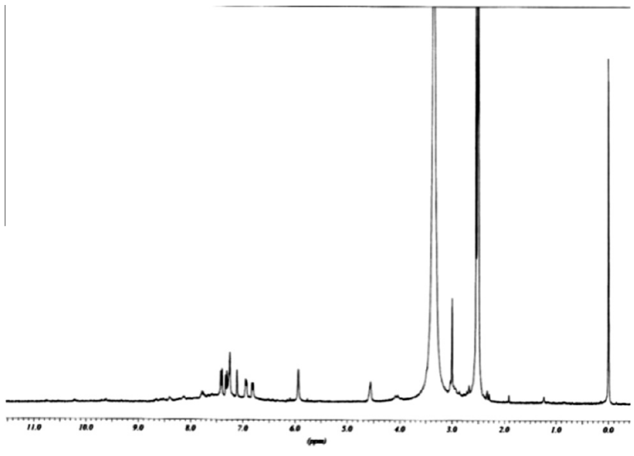
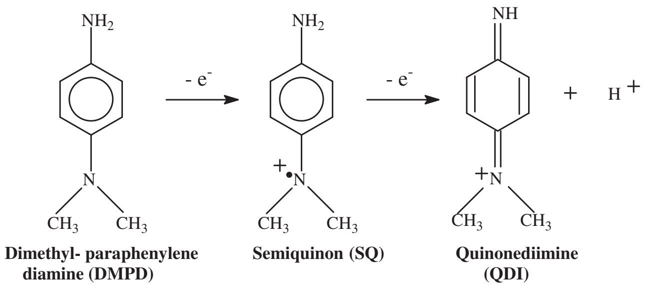


Figure 11 NMR spectrum of monomer No. 4.

Mechanism of the reaction of aniline with 4-amino-*N*,*N*-dimethylaniline (Kareem, 2000) in the presence of oxidant is expected to proceed through nucleophilic substitution reaction, and they facilitate a nucleophilic attack of the substituted aniline ring on the –NH_2 group of the reagent, through partial protonation of their –NH_2 group, forming indamine dye as shown in the Scheme 2.



Throughout the investigation on the reaction between the studied aromatic amines with 4-amino-*N*,*N*-dimethylaniline in the presence of potassium dichromate, a highly colored violet and reddish-violet condensation products have been obtained with a maximum absorbance at 550 nm for aniline, *p*-chloroaniline, p-nitro aniline, *p*-chloro-*m*-nitro aniline. The absorbance of the colored products measured versus reagent blank shown clearly in Fig. 1.

Figs. 2–6 present the IR spectra of reagent and all aromatic diamine monomers. The only difference lies in the intensity of (–NH_2) peak of the product in comparison to that reagent. Since the expected structure contains two (–NH_2) groups leading to higher absorbance intensity, and the effective at the activated group (–Cl, –NO_2) also increasing of the intensity of (–NH_2) peak of the monomer in comparison to that reagent, as shown in the Table 1.

^{1}H NMR spectroscopy was used to deduce the reaction intermediates of aniline derivates oxidative couplings. The nuclear magnetic resonance of the prepared monomers compared with reagent as shown in Table 1. Figs. 7–11 show the ^{1}H NMR spectra and peak assignments of reagent with all purified monomers. By comparing the relative signal intensities of different protons (protons in the aromatic ring: δ range 6.6–7.4 ppm, protons in the methylene group: δ range 3.3–4.4 ppm, protons in the amine group: δ range 2.5–3) (Yo and Noriko, 2002; Faiq and Faroq, 2000), the compositions of monomers were obtained (Kareem, 2000).

Since the reaction was performed in highly acidic medium (1 M H_3PO_4) so amine salt formation as phosphate must be taken into consideration throughout the theoretical calculations of the elements on the bases of this expectation. It has been found that the practical percentages are in good agreement with these calculations, as shown in the Table 2.

4. Conclusion

Oxidative coupling reaction of aromatic amines has got wide applications. The reaction may be defined as reaction two or more organic compounds in the presence of a suitable oxidant potassium dichromate ($K_2Cr_2O_7$). Oxidative coupling reactions are applied successfully in many fields such as pharmaceutical, agricultural, industrial and environmental analyses.

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