CHAPTER III

SYNTHESIS OF LIGANDS
SYNTHESIS OF AZO DYES

All the ligands chosen in the present investigation are azo dyes which can be obtained by diazotising the corresponding aromatic primary amines and then coupling the diazo compound so obtained with specific phenolic compound.

Synthesis of azo dyes involves the following three steps:

(a) Diazotisation of amine.

(b) Coupling the diazo compound with phenolic compound.

(c) Isolation and purification of dye.

(a) **Diazotisation**:\n
There are several methods of preparing diazonium salts, but the most convenient preparative route is the action of nitrous acid on amines, known as diazotisation. Practically any aromatic amine can be converted into a diazo compound by this method. The reaction proceeds as:\n
\[
(\text{Ar NH}_3 ) X + \text{HNO}_2 = (\text{Ar N}_2) X + 2\text{H}_2\text{O}
\]

In practice, nitrous acid is replaced by a mixture of sodium nitrite and hydrochloric acid and the reaction is represented by the following equation:

\[
\text{Ar NH}_2 + \text{NaNO}_2 + 2\text{HCl} = (\text{ArN}_2)\text{Cl} + \text{NaCl} + 2\text{H}_2\text{O}
\]
There are a number of ways of diazotisation depending upon the nature of amine, viz.,
(i) Direct method\(^3\), (ii) Invert method also called as indirect method\(^4\), (iii) Diazotisation in concentrated acids\(^5\), (iv) Diazotisation in nitrous acid\(^6\), (v) Self diazotisation\(^7\), and (vi) Diazotisation with alkyl nitrites (Knoevenagel's method)\(^8\).

The direct method has been used here. The method consists in taking the amine in aqueous hydrochloric acid and then adding calculated amount of sodium nitrite. As the diazotisation is an exothermic reaction and diazonium salts are unstable to heat and light, it is usually carried out between a temperature 0 - 5\(^\circ\)C. attainable by efficient cooling and regulating the speed of mixing the principal agents.

Excess of mineral acid stabilises the diazonium salt and checks the condensation of diazo compound with undiazotised amine\(^9\). It should be noted, however, that the concentration of hydrochloric acid should not exceed 20%, as it reacts with nitrous acid to induce side reactions. The process of diazotisation completes within about twenty minutes. Negative substituents present in the amine increase the stability of diazo compound\(^10\). The slight excess of nitrous acid at the end of diazotisation process is normally immaterial in a technical coupling, but in laboratory and where there is a danger of nitrous acid reacting with the second component, it should be destroyed by adding a little urea.
(b) The coupling reaction:

Diazonium compounds can be regarded as strong electrophilic reagents and attack anionoid and nucleophilic centres such as ortho and para positions in a phenol or an aryl amine. Out of the two positions of high electron density, the para position is much more favoured. In case para position is occupied, coupling readily takes place in ortho position, but if both positions are occupied, the coupling does not take place or one of the substituents would be displaced. The meta position is never favoured. When in a phenolic compound, both these positions are free, excess of diazonium salt may result in the formation of a bisazo derivative. As in the present work, 5-sulphosalicylic acid is taken as phenolic residue, there is no possibility of any formation of bisazo derivative since the para position is occupied by sulphonic group. The coupling is expected exclusively in ortho position.

Although diazonium salts are, in general, unstable at the pH of coupling and are liable to undergo decomposition, a normal coupling reaction proceeds so rapidly at low temperature that it is complete before any noticeable decomposition of the diazo compound takes place. It is necessary to take alkali in slight excess to keep the phenolic compound in solution in form of its sodium salt, but a large excess of alkali slows down the coupling due to formation of an antidiazotate which lacks power
of coupling. Usually a pH range of 7 - 9 is found most suitable.

There is a deactivating effect of electronegative groups such as sulphonic, carboxyl, nitro and chloro, due to which the rate of coupling slows down to some extent.

Aqueous pyridine can facilitate the coupling reaction in cases where little or no coupling occurs in aqueous sodium hydroxide or sodium carbonate, though nothing is known about the role of this reagent. In one patent pyridine is suggested as 'acid binding agent' in the coupling of diazotised mononitro-c-aminophenol with 1-hydroxy-2-acylamido-4-alkyl benzenes. There are instances where coupling takes place to a very small extent even after prolonged agitation in aqueous alkaline solution of a phenol or maphthol, but in pyridine medium substantial yields have resulted.

The most important single factor responsible for the yield, is the pH of the reaction medium which must be kept within certain optimum limits for any pair of diazo and coupling compound. Working with phenolic compound, normally, neutral or slightly alkaline medium (pH 7-9) is most favourable and this has been controlled in the present work while carrying on the preparation of azo dyes.

(c) Isolation and purification of dyes:

Barium salt method was used here for isolation of dye after the coupling reaction. As the dye exists in the form
of its disodium salt, which is highly soluble, this method was preferred. The method has been used by Griess\textsuperscript{13} and a number of other workers\textsuperscript{14} while working with 4-hydroxy azo benzene-3-carboxylic acid- 4'-sulphonic acid.

