PART I

GENERAL INTRODUCTION
The fascination for colour of man since time immemorial is evident from the still undiminished coloured representations on walls of dwellings of early cave men. This visual aesthetics persisted through ancient Indian, Chinese, Egyptian, Greek and Roman civilisations right up to the present time. The origin of colouring matters is lost in antiquity. Until the middle of the last century, colouring matters of natural origin were the only ones used in technical practice. Brazilwood, logwood, kermes, lac dye, cochineal, Persian berries and madder root were the important sources of natural colours. The active constituents of these natural dyes were fixed on the substrate (usually fabric) with crude inorganic materials such as clay, ash, slate dust, powdered brick and various gums, all with the objective of achieving the best shade, intensity and fastness. These insoluble combinations prepared on the substrates were known as lakes (from sanskrit 'laksha'). Gradually it came to be recognised that the results obtained could be improved by replacing the crude inorganic materials by alum and other metal salts of aluminium, iron, chromium or tin, and mordant dyeing was born. (mordant from latin 'mordere' means to bite or corrode).
It can be seen that, although the active constituents of the various natural dyestuffs differed widely in chemical structure, all contained a metal chelating system. Complex formation with the metal ion present in the mordant was responsible for the deep colour and excellent fastness properties of the dyeings. As methods of dyeing became better understood, the foundation for the development of modern metal complex dyestuffs was firmly established. Now it is well recognised that coordination phenomena are involved even in the crudest form of mordant dyeing.

The production of 'mauve', the first man-made organic dye, by Sir William Perkin in 1856, marked the beginning of the era of synthetic dyes. The tremendous growth of synthetic dyestuff industry is evident from the fact that by the end of the last century synthetic dyes of varied structures accounted for over 90% of the dyes used. It can be stated without much exaggeration that the present organic chemistry is an offshoot of dyestuff industry, and that they are inextricably linked.

Among the synthetic dyes, azo dyes constitute an extraordinarily interesting and important class of compounds from both theoretical and practical points of view. Ready availability, cheapness and versatility of properties of azo dyes have guaranteed to them a high proportion of the range of organic dyes manufactured by industry (comprising over 50% of world dyestuff production). There are
azo dyes for dyeing natural substances such as cotton, paper, silk, leather and wool; for synthetic materials such as polyamides, polyesters, acrylics, polyolefins, viscose rayon, cellulose acetate, etc., for colouring of paints, varnishes, plastics, printing inks, rubber, food, drugs and cosmetics; for staining polished and adsorbed surfaces, and for use in diazoprinting and photography. Azo dyes have also wide application in the laboratory as acid-base, redox, metallochromic and other indicators, as stains for bacteriological and histological investigations, as standard materials for adsorption chromatography, etc.

The study of azo compounds has been of great value in the development of theoretical organic chemistry, used in developing and testing theories of colour and constitution, indicator action, and acid-base and tautomeric transformations. The tautomeric properties of certain aromatic azo compounds were detected as early as the beginning of the twentieth century. It can be seen that almost all known methods of investigating tautomeric equilibrium have been used for the study of tautomeric relations in various classes of azo compounds. Many of these methods have in fact been developed in connection with such azo compounds.

Azo compounds are characterised by the presence of one or more azo (–N=N–) group. A monoazo compound can be represented as A–N=N–B where A and B are organic groups. In dyestuff industry A is the
diazo component and B the coupling component. Depending upon the nature of the diazo (A) and coupling (B) groups, azo compounds can be broadly classified into the following types.

a) Aliphatic azo compounds (both A and B aliphatic)

b) Aromatic azo compounds or diarylazo compounds (both A and B aromatic).

c) Mixed azo compounds (A or B is aliphatic or aromatic).

d) Heterocyclic azo compounds in which either A or B or both are aromatic heterocycles.

(Cyclic azo compounds have been excluded in view of their unique structure and properties compared to exocyclic azo compounds)\textsuperscript{22,23}.

