Synthesis and Characterization of some Anilines Oxidative Coupling Products

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(**Received:** 29 / 6 / 2008 ---- **Accepted:** 25 / 10 /2009)

Abstract:

Condensation reactions of aniline, benzidine, p-toluidine, p-anisidine with 4-amino-N, N-dimethylaniline (2:1) (aniline: reagent) in the presence of potassium dichromate in acidic media yielded condensation products of a highly colored violet and reddish-violet, and their identification was confirmed by IR, ^{1}H-NMR, and CHN analyses.

Key words: Aniline, Oxidative coupling.

1. Introduction:

Aromatic amines are widely distributed compounds in nature [[1], and are widely used in industry and pharmacology [2]; Aniline compounds [3] are used in many industries including dyes, agrochemicals by further reaction functionalization [4] and pigments. Both amines and some of its salts are excellent bactericides, fungicides and algaecides [5]. Aromatic amines are of growing significance in environmental chemistry due to their hazardous wastes and potential carcinogenic properties [6].

Oxidation coupling reactions of aromatic amines [7], have got a wide applications in the recent year. These reactions involved coupling between two or more aromatic amines in the presence of a suitable oxidant. Throughout literature cited it was found that little attention has been considered on studies of aromatic amines oxidative coupling.

Aniline is readily oxidized by tert-butyl hydroperoxide in the presence molybdenum and vanadium compounds as a catalyst [8]. 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 [9]. Kinetics of oxidation of aniline and substituted anilines by sodium iodate in aqueous acetic acid medium and in the presence of perchloric acid has been studied the reactions are catalyze by Ru (III) [10] . The kinetic studies of oxidation of aniline with fresh solution of perborate in acetic acid, showed that the oxidation is sluggish at room temperature but is smooth at 45 – 65C^O, the product formation confirms pseudo-first order kinetics [11].

Poly dihaloanilines have been synthesized from dihaloanilines [12] in protic and aprotic solvent media with different oxidizing agents such as copper perchlorate, potassium dichromate and potassium permanganate.

2. Experimental:

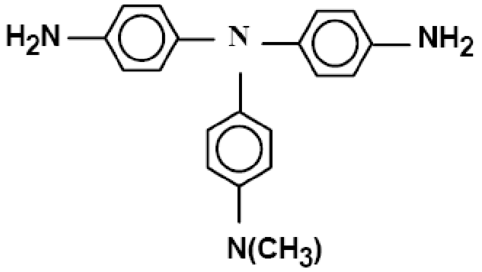
2.1 General:

Melting points were determined using Gallen Kamp melting point apparatus. Infrared spectra were recorded using a pye unicam Sp3-300 spectrophotometer in which solid materials were taken as a disc with KBr. The nuclear magnetic resonance results were obtained on a Varian A-60 instruments with tetra-methyl silaine (TMS) as internal standard. As well as, an elemental analysis (C, H and N) was recorded on Carlo Erba type 1106.

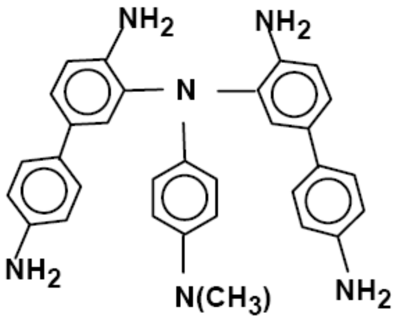
2.2- Experimental:

0.186 gm (2 mmole) aniline (in 6 ml ethanol) or substituted aniline was mixed with 0.234 gm (1 mmole) reagent (in 6 ml distilled water), 7.4 ml (1M) H_3PO_4 was added and followed by 0.187 gm (0.636mmole) $K_2Cr_2O_7$ (in 6 ml distilled water).

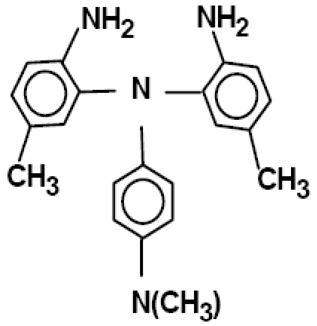
The solutions were mixed well, left a side for one hour and then evaporated on water bath to avoid any possible decomposition by excess heating. The dry product was recrystallized in tetrahydrofuran (THF) giving the coupling products (1-4) [7].



