STUDIES TOWARDS THE SYNTHESIS AND CHARACTERISATION OF DIPHENYLAMINE & ITS INTERACTIONS WITH VARIOUS METAL IONS

A Thesis

submitted in partial fulfillment of requirements for the award of the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

Under the Supervision of

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Place:Patiala

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Date:

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Candidate's Declaration

I hereby declare that the work, being presented in the dissertation entitled "**Studies towards the synthesis and characterization of diphenyl amine & its interaction with various metal ions**" in partial fulfillment of the requirements for the award of degree in Master of Science in Chemistry to School of Chemistry and Biochemistry, Thapar University, Patiala is an authentic record of my work. The work has been carried out under the supervision of Dr. Manmohan Chhibber, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala from January 2012 to July 2012. This is to certify that the work has not been submitted for the award of any other degree or certificate.

Nirmaljeet Kaur

Place: Patiala

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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Certificate

This is to certify that the dissertation entitled "**Studies towards the synthesis and characterization of diphenyl amine & its interaction with various metal ions**" being submitted by Ms. Nirmaljeet Kaur (Regd. No. 301002024) in partial fulfillment of the requirements for the award of degree in Master of Science in Chemistry to School of Chemistry and Biochemistry, Thapar University, Patiala is the work carried out under my supervision and that no part of this work has been submitted for award of any other degree or certificate.

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Table of Contents

STUDIES TOWARDS THE SYNTHESIS AND CHARACTERIZATION OF DIPHENYL AMINE AND ITS INTERACTION WITH VARIOUS METAL IONS

1. Introduction

Diphenylamines (DPA) are the compounds that consist of two aromatic groups and hydrogen attached to nitrogen atom. **Figure-1** below illustrates a generic structure of diphenylamines. DPAs are the group of compounds that find use in various industries due to their antioxidant properties. Antioxidants are the chemicals which inhibit oxidation, caused by several factors such as high temperature, presence of metals and mechanical stress, by reacting with the free radicals generated by oxidation thus preventing further oxidative decomposition of molecules and macromolecules.

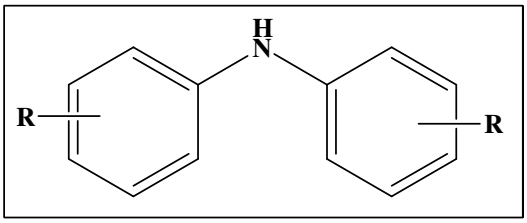


Figure -1: Generic structure of diphenylamines

These compounds are also useful as organic intermediates for manufacturing dyes, agrichemicals, and pharmaceutical products. In materials, DPAs find their use in heat-sensitive and pressure-sensitive compounds that are used in recording paper. Major applications of diphenyl amines are in their use as stabilizers in nitrocellulose-containing explosives, propellants, in the rubber and elastomer industry due to their antioxidative properties [14]. They are also used in the perfume industry as stabilizer, for the detection of DNA and to prevent the post-harvest deterioration of apple and pear crops. When alkylated, diphenylamines find its largest application as stabilizer for oils, greases and polymers.

Studies of DPA antioxidants by the dermal and oral routes of exposure indicate that these substances are relatively low in acute toxicity. Due to their low vapor pressure, inhalation toxicity is not expected to be an issue. Signs of systemic toxicity occur in test animals only at very high dose levels that are much greater than typical human exposure. However, some DPA antioxidants may cause skin irritation but are not known to be skin sensitizers. These chemicals are not expected to cause prolonged or significant eye irritation. These chemicals are not expected to be of concern with regard to reproductive and developmental toxicity.

Present work deals with the synthesis, characterization and spectrophotometric studies in the presence of different metal ions.

2. Literature

As discussed above, diphenyl amines find their use in diverse fields and are one of the very ancient compounds known. Due to their diverse use they are commercially important also. A lot of efforts have been put in to synthesize them and find their usefulness in various fields. The lines below describe the recent development in their synthesis starting from the earlier procedures. Recent applications of DPAs have also been discussed along.

2a. Synthesis

Ullmann-type coupling reactions between aryl halides and N-containing reactants **(Figure-2a)**, phenols, and other related nucleophilic agents are now a common method for the preparation of the corresponding aromatic compounds, which are important for the pharmaceutical and material sciences. However, a significant drawback of these reactions is the requirement of a high reaction temperature, which greatly limited its scope of application [1]. Another method for their synthesis is the Chapman rearrangement [2,] **(Figure-2b)** of phenylbenzimidates to benzoyldiphenylamines. This also required higher temperatures (250-300^{o}C). However, in late sixties the method was improved by showing the use of tetraethylene glycoldimethyl ether (tetraglyme) (b.p. 276^{o}C) or triethylene glycol (b.p. 285^{o}C) instead of more hazardous solvents like nitrobenzene [3]. But the high temperatures for both the reactions still limited the scope of its applications.

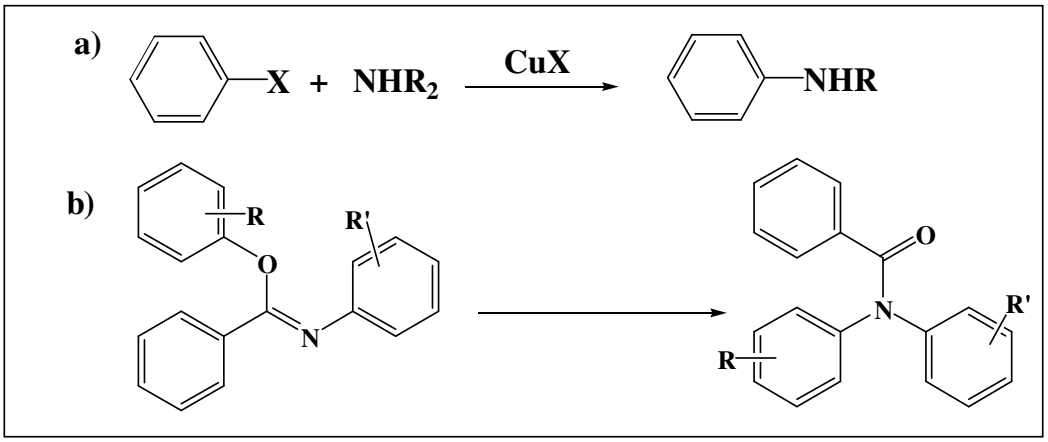


Figure-2: (a) Ullmann coupling reactions between aryl halides and N-containing reactants, **(b)** Chapman rearrangement of phenylbenzimidates to benzoyldiphenylamines

This shortcoming stimulated considerable efforts to develop relatively mild coupling conditions to synthesize diaryl products. This included use of special ligands such as N, N or N,O-bidentate compounds.