Although, as a class, aliphatic azo compounds have been known for well over a century and are of synthetic and theoretical interest\textsuperscript{10,23}, their application in dyestuff industry is insignificant. Commercially useful types of azo compounds consists of atleast one aromatic group attached to the azo link. Though majority of the azo dyestuffs are of the diarylazo type, significant number of mixed azo compounds are also in use. The same is true in the case of analytical and other applications of azo compounds. However, these mixed azo compounds have not received as much attention as they deserved, especially on their structural aspects. The present investigation is mainly on synthetic and structural studies on a new type of mixed azo compounds.
The most important synthetic method for azo dyes involves diazotisation of an aromatic amine and coupling of the diazonium salt with a suitable substrate — the coupling component. In the realm of organic chemistry probably no reaction is more reliable than that between nitrous acid and a primary aromatic amine yielding a diazonium salt. The certainty and the smoothness with which the reaction can be carried out and the high reactivity of the product (aryldiazonium ion) make it invaluable in both academic research and industry. This reaction of Peter Griess is generally known as diazotization reaction. Many variations of diazotization have been developed in accordance with the differing properties of arylamines and the use for which the products are required.

In general, a compound containing the group, \( \geq C-NH_2 \) and one other centre of unsaturation, is diazotisable using nitrous acid. Thus many aromatic heterocyclic diazo compounds are known, and the amine from which they are derived include a wide range of structures leading to great variation in diazotisability, and in properties of the diazo compounds. A dominant characteristic of arylidiazonium ion is its behaviour as a powerful electrophile, effecting substitution in compounds having one or more of the necessary nucleophilic centre(s).

Usually a proton is ejected and an arylazo group becomes covalently attached (coupled) to the substrate at the position of displacement.
An azo group can be attached to a carbon atom only when that atom is in a region of high electron density. The diazonium ion can then acquire an electron from a C-H bond so that a proton is removed and a C-azo compound results. Such compounds which can be coupled comprise several genera and many species. As a result, the possible permutations in azo coupling reactions runs into millions\(^{10,11}\).

Majority of the coupling components are derived from aromatic hydroxy compounds and amines. However, there are several aliphatic compounds that are able to couple with aryldiazonium ion\(^ {10}\). Nearly all such compounds may be regarded as methane derivatives bearing one or more ionisable or resonating substituents which bestow upon the coupling carbon site sufficient electron density to allow substitution by the diazonium ion\(^ {31,32}\). Coupling components of these types are often classed as compounds containing reactive methylene or methine groups. The number of azo compounds so derived is large and new examples are frequently reported. Victor Mayer\(^ {33-35}\) as early as in 1875 recognised these types of compounds and termed them mixed azo compounds.

The 1,3-dicarbonyl compounds constitute an important class of active methylene compounds that are able to couple readily with aryldiazonium ion\(^ {10,32}\). Several technically important dyes and
pigments are prepared from diazo-coupling of aryldiazonium ion with 1,3-dicarbonyls. For example, the well known Hansa Yellows are obtained by coupling acetoacetanilides with various aryldiazonium salts\textsuperscript{36–38}. Many variations in the dicarbonyls, as well as on the diazonium salts have been examined in attempts to improve colour, solubility and fastness of the resulting dyes. In most cases, the diazo components are from aromatic carbocycles. Only one or two reports exist on coupling of heterocyclic diazo compounds with 1,3-dicarbonyls\textsuperscript{39,40} inspite of the fact that such products exhibit interesting structural variations and have considerable applications. Therefore, the present investigation is on azo compounds derived from heterocyclic diazo components and 1,3-dicarbonyl coupling components.

\textbf{Heterocyclic azo compounds}

In the early days of the dyestuff industry, the majority of azo dyes prepared were diaryl ones. However, recently a number of aromatic heterocycles also have been prepared and used. Thus hitherto unobtainable shades, especially blues and greens, and properties such as brightness have been obtained, and this has increased even further the commercial importance of azo dyes.\textsuperscript{41}

The most important heterocycles are those with 5- or 6-membered rings, which may be fused to other aryl rings. Nitrogen, sulphur, and to a lesser extent, oxygen are the most frequently encountered hetero atoms.
Perhaps the most popular applications of heterocyclic azo compounds is in analytical chemistry. Several excellent reviews are available on these aspects. Frequently encountered typical examples of heterocyclic azo compounds (derived from heterocyclic diazo components) are shown in structures 1-5.

**Metal complexes of azo dyes**

Several applications of substituted azo compounds depend on their ability to form complexes with metal ions. Hence coordination characteristics of these compounds have been examined by a number of investigators, and are briefly mentioned below in order to emphasise the need for further studies in this direction.

Metal complexes of azo dyes are equally important as azo dyes themselves. Azo dyes are metallised for several technical reasons. The most important are:

- a) to achieve better fibre affinity and
- b) to improve certain specific property of the dye, especially light fastness.