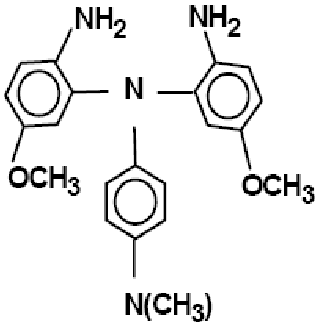
Product 1 : Aniline with reagent 4-amino-N,N-dimethylaniline



Product 2: Benzidine with reagent 4-amino-N,N-dimethylaniline



Product 3: Toluidine with reagent 4-amino-N,N-dimethylaniline



Product 4: Anisidine with reagent 4-amino-N,N-dimethylaniline

2.Results and Discussion:

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 benzidine, P-toluidine, and P-anisidine.

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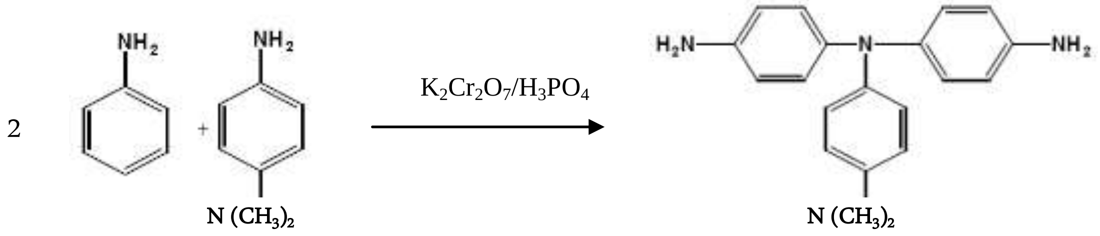
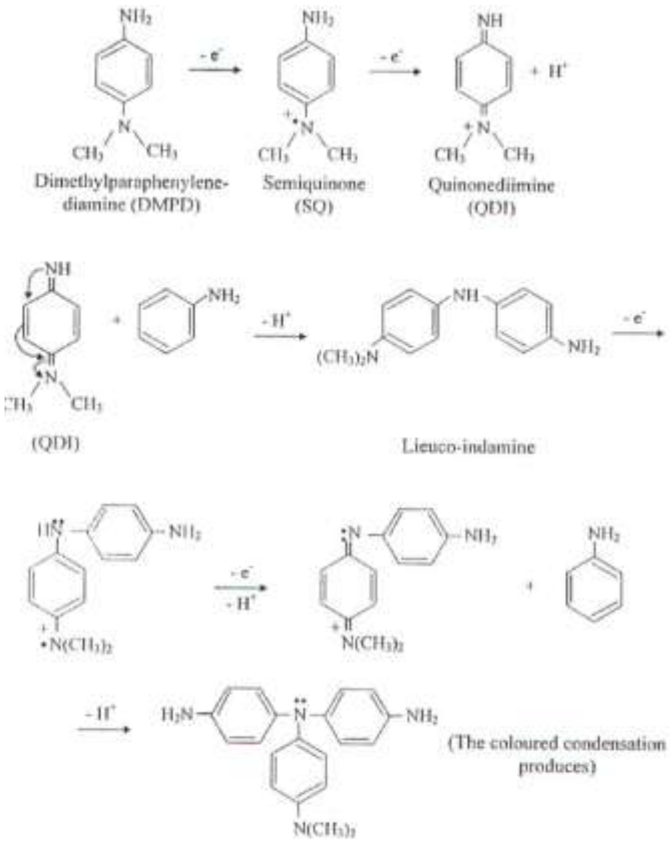


Aniline Reagent the colored condensation produces

Mechanism of the reaction of aniline with 4-amino-N,N-dimethylaniline[7] in the presence of oxidant is expected to proceed through nucleophilic substitution reaction, and they facilitate 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 (1):



Scheme (1): Mechanism of the reaction of aniline with 4-amino-N, N-dimethylaniline in the presence of oxidant

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 were obtained with a maximum absorbance at 550nm for aniline, benzidine, p-toluidine, and p-anisidine. The absorbance of the colored products measured versus reagent blank is shown in figure (1).