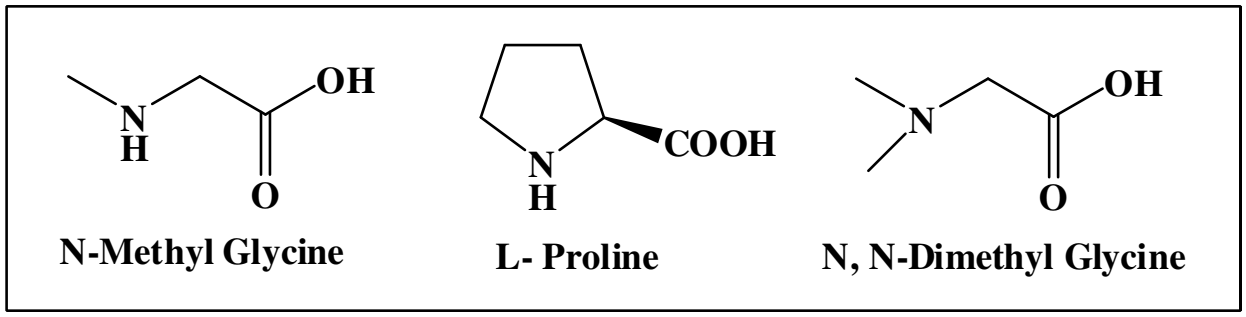


Figure-3: Secondary and tertiary amino acids used for coupling reactions by Dwai Ma et al.

Between 1999 and 2002, several groups reported that some bidentate compounds like 1,10-phenanthroline, 1,2-diamines,and 1,2-diols could serve as ligands to facilitate Ullmann-type aryl amination at relatively low temperatures. [4,5] Stimulated by these results, Dwai ma et. al. screened amino acids as possible ligands and found that both α and β- amino acids could promote the coupling reaction of aryl iodides and benzylamine [6,7]. However, only secondary and tertiary amino acids such as N-methylglycine, L-proline, and N, N-dimethylglycine **(Figure-3)** were selected for the reaction because they were found to be less reactive toward the coupling with aryl halides in competition with the reactants amines. [6]

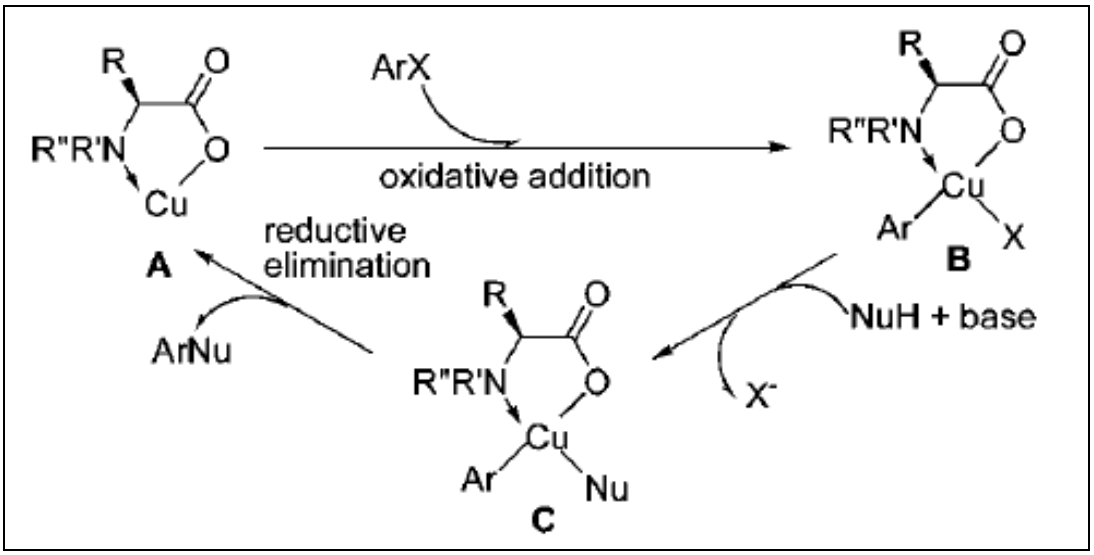


Figure-4: Catalytic cycle for amino acid promoted reactions for synthesis of diaryl amines.

The reactivity order of ligand efficiency was found to be N-methylglycine > L-proline > N,N-dimethylglycine because of difference in steric hindrance of the related copper chelates. The reaction has been proposed to proceed through an oxidative addition / reductive elimination pathway as depicted in **Figure-4**. The chelation of Cu (I) with an amino acid makes Cu (I) species more reactive toward the oxidative addition or stabilizes the oxidative addition intermediates B, thereby promoting the coupling reaction.

Stephen L. Buchwald, Hartwig, and others have impressively advanced the scope of C-N bond formation. [8,9] Modern and reliable methods for the Pd- and Cu catalyzed couplings of aryl, alkenyl, and alkynyl halides (and sulfonates, etc.) with various nitrogen nucleophiles have provided new tools for the large-scale manufacture of such molecules.