The factors that influence the structure and tautomeric behaviour of the azo compounds, and formation, structure and stability of their metal complexes are all important in determining their use not only in dyestuff industry but also in analytical and synthetic chemistry.
The types of azo compounds capable of forming metal complexes may be conveniently divided into two classes based on whether the azo group is involved in coordination with the metal ion or not. The former, usually termed as medially metallisable, are by far the most important and are derived from azo compounds having metallisable substituents at suitable positions, as illustrated in structure 6. The second category of azo compounds, terminally metallisable, are based on metallisable coupling components such as salicylic acid, salicylaldehyde, 8-hydroxyquinoline, etc.
The donor properties of azo group are weak and its ability to coordinate with metals was originally inferred from the observation that azobenzene having ortho-hydroxy or ortho-amino group forms metal complexes, whereas those groups placed meta or para to the azo group, do not. It is to be pointed out that stable complexes cannot result from the donor strength of azo group alone.

Unsubstituted arylazo compounds are known to form different types of weak metal complexes through lone pair orbital or filled molecular orbital of the –N=N– function. Some of the typical examples are illustrated in structures 7-10.

Medially metallisable azo compounds form stable metal chelate rings with metal ions through the azo group and other adjoining functional groups. X-Ray data on several such complexes have shown that only one nitrogen atom of the azo group is involved in coordination. The practical value of metal complex azo dyes are strongly dependent on the factors affecting their formation and stability.

Factors affecting stability of metal complex azo compounds

The stability of a metal complex, in general, depends on the following factors.
\[
\text{Ni(CN_Bu)_2}
\]

\[
\text{(CO)_4 Mn}
\]

\[
\text{Rh(CO)_3 Fe-Fe(CO)_3}
\]
i) Relative strength of donor and acceptor atoms

Since metal ions are Lewis acids, basic strength of the donor atoms is important to the metal-donor atom bond. However, the donor atoms must be considered together with the metal ions. Metal atoms have been divided into two classes depending on their preference for the size and type of the donor atoms. Thus class A or hard metal ions form more stable complexes with smaller donor atoms such as N, O and F, while class B or soft metal ions form stable complexes with larger donor atoms such as P, S and Cl. They are often small with high charge and have no valence shell electrons to be easily distorted or removed. Mono positive alkali metals, dipositive alkaline earths, tripositive aluminium group, VO$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, etc. belong to this class. Hard metal ion bear similarity to the proton. Soft metal ions are those which have large size with low charge and have valence shell electrons which can be easily distorted or removed (Cu$^+$, Ag$^+$, Au$^+$, Tl$^-$, Hg$^+$, etc.).

Since hard and soft demarcation is gradual and empirical, there is considerable overlap between the two classes and some of the most interesting metal ions lie in the borderline region (Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, etc.).

Ligands with donor atoms preferred by hard and soft acids are correspondingly classified as hard and soft bases. A general observation is that hard-hard and soft-soft interaction lead to stable complexes.
The basic strength of the donor atoms also is a decisive factor in complex stability. For instance the relative coordinating ability observed of O and N donor atoms for typical hard acids is as follows:

\[ \begin{align*}
O & > N \quad : \quad \text{Be}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Co}^{2+}, \text{Al}^{3+}, \text{Ti}^{4+}, \text{Zr}^{4+}, \text{U}^{6+} \\
O & \approx N \quad : \quad \text{Fe}^{2+}, \text{Cr}^{2+} \\
N & > O \quad : \quad \text{Cu}^{2+}, \text{Ni}^{2+}, \text{V}^{3+}, \text{Co}^{3+}
\end{align*} \]

Metallisable azo compounds generally show hard character. Hence important metal complex azo dyes contain hard or borderline metal ions. The difference in stability of the transition metal complexes was well explained theoretically on the basis of ligand field and molecular orbital theories. In this investigation attention was concentrated mainly on metal ions like Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), etc. which are known to form complexes with relative ease.