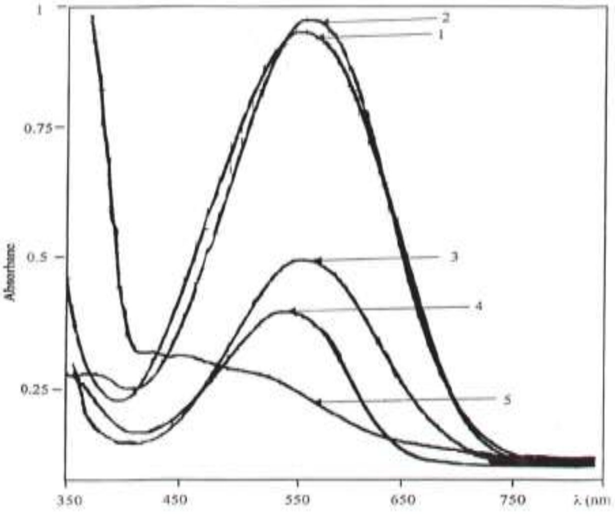


Figure (1): Absorption Spectra of the product obtained by the reaction of 4-amino-N, N-dimethylaniline with 10µg/ml of:

1- Aniline
2- Benzidine
3- P-toluidine
4- P-anisidine, all versus reagent blank
5- Absorption spectrum of blank versus distilled water

Comparing the IR spectrum of the reagent figure (2) and that of the colored products figure (3-6), since both are aromatic amines, the only difference is in increasing of the intensity of (-NH_2) peak of the product compared to that of the reagent, since in the expected structure there are two (-NH_2) group leading to higher absorbance intensity, and the effective of activated group (-CH_3, -OCH_3, -$PhNH_2$) also increasing of the intensity of (-NH_2) peak of the product compared to that of the reagent, as shown in the table (1).

^{1}H NMR spectroscopy [13] was used to deduce the reaction intermediates of aniline derivates and phenols oxidative couplings. The nuclear magnetic resonance of the product figures (8-11) compared with reagent figure (7) showed the shifting of all peaks forward a higher field table (1). A broad multiple signal at δ (7.2-6.6) corresponding to four aromatic protons of the benzene ring of the reagent, but a broad multiple signal at δ (7.1-6.5), δ (7.2-6.9), δ (6.7-6.6) and δ (7.25-6.6). Corresponding to twelve protons of the three benzene ring of the products (1, 3, 4) and corresponding to twenty protons of the five benzene ring of the product (2). Sharp singlet peak at δ (4.4), δ (3.6), δ (3.4), δ (3.4), δ (3.4) corresponding to six protons of the two(-CH_3) groups of the reagent and the products (1,2,3,4) and another sharp singlet peak at δ (3), δ (2.9), δ (2.5), δ (2.5), δ (2.5) corresponding to two protons of -NH_2 of the reagent, and the products (1,2,3,4) [14].

Since the reaction was performed in highly acidic medium (1M H3PO4) 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 is found that the practical percentages are in good agreement with the theoretical calculations, as shown in the table (2).

Table (1): The IR and ^{1}H- NMR data of the reagent and colored products (1-4).

				Chemical shifts of		
Compounds	**√ NH2(cm^{-1})**	**√C—N(cm^{-1})**	**√C=C-ring(cm-1)**	**H-ring**	**(-CH3)2**	**-NH_2**
Reagent	3378	1109	1510	7.2-6.7	4.4	3
Aniline	3419	1099	1509-1604	7.1-6.7	3.6	2.9
Benzidine	3412	1072	1503-1613	7.25-6.6	3.4	2.5
P-toluidine	3430	1100	1515-1636	7.2-6.9	3.4	2.5
P-anisidine	3436	1120	1513-1639	6.7-6.6	3.4	2.5

Table (2): elemental analysis of the reagent and colored products (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
Benzidine	43.059	4.282	9.415	41.88	4.06	6.98
P-toluidine	35.694	4.79	7.567	35.33	5.25	7.34
P-anisidine	34.215	4.633	7.255	34.95	4.81	7.46