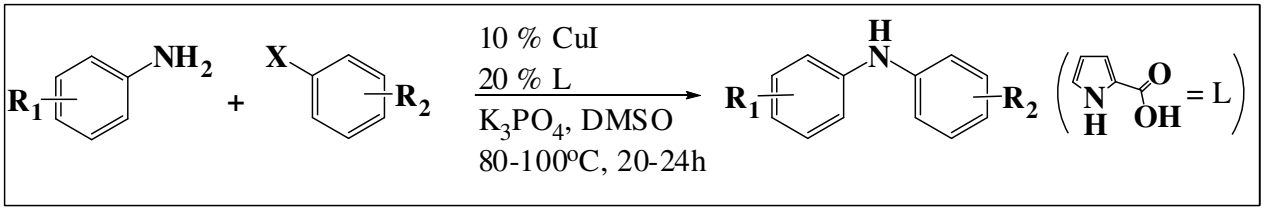


Figure-5: Pyrrole-2-carboxylic acid as Ligand for Diphenyl amine synthesis

Recently, Butchward et. al. have employed pyrrole 2-carboxylic acid as a ligand for the Cu-catalyzed monoarylation of anilines with aryl iodides and bromides [10]. They have shown that anilines and aryl halides possessing diverse electronic properties and useful functional groups were all tolerated **(Figure-5)**. Present work has employed the same methodology with slight modification for the synthesis of aromatic C-N bond. We have used aryl fluoride with aniline in presence of L-proline using CuI in catalytic amount.

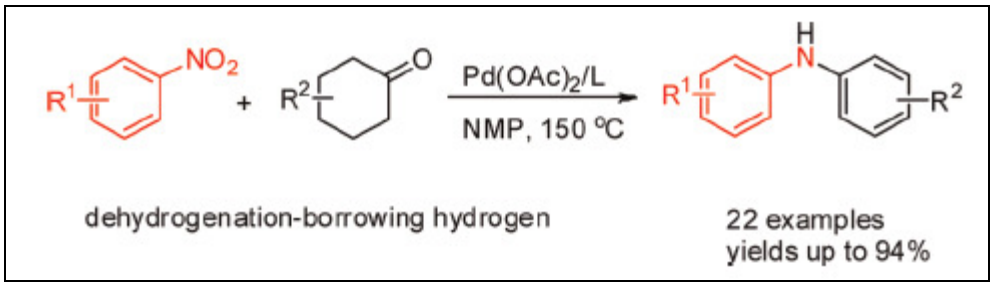


Figure-6: Cyclohexanone derivative used for the synthesis of diphenyl amines.

A very recent report has shown novel Pd-catalyzed direct arylation of nitroarenes with cyclohexanone derivatives using the dehydrogenation and borrowing hydrogen methodology

where cyclohexanone derivatives acted as both hydrogen donors and aryl sources with no external reducing reagent required **(Figure-6)** [11.] Various diarylamines were formed in good to excellent yields. The reaction showed very good selectivity, and secondary arylamines were formed as the sole products in all cases.

2b. Applications

N-Phenyl anthranilic acid, a common indicator used in redox titrations is a derivative of diphenyl amine. The indicator is used in the titration of iron with dichromate solution [12]. Diphenylamine is also a very sensitive indicator of the end point of the reaction between ferrous ion and vanadic acid [13].

Diarylamines (Ar_2NH) constitute the bulk of radical-trapping antioxidant (RTA) additives to petroleum-derived products because of their ability to slow hydrocarbon autoxidation through the following rate-controlling inhibition reactions [14].

$$Ar_2N\text{-}H + ROO^{\cdot} \longrightarrow Ar_2N^{\cdot} + RCOOH$$

Diphenylamines substituted at 4, 4'-positions with alkyl groups have N–H BDEs of 82 kcal/mol[2] in PhCl at 37°C [15]. Pratt et. al. showed that when diphenylamine is substituted with increasingly electron-donating groups at the 4 and 4'- positions, the N–H BDE is predictably weakened (e.g.,by 4.0 and 6.3 kcal/mol for alkoxy and dialkylamino groups,respectively) [16] thus increasing their radical scavenging activities. A recent study by the same group incorporated ring nitrogens into diphenylamines that proved excellent antioxidants at ambient temperatures where as compound A **(Figure-7)** is most effective as antioxidants at higher temperatures (>120 °C), such as those commonly attained by the lubricants of operating combustion engines [17].

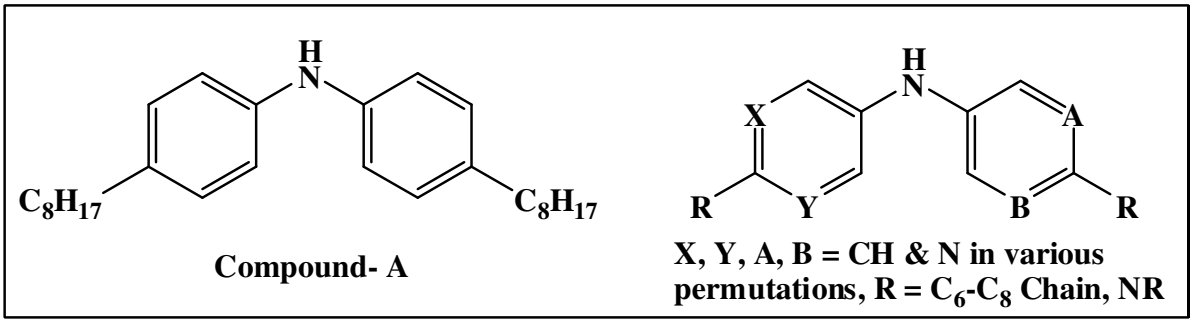


Figure-7: Commercially available compound-A available as high temperature antioxidant and its synthesized derivatives.

In a recent study, diphenylamine-vinyl conjugated polythiophene (DPAV-PT) polymer has been synthesized by the Stille coupling reaction. The polymer possesses good solubility in common organic solvents. The preliminary results indicate that DPAV-PT could be a good candidate for applications in polymer solar cell and organic field effect transistors. [18]

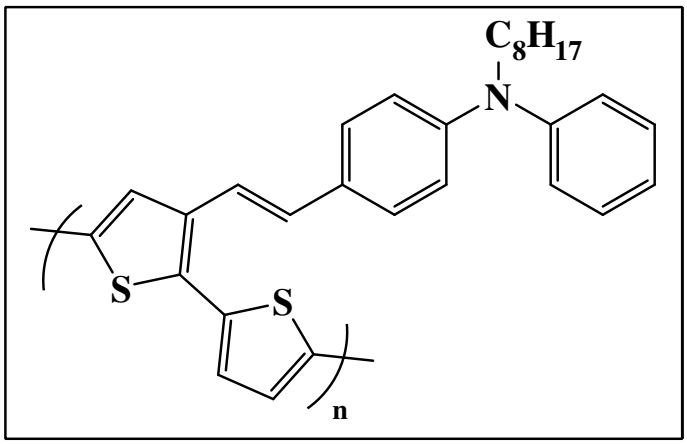


Figure-8: Chemical structure of DPAV-PT

Diphenylamine (DPA) has also been shown to enhance the ionic conductivity and long-term stability in poly(ethylene oxide) (PEO) in the presence of potassium iodide (KI) and titanium dioxide (TiO_2) nanoparticles having high surface area. DPA that has been used as a charge transport enhancer also enhances the interaction of the TiO_2 nanoparticle film. By reducing the sublimation of iodine it increases the device stability with 89% of the overall efficiency preserved even after 40 days [19].