The solution containing the disodium salt of dye was just heated to boiling and acidified with hydrochloric acid, and excess of a saturated solution of barium chloride was added. The strong acid sulphonic group reacts with barium chloride forming an insoluble acid barium salt of dye. On allowing the mixture to stand on a boiling water bath for some time and then cooling, the insoluble barium salt of the dye crystallises out.

The crystalline barium salt was filtered, washed thoroughly with distilled water and finally with alcohol. The solid was transferred to a beaker and again stirred well with wash liquid to ascertain complete washing. It was finally filtered, dried and weighed.

The barium salt of dye was now taken in boiling water and a calculated amount of sodium sulphate (as its hot solution) was gradually added with stirring. The barium salt of dye decomposed precipitating out barium sulphate. A slight excess of sodium sulphate was taken to ensure complete precipitation of barium sulphate which was later filtered off. Thus the monosodium salt of dye was obtained in solution with a trace of sodium sulphate as an impurity.
The solution was concentrated on a water bath to yield crystals of the dye. The crude product was recrystallised alternatively from water and then 60% alcohol. The final crystallisation was effected from 60% alcohol which yielded better crystals. A sintered glass crucible was used to avoid any chance of filter paper fluff contaminating the compound.

In these steps of isolation and crystallisation the organic impurities like unreacted amine, sulphosalicylic acid are removed. The isolation of dye in the form of its insoluble barium salt removes practically any unreacted amine. The soluble sulphosalicylic acid is also washed off here. The inorganic impurities like barium chloride and sodium sulphate, being highly soluble in water are removed during repeated washings and crystallisations.

The compound was dried in an air oven at 110°C. for about six hours and then left in a vacuum desiccator overnight to ensure a perfectly dry sample.

**PRACTICAL PROCEDURE:**

All weighings were made just before the start of the preparation.

(1) Phenyl azo 5-sodiosulphosalicylic acid (unsubstituted dye):

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{OH} & \quad \text{COOH} \\
\text{SO}_3\text{Na}
\end{align*}
\]
18 ml. of aniline (0.2 M) was taken in 50 ml. of hydrochloric acid in a 500 ml. beaker. The beaker was surrounded with freezing mixture. Some crushed ice made from distilled water was added to effect internal cooling as well as dilution of acid. The temperature was maintained well below 5°C. throughout by external as well as internal cooling.

13.8 g of sodium nitrite (0.2 M), dissolved in 20 ml. of water was run in slowly with whisk stirring. When the addition was complete the contents of the beaker were allowed to stand for about 15 minutes with occasional stirring. The excess of nitrous acid was ensured by starch-iodide paper.

50.8 g (0.2 M) of 5-sulphosalicylic acid was taken in another beaker and dissolved in 25 g of sodium hydroxide in 100 ml. of water. The resulting solution was cooled in ice as before. To the well cooled solution of 5-sulphosalicylic acid, was added well stirred diazo salt and the temperature was never allowed to rise above 5°C. After the addition was complete, the stirring was continued for about 5 minutes and then the beaker was left in the ice box for six hours, and then at laboratory temperature overnight. The dye was then isolated as its barium salt and purified as described earlier in this chapter.

There was no untoward development of colour or any foaming which indicated smooth coupling. The yield was fairly good but losses occurred in large quantities in a number of crystallisations in ensuring a pure dye. The preparation was repeated
to get enough yield of the pure dye.

(ii) p-methyl phenyl azo -5-sodiosulphosalicylic acid :
      (Methyl dye).

\[
\text{CH}_3\text{N} = \text{N} - \text{OH} - \text{COOH} - \text{SO}_3\text{Na}
\]

21.4 g (0.2 M) of p-toludine was diazotised as described above and coupled with 50.8 g (0.2 M) of 5-sulphosalicylic acid, using the same practical procedure as in case of unsubstituted dye.

(iii) p-methoxy phenyl azo-5-sodiosulphosalicylic acid :
      (Methoxy dye).

\[
\text{CH}_3\text{O} \text{N} = \text{N} - \text{OH} - \text{COOH} - \text{SO}_3\text{Na}
\]

24.6 g (0.2 M) of p-anisidine was diazotised and coupled with 50.8 g (0.2M) of 5-sulphosalicylic acid. The method was exactly similar to that in case of unsubstituted dye.

(iv) p-chloro phenyl azo-5-sodiosulphosalicylic acid :
      (Chloro dye).

\[
\text{Cl} \text{N} = \text{N} - \text{OH} - \text{COOH} - \text{SO}_3\text{Na}
\]

25.5 g (0.2 M) of p-chloroaniline was diazotised and coupled with 50.8 g (0.2 M) of 5-sulphosalicylic acid, employing the same procedure as in case of unsubstituted compound.

In all the cases the coupling was smooth. The preparations were repeated to obtain enough yield of the pure dye.
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