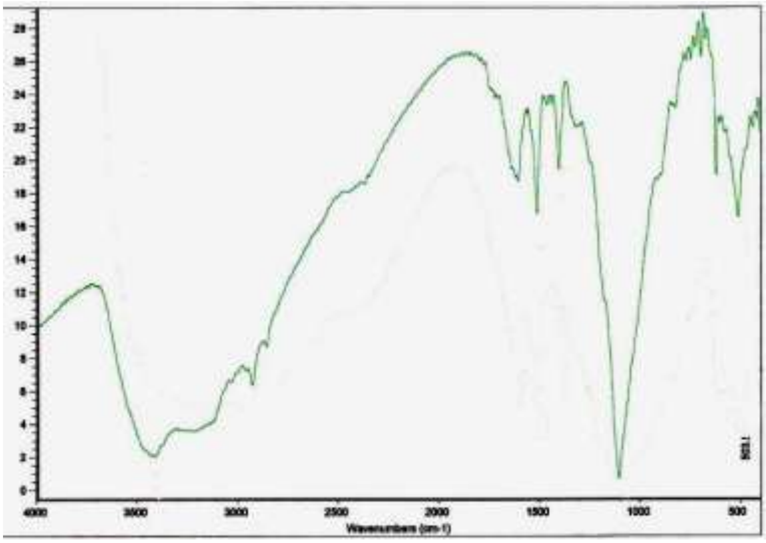


Figure (2): IR spectrum for the reagent 4-amino-N, N-dimethylaniline

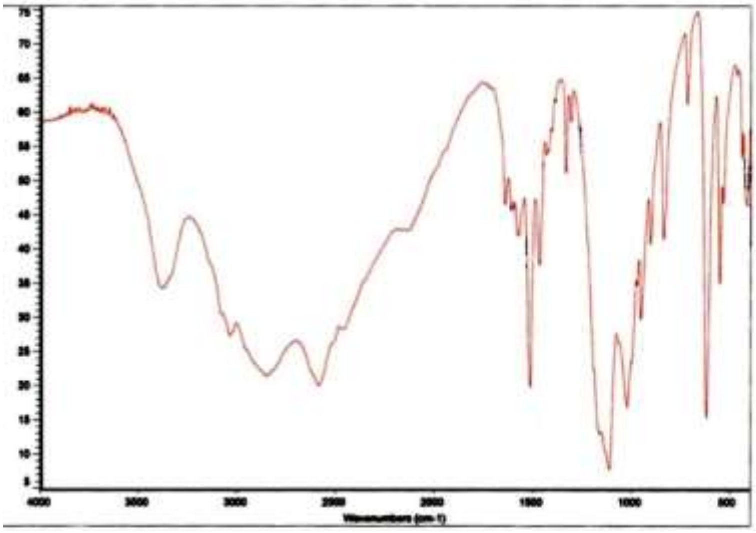


Figure (3): IR spectrum for the colored product of aniline with 4-amino-N, N-dimethylaniline

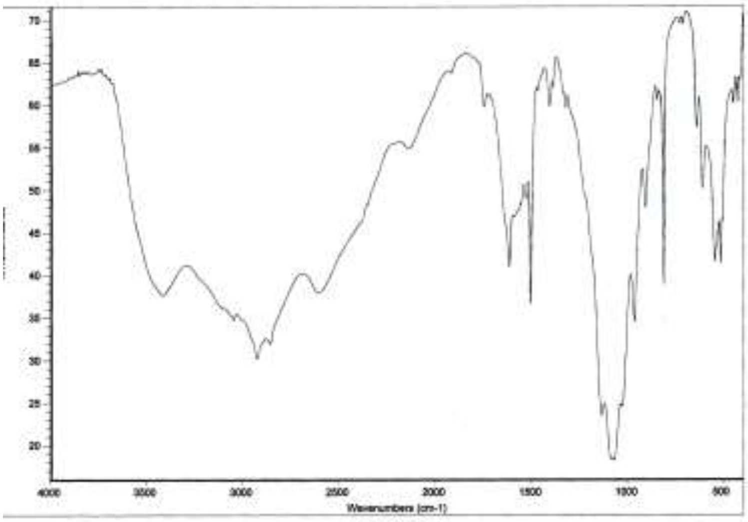


Figure (4): IR spectrum for the colored product of Benzidine with 4-amino-N, N-dimethylaniline