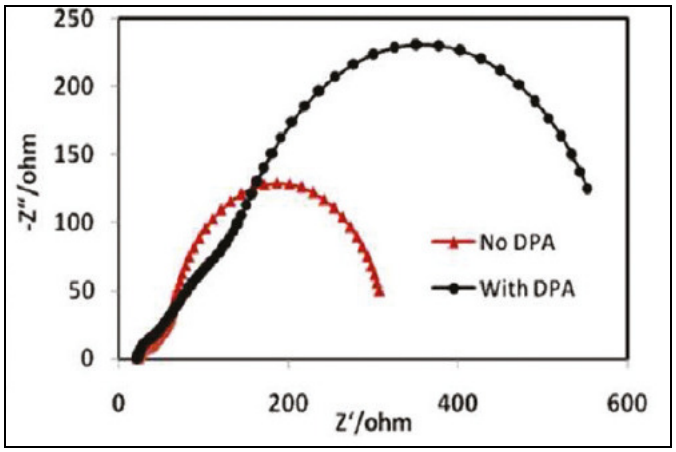


Figure-9: Enhanced ionic conductivity in the presence and absence of diphenyl amines.

Li et. al. developed an 2-adpa structure based co-polymer with potential to scavenge Hg^{2+} and Pb^{2+} metal ions in waste water [20].

Qian et. al made use of diphenyl amine moiety as potential metal ion binding site where diarylamino "NH" fragment was a potential deprotonation carrier. They designed and synthesized a 1,8-naphthalimide chromophore integrated with a 2-aminodiphenylamine (2-adpa) moiety to develop a Cu^{2+} specific colorimetric sensor. The "naked-eye" sensor had high selectivity and sensitivity for Cu^{2+} in a neutral aqueous solution, with an analytical detection limit (ADL) of 3.0 X 10^{-7} M [21].

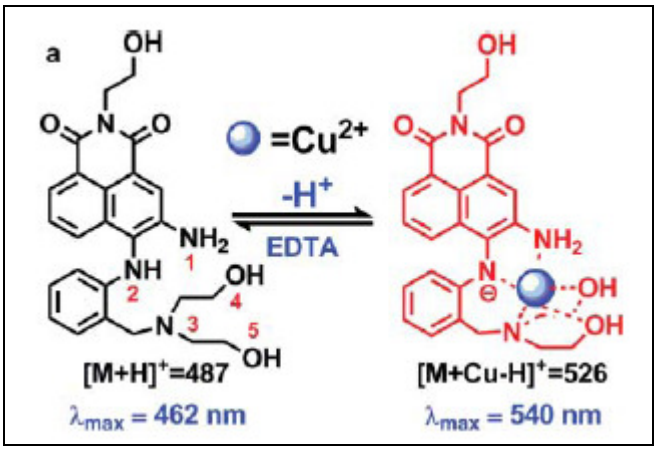


Figure-10: Deprotonation mechanism and coordination mode of 2-adpa based sensor.

Present work deals with the synthesis, characterization of a diphenyl amine and an attempt has been made to carry out spectroscopic studies in the presence of different metal ions.

3. Research Gap

Diphenyl amines find their use in diverse fields and are one of the very well-known. Due to their diverse use they are commercially available. A lot of efforts have been put in to synthesize them and find their usefulness in various fields. As discussed above, many new and convenient methods for their synthesis have been developed recently. Starting from Ullmann-type coupling the chemistry of diphenyl amines has come a long way to Buchwald- Hartwig synthesis.

Considering the ease of synthesis available not much science has been explored for the development of various materials like sensors, ionophores, catalysts and more competitive antioxidants.

4. Objectives

- To synthesize N-[2-(2-Nitro-phenylamino)-phenyl]-acetamide, diphenyl amine.

- To purify and characterize the compound and its various intermediates.

- To use all the synthesized compounds individually and in the presence of various metal ions (cations) and anions.

5. Materials and Experimental methods

All the reagents used were of LR grade and procured from Aldrich and S.D. Fine-Chem. Limited, Mumbai, India. All the solvents used for the synthesis and column chromatography were distilled before use. ^{1}H and ^{13}C NMR analysis was performed on BRUCKER ADVANCE 2 400MHz spectrophotometer from SAIF, Punjab University, and Chandigarh. All the UV-VIS spectroscopic studies were done in analytical grade solvents using Specord 205 UV-VIS spectrophotometer by Analytik jena using slit widths of 1.0 nm and quartz cuvettes.

N-(2-Nitro-phenyl)-acetamide (Compound-1) : 2-Nitro-aniline (2.6 m moles, 364 mg), acetic anhydride (0.023 m moles,2.4 ml), glacial acetic acid (0.04 m moles, 2.4 ml) and zinc dust (0.30 m moles, 20 mg) were taken in a 100ml round bottom flask and refluxed gently under anhydrous conditions for 10-15 minutes. The hot reaction mixture was poured with stirring into ice-cold water (40ml). Yellow precipitates formed were filtered and washed with water to remove excess of acid and acetic anhydride. TLC was done with pet ether: ethyl acetate (75:25) to check the purity of the product. The yield of the product was 53 %. Reaction was repeated many times to build up the product. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.7 (bs, 1H), 8.2 (d, 1H), 7.6 (t, 1H), 7.2 (t, 1H) 10.0 (s, 1H) 2.2 (s, 3H).

