SECTION (i): LITERATURE SURVEY ON SCHIFF BASES

Chemistry of Schiff Bases
The condensation products of carbonyl compounds and primary amines are often named as Schiff bases. They are also known as azomethines or anils or imines.

Schiff bases can be prepared by (I) the reaction of carbonyl groups with amino groups and related reactions, (ii) nitroso-methylene condensation, (iii) formation of oximes via c-nitrosations, (iv) diazonium salt-methylene condensations, (v) additions to carbon-carbon double or triple bonds, (vi) through ylids (vii) tautomerization of amides and thioamides and related reactions, (viii) addition reactions to nitriles, isonitriles, nitrile oxides and related compounds, (ix) oxidation and elimination from nitrogen compounds, (x) reduction of nitro compounds, (xi) rearrangements and photochemical reactions and (xii) electrochemical synthesis at lead electrode.

The condensation of primary amines with carbonyl compounds was first reported by Schiff [1]. The reaction was reviewed [4,53]. The experimental conditions depend on the nature of the amine and the carbonyl compounds which determine the position of the equilibrium.

\[ \text{RR'}\text{CO} + R''\text{NH}_2 \quad \xrightarrow{\text{equilibrium}} \quad \text{RR'C} = \text{NR}'' + \text{H}_2\text{O} \]

Usually, it is advisable to remove the water as it is formed by distillation or by using an azeotrope forming solvent [10,18,197]. This is necessary with diaryl or alkyl aryl ketones, but aldehydes and dialkyl ketones can usually be condensed with amines without removing the water. Aromatic aldehydes react smoothly under mild conditions and at relatively low temperatures in a
suitable solvent or without it. In condensation of aromatic amines with aromatic aldehydes, electron attracting substituents in the para position of the amine decrease the rate of the reaction, while increasing it when on the aldehyde [49]. In both cases a linear sigma-rho relationship was observed. With ketones, especially with aromatic ones, higher temperatures, longer reaction times and a catalyst are usually required in addition to the removal of water as it is formed.

The reaction is acid catalysed. However, only aldehydes and ketones which do not aldolize easily in acidic media can be condensed with amines in the presence of strong acid catalysts, e.g. concentrated protic acid [39], BF$_3$-etherate [48, 205], ZnCl$_2$ [2, 18, 20, 39, 54], or POCl$_3$ [50]. For methyl ketones, only weak acids should be used, while for methylene ketones, which are less sensitive to acid-catalyzed aldolizations, stronger acids may be used as catalysts [4]. Ultraviolet irradiation is reported [20] to promote the formation of azomethines from aldehydes. This is explained [55] as a light-promoted autoxidation of part of the aldehyde to the corresponding acid, which in turn acts as catalyst. Schiff bases have also been prepared using piperidine [200], dimethylacetamide and 5% lithium chloride [251] and platinum group elements [312] as catalysts. Aromatic aldehydes and aliphatic or aromatic ketones give with the amines quite stable azomethines. Primary aliphatic aldehydes can give azomethines with various amines if the reaction is carried out at 0°C, and the product is distilled from KOH [11, 17]. The effect of solvent in the preparation of schiff bases was also studied as a function of Reichardt E$_{11}$N and modified Kamlet-Taft B$_{KT}$T parameters by Nagy et al. [295].
The intranuclear distance quoted for the >C=N- double bond is 1.29 –
1.31 Å for the non-conjugated group and 1.35 or 1.36 Å for azo-aromatic
compounds [37]. Symth [3,25] estimated the dipole moment of >C=N- bond
be 0.9 D. Cottrell [40] calculated the bond energy for >C=N- bond from the
original data of Coates and Sutton [12] and found to be 147.0 K. cal/mole.
Palmer's book [42] gave some detailed examples of the calculation of bond
energies from thermochemical data and found to be 142.0 K. cal/mole.