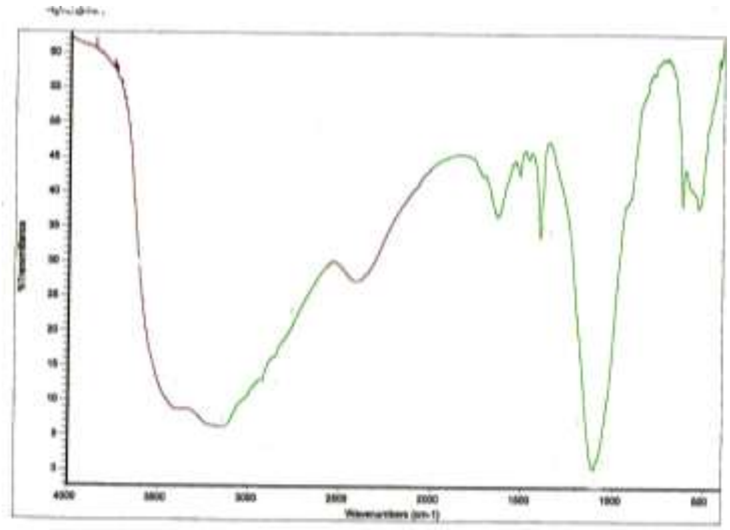


Figure (5): IR spectrum for the colored product of P-toluidine with 4-amino-N, N-dimethylaniline

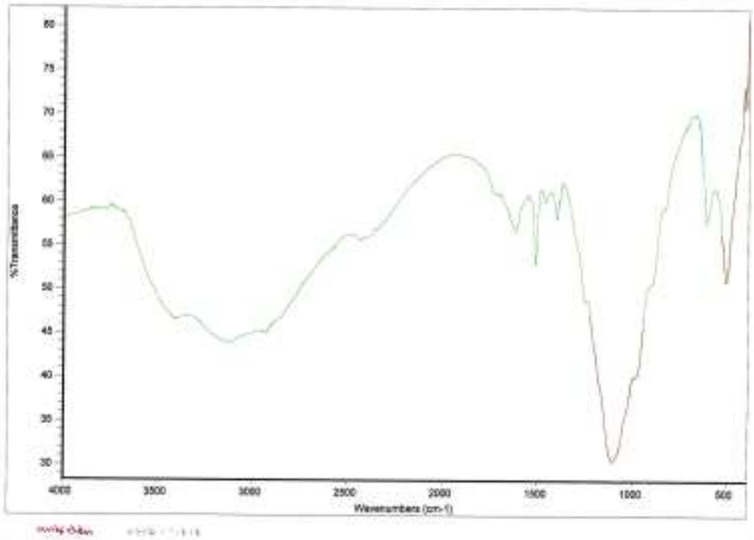


Figure (6: IR spectrum for the colored product of Anisidine with 4-amino-N, N-dimethylaniline

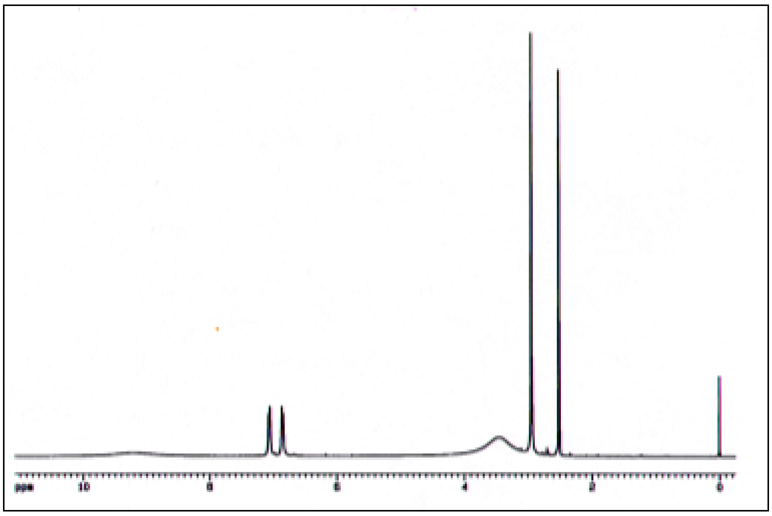


Figure (7): ^{1}H-NMR spectrum for the reagent (4-amino-N, N-dimethylaniline)