N-(2-Amino-phenyl)-acetamide (Compound-2): Compound-1 obtained above ((1.6 m moles, 636 mg), iron (5.3 m moles, 300 mg), iron sulphate (0.7 m moles, 200 mg), acetic acid (catalytic amount) and water (30ml) was taken in 100ml round bottom flask. The contents were sonicated to mix them properly. This was followed by refluxing for 8 hours. After TLC [pet ether : ethyl acetate (75:25)] monitoring confirmed the completion of the reaction, 20 ml ethyl acetate was poured from all sides and refluxing for half an hour to dissolve the compound.

Potassium hydroxide (10% aq) was added to reaction mixture to neutralize the acetic acid till a basic pH was achieved. Common salt was also added to make water dense and filtered the contents using a bed of celite. Silica column (pet ether: ethyl acetate) was used to separate the unreacted compound 1 from the product. The yield of the product was 66 %. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.7 (bs, 1H), 7.5-7.6 (m, 2H), 7.2-7.3 (m, 2H), 2.7 (s, 3H)

N-[2-(2-Nitro-phenylamino)-phenyl]-acetamide(Compound-3): Aromatic aniline (Compound-2) as prepared above (1.6 m moles, 250 mg), Cuprous iodide (0.16 m moles, 31.7 mg), proline (0.3 m moles, 38.6 mg), Potassium carbonate (3.3 m moles, 460 mg) and 1-fluoro,2-nitro benzene (0.24 m moles, 0.26 µl) were taken in dimethyl formamide (15ml) a 50 ml round bottom flask. The reaction mixture was stirred in an oil bath on magnetic stirrer and a temperature of 120^{o}C was maintained. Progress of the reaction was monitored with the help of TLC [pet ether: ethyl acetate (50: 50)]. After 13 hours, reaction mixture was taken out of oil bath dissolved in ethyl acetate (25ml). Washings with water were given to remove inorganic salts. After the completion of reaction, some water (approx. 3ml) was added to the reaction mixture to remove any unreacted K_2CO_3 and CuI. Salt was added to saturate excess water. Pure product was obtained with alumina column chromatography. The yield of the product was 28 %. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.2 (m, 1H), 7.8 (m, 1H), 7.7 (m, 2H), 7.5 (m, 1H), 7.2 (m, 1H), 7.1 (m, 1H), 6.9 (m, 1H), 2.4(s, 3H). **^{13}C NMR ($CDCl_3$):** δ 14.05, 109.0, 119.3, 122.9, 123.2, 126.0, 129.6, 131.0, 131.1, 134.5, 136.4, 142.6, 151.6.

UV-VIS Spectrophotometric studies: Compounds **1** (2.3 mg), **2** (2.8 mg) and **3** (4.2 mg) were dissolved in 5ml of distilled water each in separate volumetric flasks to get their 3.0 mM solution. A UV spectrum was observed for each of the compounds. **Table-1** below shows the λ_{max} and ε values for each of the compounds.

Table-1

S.No.	Compound	λ_{max} Value (nm)	ε Value
1.	Compound-1	230.0, 280.0	9352, 2786
2.	Compound-2	245.1, 275.0	6243, 5899
3.	Compound-3	245.4, 280.8	3176, 1626

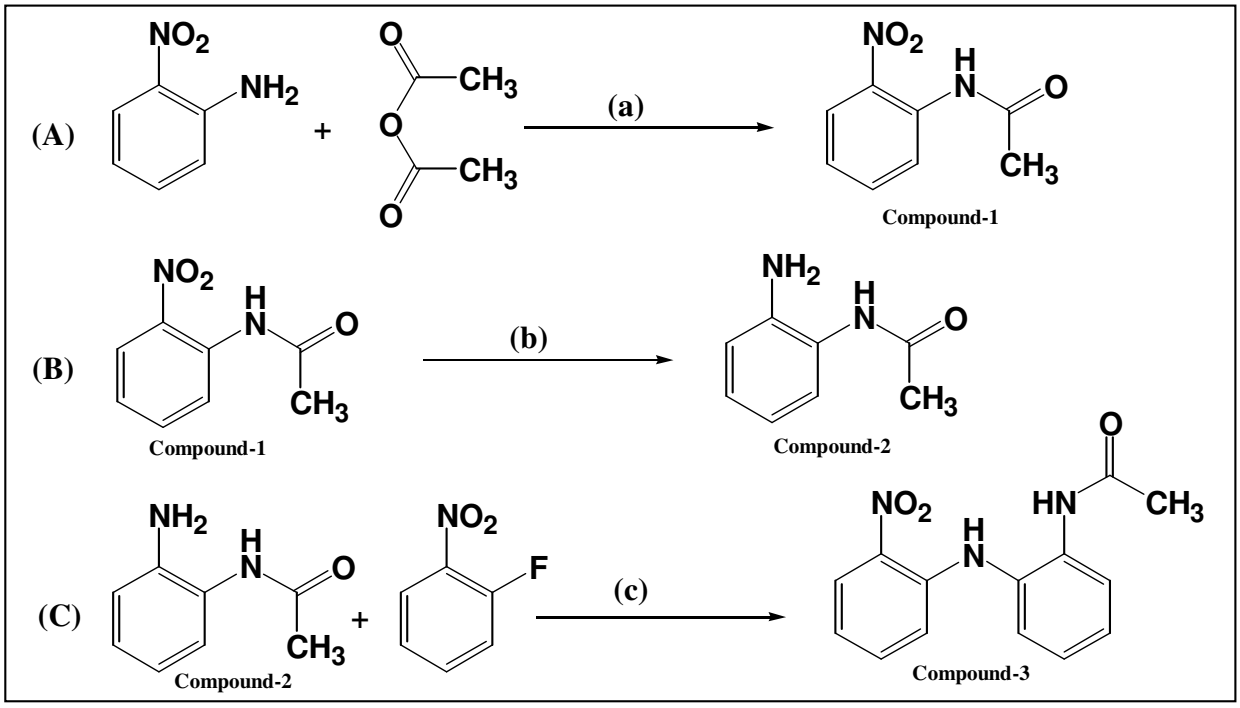
A 3.0 mM solution of Zinc (Zn^{2+}), Copper (Cu2+), Nickel (Ni^{2+}), Cadmium (Cd^{2+}) and Mercury (Hg^{2+}) were made from their respective stocks using their respective nitrates. The concentrations of Cobalt and Iron were 0.1mM and 1.0 mM respectively.