The IR data found in the literature revealed that the acyclic >C=N-
double bond most commonly encountered in Schiff's bases (azomethines)
absorb in the 1690-1640 cm\(^{-1}\) region. In most cases it is a strong and fairly
sharp band located at somewhat lower frequencies than the bands of
carbonyl groups and close to >C=C< stretching frequencies. In the absence
of strain, steric hindrance or other complicated factors and in dilute solutions,
prepared from neutral solvent, the stretching frequency of >C=N- is found to
be 1670 cm\(^{-1}\). The corresponding force constant, 10.6 dynes cm\(^{-1}\) is in the
harmonic oscillator approximation. If there are one or more groups conjugated
with the >C=N- group the frequency is usually lowered. Generally speaking
there is very little difference between infrared and Raman frequencies and
between the spectra of pure liquids and solids and their solutions in CC\(_4\) or
other not very associative solvents. In general >C=N- vibrations exhibit a
lesser degree of localization than >C=O vibrations.

Little is known about the electronic spectrum of the C=N group itself in
a purely aliphatic environment. Platt [31] and Sidman [38] estimated that \(\Pi\)-n
transition lies at 2100 Å if the >C=N- group carries only aliphatic substances,
at 2500 Å if conjugated with a vinyl group and at 2900 Å if on a benzene ring. Much more is known about the spectra of compounds in which the >C=N- group is substituted by aromatic rings. Charette, Faltihanal and Teyssie [54] studied the ultraviolet spectra of a series of N-salicylidene alkyl amines and their aryl-substituted derivatives in different solvents. Spectacular changes occur when the inert solvents are replaced by hydrogen bonding solvents. Gawinecki, Ryazard et al., prepared some Schiff bases derived from aryl groups and carried out the UV studies [175]. Kinetics and mechanism of hydrolysis of schiff bases were studied by pishchugin et al., [247,248]. Hydrolysis of various oxazolidines and N-acylated oxazolidines was carried out to explore their suitability as potential prodrugs [270]. Mahmoud et al., reported the kinetics of hydrolysis of Schiff bases and indicated that the rate-determining step is changed from –OH attack on the free Schiff base in alkaline media to attack by water on the protonated schiff base neutral and weakly acidic media. The results of study of solvent effects on base hydrolysis rates suggest that specific solute-solvent interaction, viz., dispersion forces and intermolecular hydrogen bonding play important roles [272]. Pramila and coworkers examined the rates of hydrolysis of Schiff bases at pH 4-13 in a 10% dioxane-water system and in various non-ionic surfactant system [406]. Angeles et al. studied the hydrolysis of Schiff bases in aqueous and non-aqueous media [413].

Determination of proton – ligand stability and stability of Schiff base were reported in the literature [60,70, 113, 114, 120, 143, 299, 335]. Salman et al. [414] studied some new 0-hydroxy Schiff bases in four solvents using UV spectra and reported that the appearance and intensity of band at >400nm
which belongs to the keto form of the schiff base depends on the electronic and not steric effect of the substituent. Potentiometric investigation of effects of several electron donating and withdrawing substituents on the basicity of azomethine group of salicylidene aniline in nitrobenzene was carried out by Gunduz et al., [313]. Potentiometric study of some Schiff base ligands was reported by Bera et al., and discussed the effects of hydrogen bonding and substituent effects on the stability constants and the proton affinities of nitrogen atoms in the Schiff bases [143]. Polarographic bahaviour of Schiff bases has also been reported in the literature [314]. Madhav et al., [396] studied some Schiff bases using HMDE, square wave and cyclic voltammetric techniques and explained the results in terms of electron withdrawing and releasing effects of the substituted groups. Effects of supporting electrolytes, solvents and acid concentration on salicylaldehyde tris Schiff base have been studied polarographically by Sreenivasulu et al., [397]. Cyclic voltametric measurements ontrasition metal Schiff bases complexes been reported [440, 451].

By virtue of the presence of lone-pair of electron on the nitrogen atom and of the general electron donating tendency of the double bond, compounds containing the azomethine group should posses basic properties. The most characteristic aspect of the compounds containing the >C=N- group which show basic properties lies in the formation of complexes with metals. These complexes provide some very characteristic series of co-ordination compounds. The basic strength of the >C=N- group is inadequate by itself to permit the formation of stable complexes by simple co-ordination of the lone pair of electrons to a metal ion. Therefore, in order that stable compounds to
be formed it is necessary that there should also be present in the molecule a functional group with a replaceable hydrogen atom, preferably a hydroxyl group near enough to the >C=N- group to permit the formation of a five or six membered ring by chelation to the metal atom.