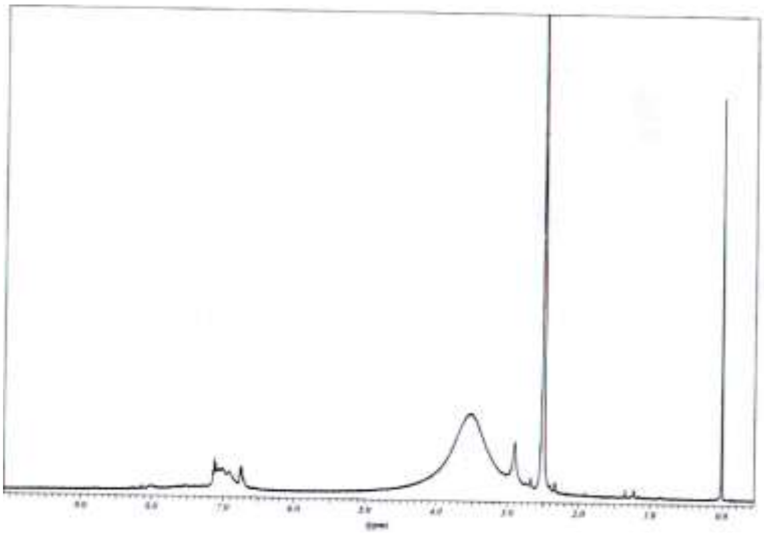


Figure (8): ^{1}H-NMR spectrum for the colored product of aniline with 4-amino-N, N-dimethylaniline

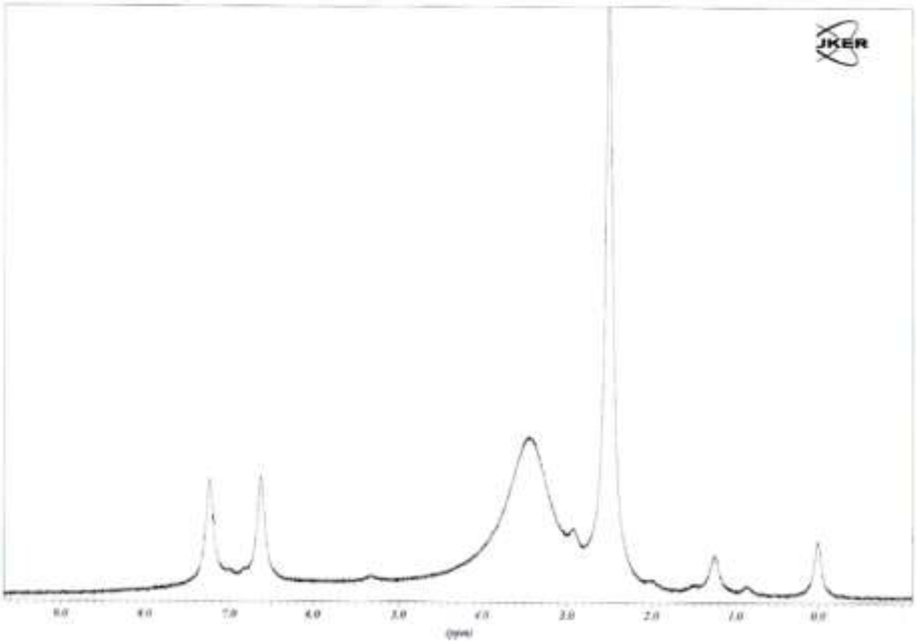


Figure (9): ^{1}H-NMR spectrum for the colored product of Benzidine with 4-amino-N, N-dimethylaniline

