

Review in Azo Compounds and its Biological Activity

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Abstract

In this review paper, we talk about Dyes are used to give colors to substances, especially fabrics. Chromophores, functional groups that absorb light, give color to these dyes. The most common chromophores are azo, nitro, and carbonyl groups. Auxochromes, functional groups that increase the intensity of the color, are also important parts of dyes. The most common chromophores are hydroxyl, amino, sulfonate, and carboxylate groups. Azo dyes have a nitrogen to nitrogen double bond as their chromophore. These dyes are created by taking a diazonium salt and adding it to a strongly activated aromatic system.

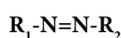
Keywords: Azo; Dyes; Coupling; Auxochrome; Chromophore

Azo Compounds

The history of dyeing can be divided into two great periods, the "pre-aniline," extending to 1856 and the "post-aniline" period. The former was characterized by a rather limited range of colors that were based on dye-producing animals and plants. The main vegetable dyes available were extracted from madder root (Asia and Europe), producing a brilliant red and leaves of the indigo plant (India), yielding the blue dye still used today in jeans. Among the most important animal based dyes is the famous and expensive "Tyrian Purple" which was obtained from the small shellfish nurez. We have the ancients' word that this dye was unbelievably beautiful, but

evidence taken from ancient samples prove that it ranges through a rather uninspiring series of reds and purples. After seeing it, we wish that Homer had written about some of today's inexpensive coal-tar purples and reds. A far more beautiful natural color was introduced to Europe from Mexico in 1518, the brilliant scarlet dye cochineal, which had been produced from tiny lice which infest certain types of cactus [1-6].

- Azo compounds contain the $-N=N-$ group:



• In aromatic azo compounds, the R groups are arene rings; the structures of these are more stable than if the R groups are alkyl groups.

• This is because the $-N=N-$ group becomes part of an extended delocalised system involving the arene groups.

• The aromatic azo groups are highly coloured and are often used as dyes.

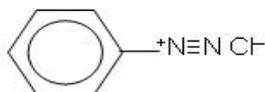
• Aromatic azo compounds are formed by a coupling reaction between a diazonium salt and a coupling agent.

Diazonium Salts

• The diazonium salts are very unstable; the only relatively stable diazonium salts are the aromatic ones, and these are not particularly stable [7].

• This is because the presence of the benzene ring with its high electron density stabilises the $\pm N \equiv N$ group.

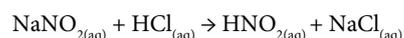
- Benzenediazonium chloride is an example of a diazonium salt:



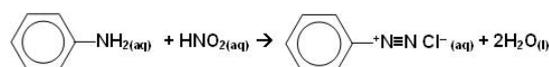
• In aqueous solution, Benzenediazonium chloride decomposes above temperatures of 5°C and the solid compound is explosive; for this reason, diazonium salts are prepared in ice-cold solutions and are used immediately.

• They are synthesised in a diazotisation reaction- a cold solution of sodium nitrate is added to a solution of arylamine in concentrated acid (below 5°C).

• The acid firstly reacts with the sodium nitrate to form an unstable nitrous acid (nitric(iii)acid):



- The nitrous acid then reacts with the arylamine:



Diazo Coupling Reactions

• In a diazo coupling reaction, the diazonium salt reacts with another arene (the coupling agent) [8].

• The diazonium salt acts as an electrophile, reacting with the benzene ring of the coupling agent.

• When the ice-cold solution of the diazonium salt is added to a solution containing the coupling agent, a coloured precipitate of an azo compound is formed; many of these compounds are dyes.

• The coupling agent always reacts in the two or four position of the benzene ring (where one position is the functional group).

• The colour of the compound formed depends on the coupling agent that is being reacted with diazonium salt.

Coupling with Phenols

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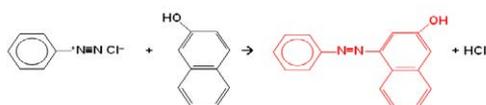
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• When the diazonium salt is reacted with a phenol, a yellow/orange azo compound is formed:

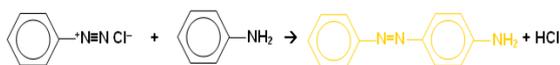


• With an alkaline solution of naphthalen-2-ol, a red azo compound is formed:



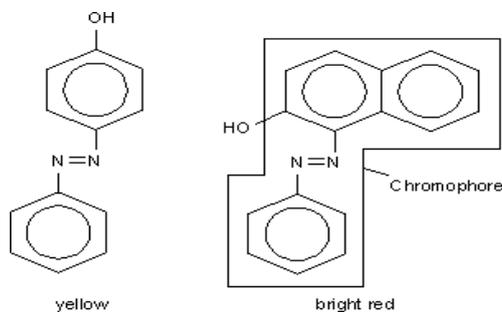
Coupling with Amines

• A yellow dye is often formed when a diazonium salt is reacted with arylamines:



• Many different azo compounds can be formed by coupling different diazonium salts with

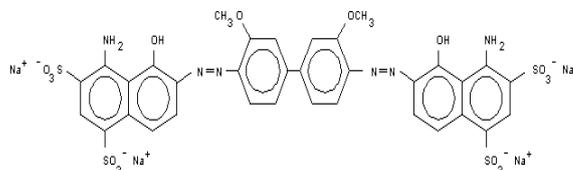
• Coupling of diazonium salts with phenols yields azocompounds, containing the azo group, -N=N-. For example, an alkaline solution of phenol (the coupling agent) reacts with benzene diazonium chloride (an electrophile) to form a *yellow* azo-dye. Coupled with naphthalen-2-ol a *bright red* precipitate is formed [9-11].



• These particular dyes are of little practical value owing to their only slight solubility in water. However, azo-dyes containing one or more sulphonic acid groups are much more soluble and of considerable commercial importance in the dyestuffs industry [12-15].

• In azo compounds the -N=N- group is part of an extended delocalised electron system involving the aromatic rings, called a chromophore. The quantised molecular electronic energy levels are closer together in such delocalised systems and light from the visible region of the electromagnetic spectrum is absorbed (DE) when electrons are promoted from lower to higher levels. The azo compound then appears a colour corresponding to the unabsorbed visible light. Also, groups such as -OH and -NH₂ are often attached to chromophores (also forming part of the extended delocalised electron system, so changing the DE values) to modify the colours of the molecules. Azo-dyes bind to fabrics in different ways. For cotton, many are insoluble and become trapped in the fibres. Others, called direct dyes, become attached to the fibres by hydrogen bonding and instantaneous dipole-induced dipole intermolecular bonding. Because intermolecular bonding is much weaker than covalent bonding, the dye molecules must be long and straight so that they can align closely with the cellulose fibres of cotton

giving more opportunities for intermolecular attractions [16,17]. The structure of the dye Direct Blue 1 is illustrated below:



Diazonium Salts

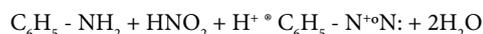
• Both aliphatic and aromatic primary amines can form diazonium salts. They do this by reacting with Nitric(III) acid (nitrous acid), HNO₂, at a temperature of 0-5°C.

• Owing to the instability of nitric(III) acid, it is always generated during a reaction, usually by the action of dilute sulphuric(VI) acid or hydrochloric acid on sodium nitrate(III) (sodium nitrite), NaNO₂. The acid used to generate nitric(III) acid provides the anion of the diazonium salt.



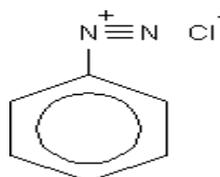
• However, alkyl diazonium salts are extremely unstable and always decompose to evolve the colourless unreactive nitrogen gas, amongst other products.

• The diazoniumcations of aromatic diazonium salts are somewhat more stable than their aliphatic counterparts. With phenylamine the benzene diazonium ion is formed:

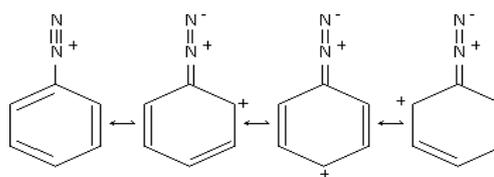


• Although benzene diazonium salts can be isolated in the crystalline form, they are usually retained in solution and used immediately as they decompose on standing even in the cold. In the solid state the salts are explosive and can be easily detonated by a slight shock or on mild warming.

• A structure for benzene diazonium chloride is shown below:



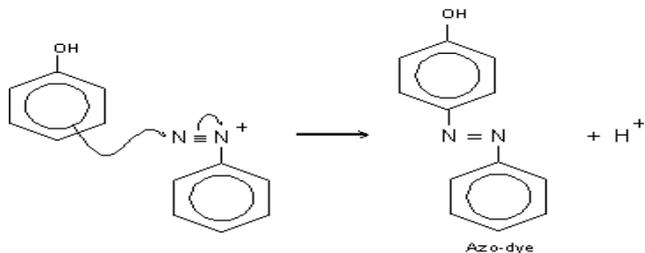
• The greater stability of the benzene diazoniumcation compared with the alkyl diazoniumcation is attributed to the diazo group being part of the delocalised system with the benzene ring and so the way in which the positive charge is distributed about the ring.