**Physico-chemical studies of Metal-Schiff base complexes**

A perusal of literature revealed that Schiff bases behave as monodentate, bidentate and polydentate ligands towards many metal ions in the formation of complexes. Metal chelates of azomethines mostly with transitional metals, lanthanides and rare-earths have been prepared and characterized using elemental analysis, conductometry, magnetic susceptibility, thermal (TG, DTA, DSC), X-ray diffraction, X-ray fluorescence, infrared, ultraviolet visible, mass, nuclear magnetic resonance, electron spin resonance and proton resonance spectra [59, 64-67, 74-76, 84-88, 91-94, 101-112, 116, 122, 126, 129, 130, 135, 141, 145, 151, 152, 155-158, 160-171, 183-198, 201-220, 222-225, 227-234, 237-240, 242-245, 283-286, 301, 340, 445, 448, 453]. The characterization of metal-Schiff base complexes synthesized electrochemically has also been reported [278, 300, 378, 399, 407, 409]. Various authors studied structural and electrochemical behaviour of Schiff base transitional metal complexes [425, 427, 433, 438, 441]. Formation of polynuclear and mixed-ligand copper(II) and nickel(II) complexes with Schiff base have been envisaged in the literature [288, 444]. Stephan and his coworkers compared electrochemically and photochemically induced electron transfer process of a series of cu(II) Schiff base complexes [444].
Studies of metal-azomethine complexes in solution have been carried out by several authors. Metal-to-ligand ratio and stability constants for the complexes were computed using pH metric and potentiometric \cite{60, 69, 71, 82, 87, 113-116, 119, 123, 137, 140, 142, 144, 146, 154, 182, 221, 298, 313, 330, 360, 374-376, 430, 431, 456}, spectrophotometric \cite{58, 72, 95, 139, 182, 246, 248, 299, 436, 455}, and conductometric \cite{385} techniques.

Solvent extraction, thin layer chromatography and spectro-electrochemical studies were carried out to study Cu(II), Zr(IV), U(VI), Co(II) and Th(IV) Schiff base complexes \cite{62, 117, 181, 219, 426}. Schiff bases were also used in the flurometric determination of beryllium \cite{214} and aluminium \cite{267}. Aoki et al., studied the effect of metal-to-ligand ratio on fluorescence properties of Zn(II) and Be(II) Schiff base complexes \cite{296}. The same authors have also determined ethylenediamine flurometrically by forming a fluorescent Be(II)-Schiff base complex \cite{373}.

Polarographic technique has also been employed by various authors in the study of metal-azomethine complexes to determine co-ordination number, stability constants, kinetic parameters and stereochemical behaviour in solution for reversible and irreversible systems \cite{9, 62, 81, 118, 120, 121, 124, 125, 127, 132, 136, 138, 147, 148, 172, 176-179, 207, 235, 236, 271, 276, 287, 327, 384, 389, 415, 465, 466, 467}.