The absorption spectra were obtained by mixing organic compounds with above mentioned metal ions. For most of the metal ions, no change in UV-VIS spectra was observed except in case of iron where serial dilution was done to observe change in λ_{max} values.

6. Results and Discussion

The objective of this project work was to accomplish the synthesis of N-[2-(2-Nitro-phenylamino)-phenyl]-acetamide (Compound-3) and carry out their UV-Vis spectroscopic studies in presence of different metal ions. The synthesis was carried out in three steps using commonly available starting material 2-nito aniline. Each of the synthetic intermediates was characterized using ^{1}H, ^{13}C NMR.

2-Nitro aniline was converted into corresponding acetamide **(Compound-1, Scheme-1)** by refluxing it in the presence of metallic zinc, acetic anhydride and acetic acid. The yellow solid, was characterized using ^{1}H nmr and the spectra was in agreement with the proposed structure.

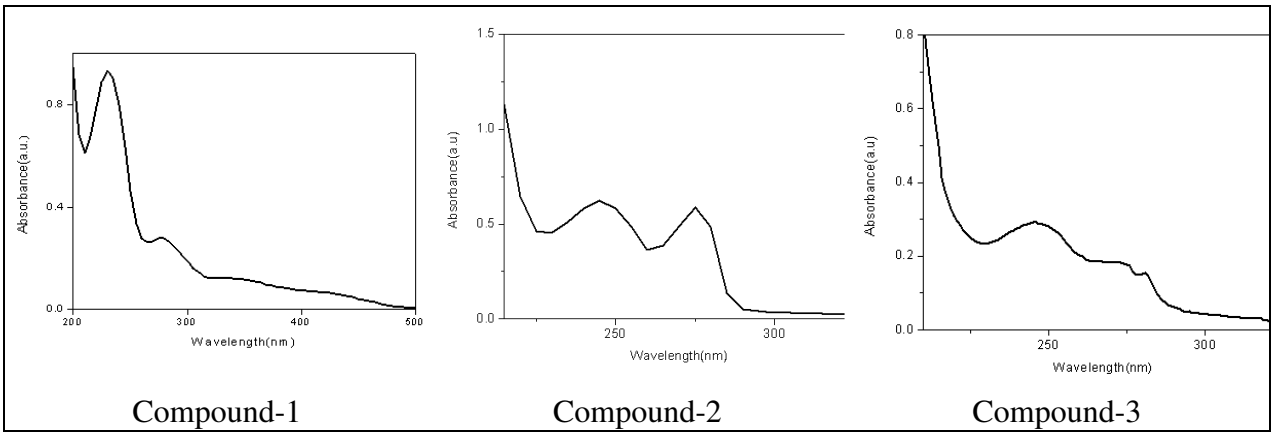


Scheme-1: (a) Zn dust, CH_3COOH, Reflux **(b)** Fe powder, $FeSO_4.7H_2O$, H_2O, Reflux, **(c)** K_2CO_3, CuI, Proline, DMF, $100^{O}C$, 24 hours.

Compound-1 obtained was reduced to corresponding amine using iron, iron sulphate and catalytic amount of acetic acid in water. The reaction mixture after refluxing for 8 hours gave corresponding amine. The black spot of ninhydrin on heating, after dipping it in its solution confirmed the presence of amino group in the molecule **(Compound-2, Scheme-1)**. The ^{1}H NMR integration equivalent to four aromatic protons and three protons corresponding to acetyl group were also observed corresponding to the structure.

For the synthesis of diphenyl amine recently, Butchward et. al. have employed pyrrole 2-carboxylic acid as a ligand for the Cu-catalyzed monoarylation of anilines with aryl iodides and bromides [Rt]. They have shown that anilines and aryl halides possessing diverse electronic properties and useful functional groups were all tolerated **(Figure-5)**. We employed the same methodology with slight modification for the synthesis of aromatic diphenyl amine. Therefore, Compound-2, ligand L-proline, copper iodide and base potassium carbonate were taken in DMF along with 2-nirofluoro benzene. The reaction mixture was refluxed for around 13 hours in an oil bath. The product obtained was initially characterized using TLC and later by ^{1}H and ^{13}C NMR analysis. Both the spectra were compatible with the proposed compound. **(Compound-3, Scheme-1).** Annexure-1 shows the ^{1}H and ^{13}C NMR spectra of N-[2-(2-Nitro-phenylamino)-phenyl]-acetamide.

All the synthesized compounds were subjected to UV-VIS Spectroscopic studies at 3.0 mM concentrations in water. The λ_{max} and ε values for all the compounds have been put into a **Table1**



Compound-1 Compound-2 Compound-3

Figure-11: UV-Vis spectroscopic studies with compounds **1**, **2** and **3**.

Studies for the interaction with anion (F^- ,Cl^- ,Br^- ,I^-) were also carried out for all the compounds but no change in the spectra was observed.

The absorbance of all the compounds was taken in the presence of 3.0m M solutions of Zinc (Zn^{2+}), Copper (Cu2+), Nickel (Ni^{2+}), Cadmium (Cd^{2+}) and Mercury (Hg^{2+}) and 0.1 mM concentrations of Co and 1.0m M solution of Iron (Fe^{3+}). No change in the UV-Vis absorption spectra were observed except in case of Fe^{3+} with **compound-2** where a blue shift was observed **(Figure-12a)** indicating the interaction of Fe^{3+} with N-(2-Amino-phenyl)-acetamide. Thus, it can be concluded that Fe $^{3+}$ interacts with N-(2-Amino-phenyl)-acetamide. A detailed investigation

was carried out with varying concentration of Fe^{3+} to observe change in spectra and attempt was made to determine the isosbestic points. Often one absorbing species, X, is converted to another absorbing species, Y, during the course of a chemical reaction. This transformation leads to a very obvious and characteristic behavior. If the spectra of pure X and pure Y cross each other at any wavelength, then every spectrum recorded during this chemical reaction will cross at the same point, called an isosbestic point. The observation of an isosbestic point during a chemical reaction is good evidence that only two principal species are present.