Azo-dyes - Coupling Reactions

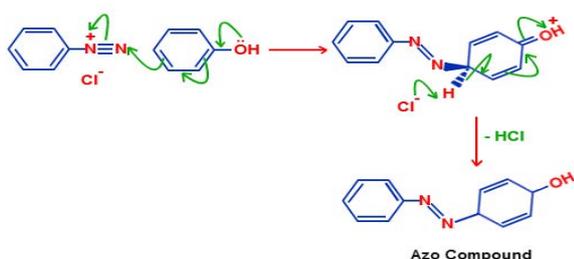
• In practice, a solution of a benzene diazonium salt is added to an alkaline solution of a phenol (or aromatic amine, such as phenylamine). The benzene diazoniumcation behaves as an electrophile, but it is a

weak electrophile and so the aromatic ring which it attacks must have attached to it an activating group such as -OH or -NH₂. An electrophilic substitution reaction occurs to form an azo-dye.



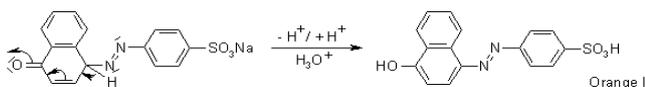
- The electrophile chlorine activates the reaction and electrophilic substitution takes place on phenol.
- Substitution reaction takes place always in para position except when the position is already occupied.

The mechanism for p-mitrobenzenediazoniumtetrafluoroborate in azo coupling with benzene or nitrobenzene.

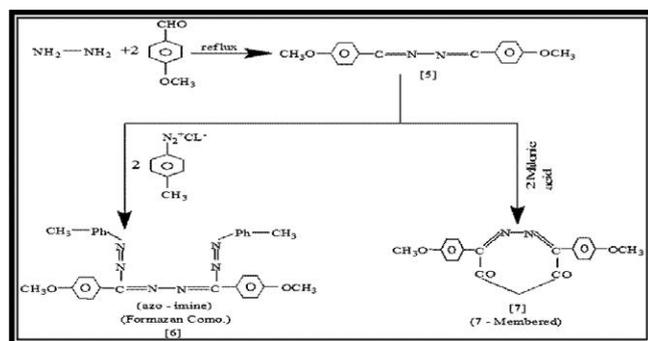


Aromatic diazonium ions acts as electrophiles in coupling reactions with activated aromatics such as anilines or phenols. The substitution normally occurs at the para position, except when this position is already occupied, in which case ortho position is favoured. The pH of solution is quite important; it must be mildly acidic or neutral, since no reaction takes place if the pH is too low [7,8].

Mechanism of Azo Coupling

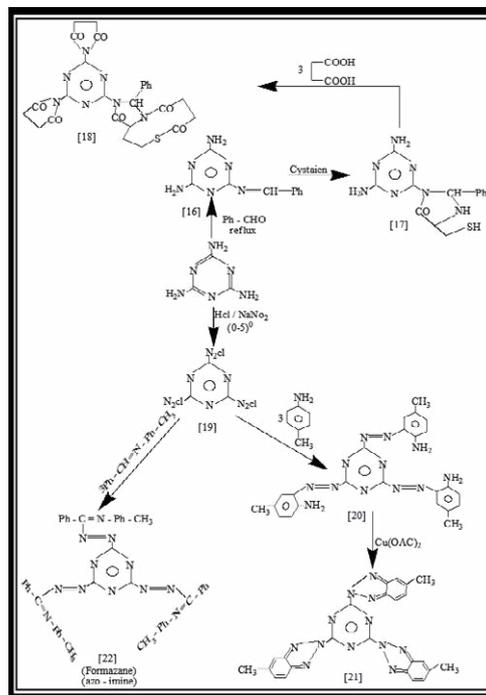


Dr. Nagham synthesized many azo groups linked with schiff base to produce various membered rings and formazane compounds [9].