ii) Chelate effect

Studies have confirmed that metal chelates are more stable than complexes of related unidentate ligands. An entropy effect is partially responsible for this phenomenon. Various considerations of geometry are also important for the stability of metal complexes. Each ligand has its own preference for a particular geometrical configuration. Position of donor atoms in functional groups of the
ligand determines the geometry of the ligand in metal complex and consequently the configuration of the metal complex itself. In the case of metallisable azo dyes it has been shown\textsuperscript{65} that when the donor functions are so placed as to form 5- or 6-membered chelate rings (as in heterocyclic ring systems), the resulting complex is most stable. Thus arylazo compounds having metallisable substituents at ortho-positions with respect to the azo linkage are able to form highly stable metal chelates. It has been observed that of two related multidentate chelating agents, the one forming the greater number of annulated chelate rings with a given metal ion yields the more stable complex. The o,o'-disubstituted azo compounds which form two chelate rings with metal ion give highly stable complexes compared to ortho-monosubstituted azo compounds which would form only one chelate ring. The relative stabilities of metal complexes of bi- and tridentate azo dyes have been shown to follow the sequence in fig. 1 with respect to the ligand\textsuperscript{65-68}.

As the power of coordination of metal ions falls off, the number of metals which form complexes also decreases, so that the last member of the series forms stable complexes only with a limited number of metal ions. The order of stability of complexes of bivalent metal ions of the first transition series is as follows: Cu > Ni > Co > Fe > Mn. This order is often referred to as the natural order of stability or Irving-Williams stability order, which has been observed in the case of metal complexes of several ligands\textsuperscript{69}. 
Fig. 1. Relative stabilities of azodyes with respect to complex formation.
Metal complexes of azo compounds containing donor atoms of heterocyclic ring(s)

Metallisable azo dyes containing one heterocyclic donor atom suitably located for the formation of annulated chelate complex are the subject of numerous patents\textsuperscript{70-76}, the most common being those containing a hetero nitrogen atom in a position adjacent to the azo group. A typical structure 11 is given below which is a copper(II) complex of 1-(2-pyrdylazo)-2-naphthalenol, (PAN).

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

11

PAN can form two annulated chelate rings with the metal ions. Their stability is comparable to that of o,o'-disubstituted azo dyes. An X-ray structure determination of the copper(II) complex of PAN has shown that the molecule is very nearly planar and has normal Cu-N and Cu-O interatomic distances and only one nitrogen atom of the azo function is involved in bonding with the metal ion\textsuperscript{77}. The double bond character of the azo group is preserved unlike in many of the metal complexes of diarylazo dyes.
Heterocyclic azo compounds in which the hetero atom is at least formally involved in chelation with a metal ion have been widely used in inorganic analysis and some of these compounds have become so unavoidable in classical methods of analysis. Since the introduction of PAN as a chromogenic reagent for metal ion by Cheng and Bray in 1955, many heterocyclic azo compounds with structures related to PAN have been investigated. Experimental methods involving heterocyclic azo compound are available for the qualitative and quantitative determinations of almost all metal and metalloid ions from a variety of matrices. Several excellent reviews are also available on these aspects of heterocyclic azo compounds.

Literature is extensive on heterocyclic azo compounds and their metal complexes derived from aromatic coupling components. However, only scanty reports exist on reaction of heterocyclic diazo compounds with active methylene compounds. The product of such reactions, especially with 1,3-dicarbonyl compounds, may exhibit interesting properties. This is because proton transfer and hydrogen-bonding are the two important aspects of the chemistry of hydrogen that respectively govern the behaviour and structure of many molecules, both simple and complex, from water to DNA. The 1,3-dicarboxyls exhibit both these features and have been subjected to detailed study for many years. They provide the best known example of keto-enol tautomerism. The present investigation has therefore been so designed as to provide information also in this respect. Thus, the
coupling components used are typical 1,3-dicarbonyls and the diazo components are from typical heterocyclic amines such as 5-membered thiazole, 6-membered pyridine, etc.

Arylazo derivatives of 1,3-dicarbonyl compounds

The 1,3-dicarbonyl compounds can be represented by the general formula R-CO-CH₂-CO-R', where R and R' are H, OH or any organic group or organic framework such as part of a ring system. The tautomeric nature and reactivity of these compounds are influenced by a variety of factors other than the nature of R and R' groups, such as solvent, temperature, substituent at the active carbon atom, etc. In general, bulky 2-alkyl substituents lead to decreased enolization, while Cl, Br, CN, COOCH₃ and SCN groups lead to almost 100% enol form. The tautomeric transformation of these compounds can be represented as in 12 and 13.
The methylene protons in the keto form and the hydroxyl proton in the enol form are acidic. Removal of a proton generates the anion 14. This anion is a powerful chelating agent, and is the source of a broad class of coordination compounds right from the time of Werner, and still serves as the starting material for the synthesis of novel compounds with unexpected properties and applications.