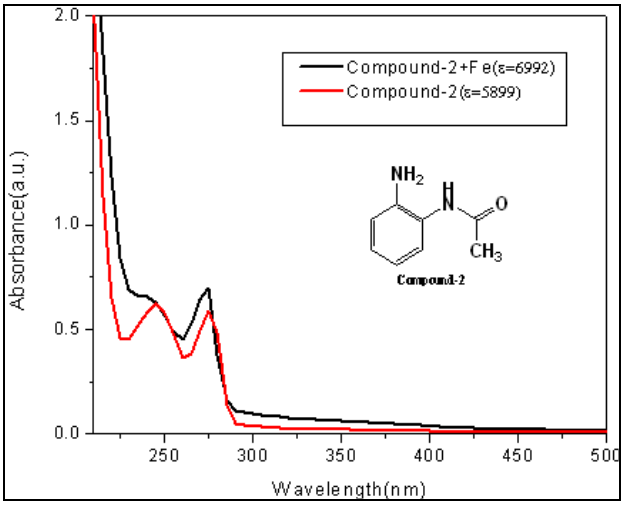


Figure-12a: Change in the UV-Vis absorbance of compound-2 with addition of Fe^{3+}.

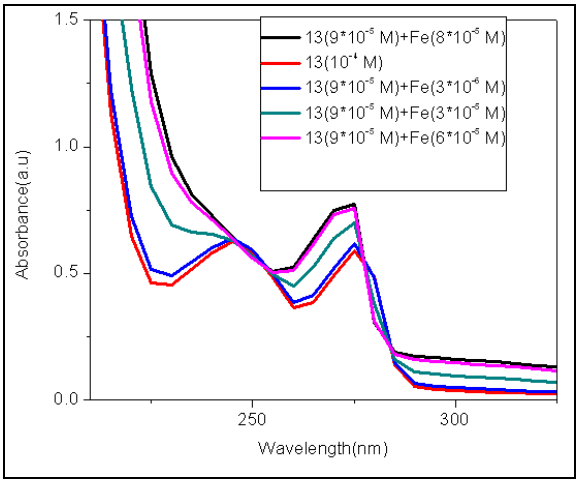


Figure-12a: Change in the UV-Vis absorbance of compound-2 (mentioned 13 in Fig. above) with increasing concentarion of Fe^{3+}.

Thus, the studies with increasing concentration of Fe^{3+} gave a visible change in UV-Vis spectra where **ε** value changed from 5899 (in absence of any Fe^{3+}) to 6992 (Fe^{3+} concentration of 8 x 10^{-5}M) **(Figure-12b)** . It has also been observed that on increasing the concentration of Fe^{3+} the UV-Vis band appearing at 245.1 nm starts disappearing suggesting the complex formation with Fe^{3+} species.

Thus, the preliminary studies with three compounds reveal that **compound-2** can be developed into a Fe^{3+} sensor by taking more variable concentrations of the iron. It remains to be investigated how the absorption spectra changes with change in pH, temperature and in the presence of other interfering ions.

7. Conclusion

Diphenyl amines (DPAs) are useful organic compounds that are used as intermediates for manufacturing dyes, agrichemicals, and pharmaceutical products. Major applications of diphenyl amines are in their use as stabilizers in oils, propellants, nitrocellulose-containing explosives, in the rubber and elastomer industry due to their antioxidative properties. They are also used in the perfume industry as stabilizer, for the detection of DNA and to prevent the post-harvest deterioration of apple and pear crops. When alkylated, diphenylamines find its largest application as stabilizer for oils, greases and polymers. In materials, DPAs find their use in heat-sensitive and pressure-sensitive compounds that are used in recording paper.

Present study was taken up to N-[2-(2-Nitro-phenylamino)-phenyl]-acetamide **(Compound-3)** and study its absorption spectra in presence of cations and anions in UV-Vis region. Compound-3 and its all the intermediates were studied in the presence of different metal ions viz. Zinc (Zn^{2+}), Copper (Cu2+), Nickel (Ni^{2+}), Cadmium (Cd^{2+}) and Mercury (Hg^{2+}) and 0.1 mM concentrations of Co and 1.0m M solution of Iron (Fe^{3+}). No change in the UV-Vis absorption spectra was observed except in case of Fe^{3+} with **compound-2** where a blue shift was observed. Studies were carried out with the compound in the varying concentration of Fe^{3+}.

Preliminary studies with three compounds reveal that **compound-2** can be developed into a Fe^{3+} sensor by taking more variable concentrations of the iron. It remains to be investigated how the absorption spectra changes with change in pH, temperature and in the presence of other interfering ions.