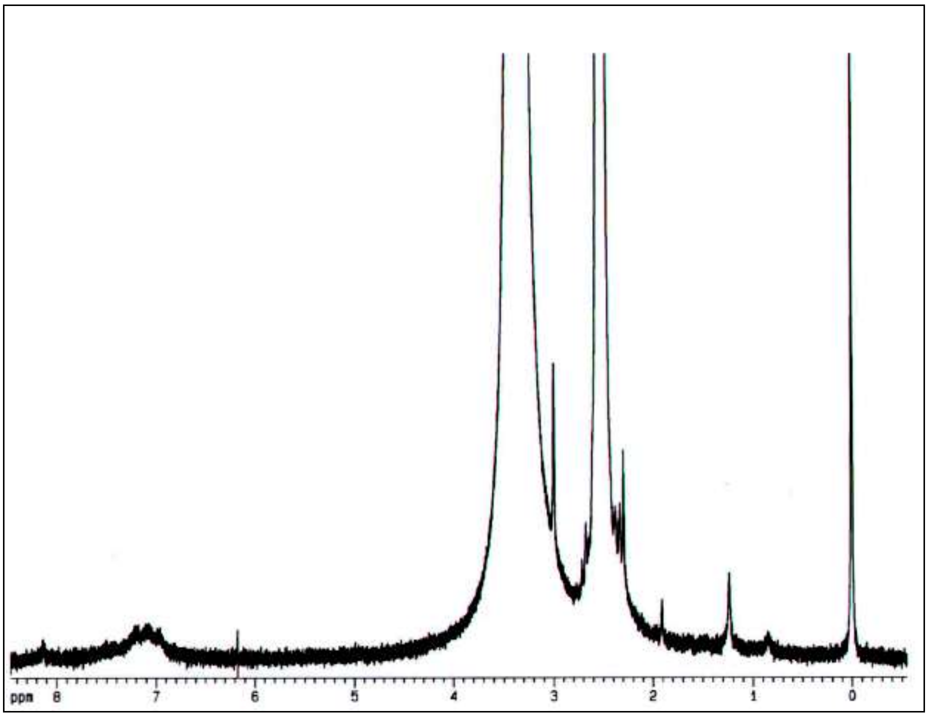


Figure (10): ^{1}H-NMR spectrum for the colored product of P-toluidine with 4-amino-N, N-dimethylaniline

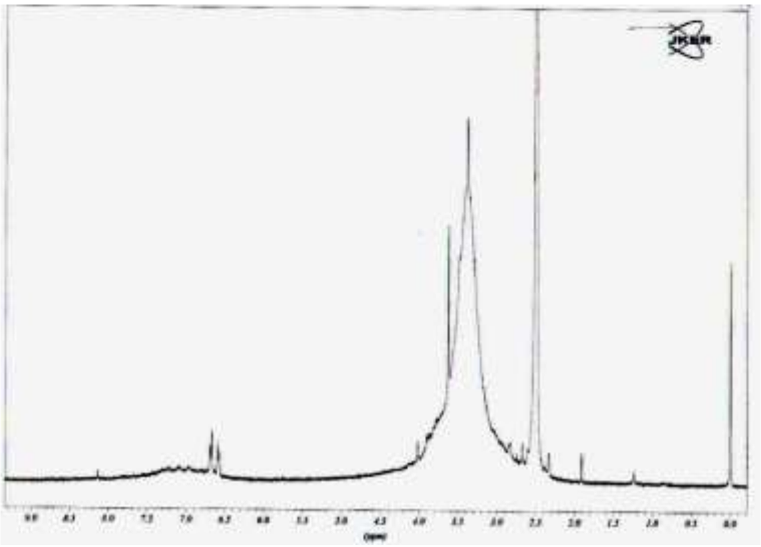


Figure (11): ^{1}H-NMR spectrum for the colored product of P-anisidine with 4-amino-N, N-dimethylaniline

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تحضير و دراسة نواتج الأكسدة المزدوجة لمجموعة انيلين و مشتقاته

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(تاريخ الاستلام: ٢٥ / ٦ / ٢٠٠٨ ---- تاريخ القبول: ٢٥ / ١٠ / ٢٠٠٩)

الملخص

ان تفاعل التكاثف لكل من aniline, benzidine , p-toluidine, p-anisidine مع 4-amino- N,N-dimethylaniline بوجود بوتاسيوم ثنائي كرومات في محيط حامضي يعطي نواتج غامقة اللون (احمر– بنفسجي)، وتم تشخيص النواتج بواسطة IR، $^{1}H^{-}$ NMR والتحليل العنصري الدقيق CHN.