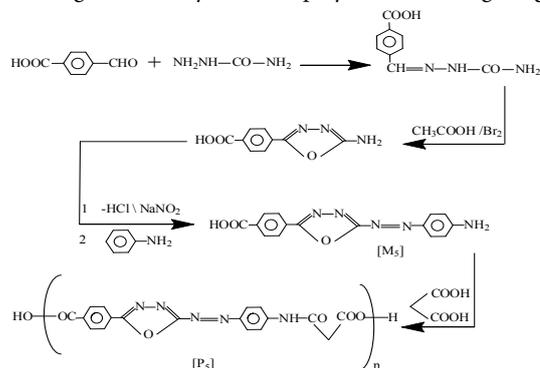


Dr. Nagham synthesized azo groups linked with schiff base to

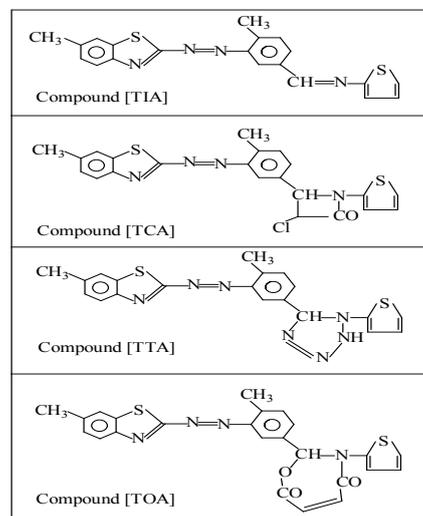
produce formazane compounds from melamine compound [10].



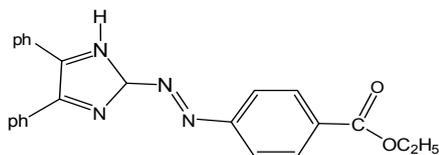
Dr. Nagham, et al. synthesized polymer containing azo groups [11].



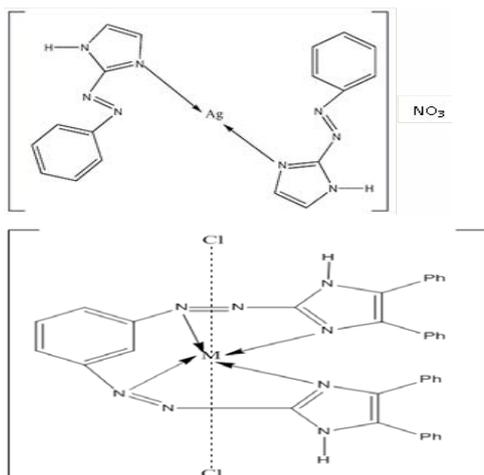
Dr. Nagham et al. synthesized various membered rings containing azo groups.



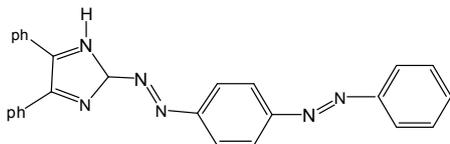
Dr. Matelf et al. synthesized imidazole rings containing azo groups.



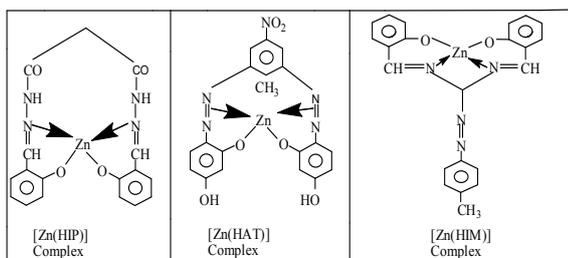
Dr. Hanser et al. synthesized imidazole azo complexes.



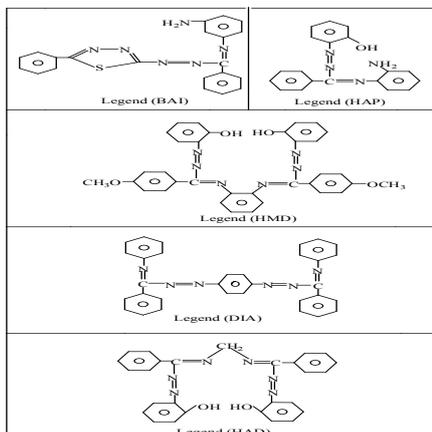
James prepared imidazole azo antibacterial and antifungal.



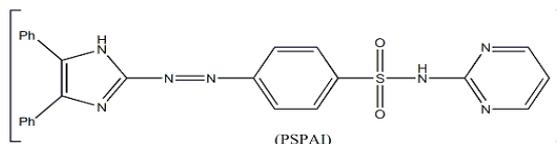
Alaa et al. prepared macroazo ligands.



Dr. Nagham Aljamali synthesized formazane compounds containing azo groups linked with imine group.



Some azo compounds used as drugs like sulphadiazine derivatives.



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