8. References

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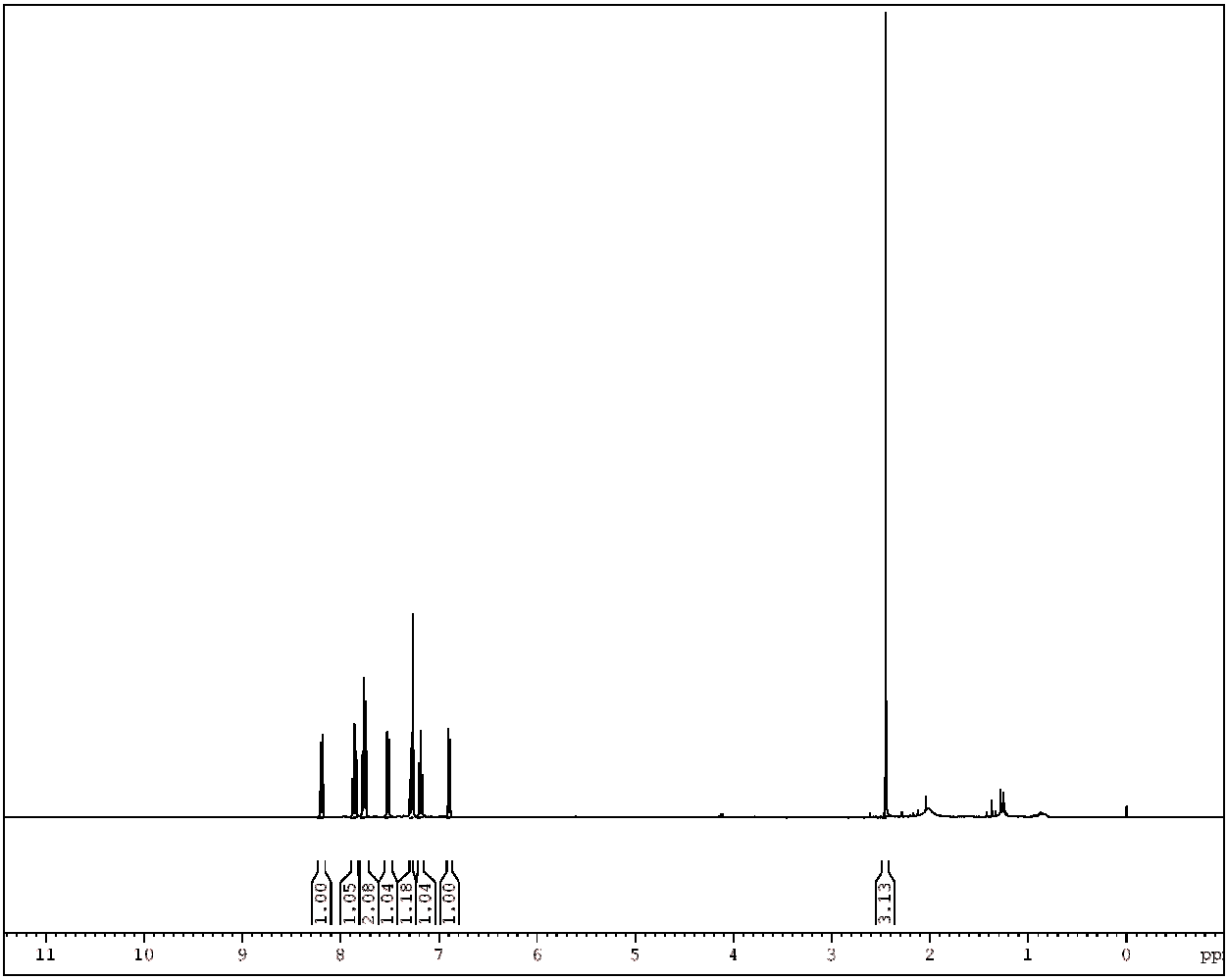
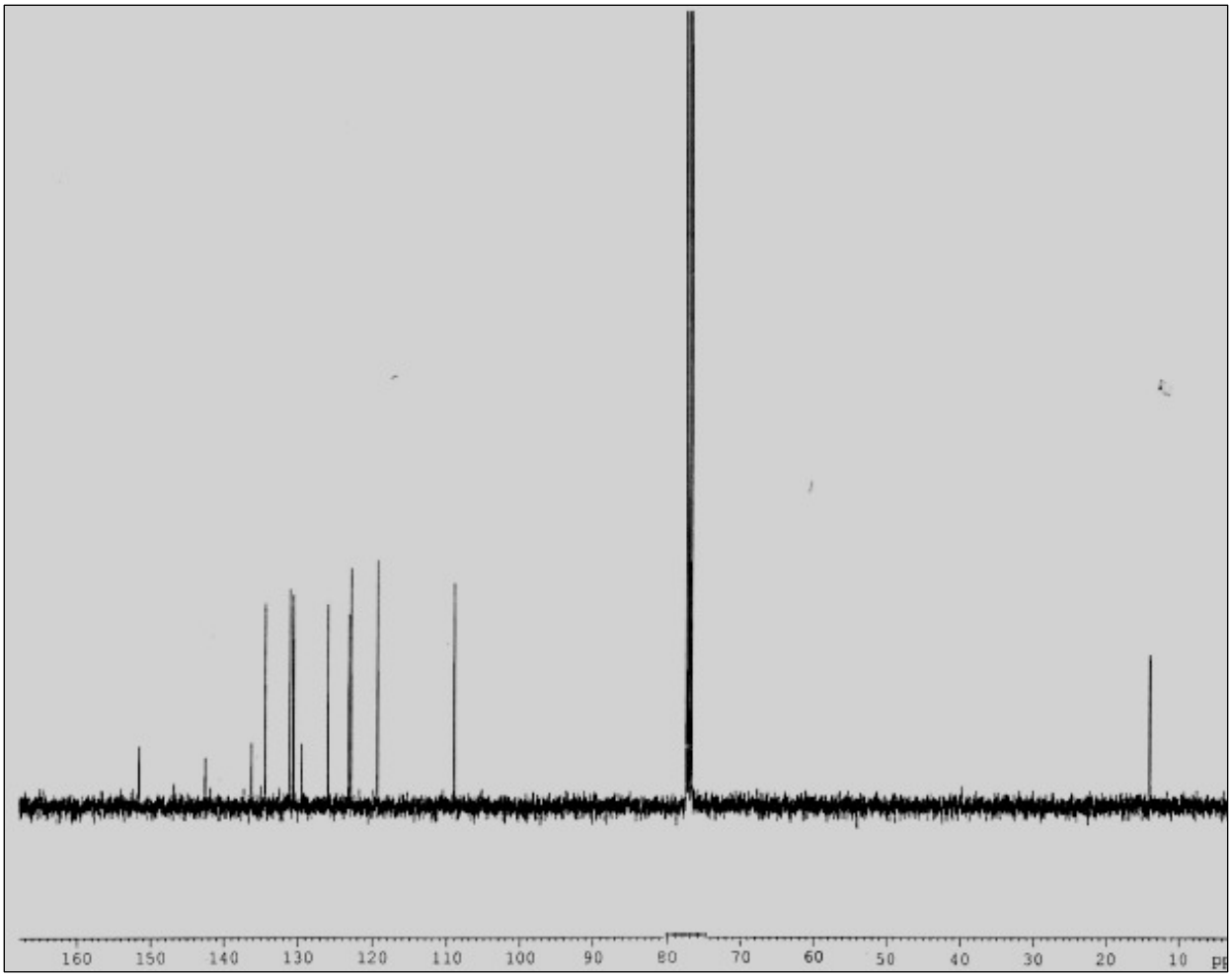
Annexure-1



^{1}H NMR Spectra of Compound-3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