Numerous monographs and books are available on these aspects of 1,3-dicarbonyls, and no attempt is made to elaborate these further. Instead, some of the salient aspects of these arylazo derivatives pertinent to the present investigation are briefly included here.

The reactivity of the active methylene group of 1,3-dicarbonyls has aroused wide interest. The active methylenic carbon in these compounds can act as a nucleophilic centre easily attacked by electrophiles such as arylidiazonium ion. The reaction, without considering the exact tautomeric form, can be represented as:
and the product can be termed in general as 2-Arylazo-1,3-dicarbonyls.

Typical 1,3-dicarbonyls that are able to couple with aryldiazonium ion include β-diketones (R and R' are alkyl and/or aryl groups), β-ketoesters (R is alkyl or aryl, R' alkoxy or aryloxy) and β-ketoanilides (R is alkyl, R' alkyamino). From a structural point of view, perhaps the most important feature of these compounds is their tautomeric behaviour.

Tautomerism of 2-arylazo-1,3-dicarbonyls

Tautomerism of these mixed azo compounds has evoked considerable interest and controversy in the past. In fact much of the early work on these compounds were directed towards settling different viewpoints.

The introduction of an areneazo group at the 2-position of the 1,3-dicarbonyls raises the possibility of azo-hydrazone tautomerism, apart from the keto-enol tautomerism of the dicarbonyls. Thus, at least the following structures (15-18) can be distinguished even in simple 2-phenylazo-1,3-dicarbonyls.

In unsymmetrical 1,3-dicarbonyls (when R and R' are different) the number of possible structures further increases.
bonding groups such as OH, SH, COOH or NH₂ are present in the phenyl ring, the tautomeric behaviour of compounds may become still complicated. Similarly the electronic efforts of R groups also have influence on the resulting structure.

The tautomeric behaviour of arylazo-1,3-dicarbonyls are comparable to that of the well studied tautomerism of ortho-hydroxydiarylazo compounds. Various studies employing several techniques including theoretical calculations have helped to build up a coherent picture on which form predominates in a wide variety of diarylazo compounds.

Thus, it has been shown that phenylazo derivatives of phenols exist entirely in the internally hydrogen bonded azo-enol form, 19. The corresponding derivatives of naphthalenols and anthracenols exist predominantly or entirely in the internally hydrogen-bonded quinone-hydrazone form, 20. Studies in the case of heterocyclic azo compounds such as 1-(2-pyridylazo)-2-naphthalenol, and 1-(2-thiazolylazo)-2-naphthalenol have shown their occurrence in the azo-phenol form, 21.

Phenylazo derivatives of 1,3-dicarbonyl compounds such as acetylacetone, benzoylaceton, dibenzoylmethane, thenoyl-trifluoroacetone, methylacetoacetate and acetoacetanilide have been shown to exist entirely in the intramolecularly hydrogen-bonded hydrazo-keto form, 22, rather than in any other tautomeric form.
Bulk of the information in this regard comes from electronic, ir, nmr and mass spectral data, quoted at appropriate places in the subsequent chapters.

In the present investigation, various spectral techniques have been employed for structural characterisation of azo compounds derived from heterocyclic diazo components and typical 1,3-dicarbonyl coupling components.

Dye chemists have been generally unconcerned about the structural variations of the ligands, and hence have represented metallised azo dyes uniformly as azo derivatives, irrespective of the type of tautomeric form of the ligands. Indeed, coordination chemists were quite aware of the structural alternatives, but in view of their non-committed stand, the structural aspect remains yet unsettled.

The net result of coupling aryldiazonium ion with the bidentate 1,3-dicarboxyls, is the introduction of a potential donor group (the azo or hydrazone function). Thus three donor groups are present in these compounds. However, it has been shown in the case of several 2-phenylazo-1,3-dicarboxyls that steric factors prevent the participation of all the three donor groups simultaneously to the same metal ion.
In the case of heteroarylazo-1,3-dicarbonyls, if the hetero atom is situated appropriately, it may also get involved in bonding with the metal ion. Thus in this investigation, coordination characteristics of the heteroarylazo derivatives of 1,3-dicarbonyls have been investigated with a view to gaining further insight into their tautomeric behaviour, and nature of bonding in their typical metal complexes.