Section (ii) Applications of Schiff bases and their metal complexes

The >C=N- group is present in many organic molecules of fundamental importance. They have got extensive applications in biological and industrial
fields. Schiff bases with potential pharmaceutical use were synthesized [26,29,45]. Anticataract pharmaceutical Schiff bases have been reported by Elsmer et al., [277]. Azomethines prepared by Nakahara and his coworkers were used as catalysts providing dental composites with excellent hardness, adhesion, on dentin and enamel, and discoloration resistance [291]. Thirty seven pharmaceutical anils were reported in the literature possessing anti-inflammatory, antipretic and analgesic properties [78,432]. Ismail and his coworkers reported antipyrine activity of copper(lli) Schiff base complexes [432]. Neomycin derivatives were recovered by converting them to Schiff bases with aromatic aldehydes at pH < 7.0. These schiff bases themselves are useful in human and veterinary medicine [45]. A potency of 725 streptomycin units/mg was reported for a number of Schiff bases prepared from salt of streptomycin [46]. Compounds of pencillin with Schiff bases of amphetamine were reported [23]. Therapeutically effective Schiff bases exhibiting cardiotonic and diuretic actions have also been prepared [8, 36,105]. Michel et al., prepared Cu & Ni new Schiff base complexes of potential interest to nuclear medicine [446]. Schiff bases having anti-inflammatory property have been synthesized [41, 206, 213]. Sivam et al., prepared some Pharmaceuticals containing Shiff base [353]. Some Schiff bases on expected chalogogic and choleretic activity were synthesized [328]. Tanaka et al., [254] prepared some Schiff bases useful as raw materials for drugs, agrochemicals and electron devices by reduction of them with molecular hydrogen in presence of palladium containing catalysts and tertiary amines. Gupta et al., studied synthetic structural aspects of lead (ll) complexes with Schiff bases of sulfa drugs [461].
Tuberculostatically active Schiff bases were condensed from aldehydes and amines with activity at $10^{-6} - 10^{-7}$ concentrations [19, 35, 89]. Shah et al., reported potential tuberculostatic azomethines which inhibited growth of Mycobacterium tuberculosis \textit{in vitro} [269].

Antiviral active anils were prepared in presence of zinc and acetic acid by Auelbekov et al., [215]. Iridium (III) Schiff base complexes also behaved as antivirucides [294]. Substituted salicylaldehyde Schiff bases of 1-amino-3-hydroxy guanidine tosylate acted as antiviral agents against coronavirus [270].

Fifty seven Schiff bases used as anticancer agents were reported by Chaudari and his co-workers [96]. Anticancer activity of Schiff bases was also cited in the literature [150,439]. Schiff bases of uracil-6-carboxaldehyde were synthesized and evaluated as potential antitumour agents by Kim et al., [418]. Metal-Schiff base complexes studied by Zishen et al., also exhibited anticancer activity against Ehrlich ascites carcinoma, with the Cu(II) complexes having the highest activity [335]. Pronounced anticarcinogenic reactivity of copper – di –Schiff bases has been studied [366]. Antineoplastic properties of different Schiff bases have been examined both \textit{in vitro} and \textit{in vivo} and reported as useful future anticancer agents [368]. Copper complexes of di-Schiff bases were used as neoplasm inhibitors and antirheumatics [338, 369]. Schiff bases derived from salicylaldehyde and 2-substituted aniline and their metal chelates with Cu(II), Ni(II) and Co(II) ions were screened for antiulcer activity. The copper complexes showed an increased activity [367].
Insecticidal compositions containing Schiff base as an active ingredient was reported [5]. The anils alone did not exhibit greater insecticidal action prepared by West [6] but exerted enhanced effect on non-aqueous solutions containing pyrethrum or rotenone. Thirteen azomethines tested against several pathogenic fungi were reported [22]. Schiff bases possessing pesticidal and fungicidal activity were reported by Gradon and co-workers [149]. Quantitative estimation of azomethine containing insecticides and frungicides was carried out polarographically [131]. Synthesis of some more Schiff bases of fungicidal activity were also reported [48, 133, 161, 173, 261-263, 273, 304, 324, 325, 336, 339]. Siddique et al., [311] evaluated the toxicities of Schiff bases and their complexes against insects and also reported the greater efficacy for the complexes than the Schiff bases.

Complexes with bidentate Schiff bases were reported to possess biocidal activity against bacteria and fungi [180]. Singh and his co-workers synthesized some boran complexes with Schiff bases and found to possess antifungal and antibacterial activity [329]. Schiff bases derived from methyl cyclo propyl ketones on addition with dialkyl phosphites showed aphicidal activity [357]. Twenty six thiazoie Shiff bases and their derivatives prepared by Mahapatra showed antifungal activity against curvularia species [200]. The antifungal property of some nickel-Schiff base complexes was studied. The complexes were more active than the free ligands against all the fungi tested [275]. Fifteen transition metal complexes with three Schiff bases have been screened against some fungal pathogens. Among these, Cu(II) and Co(II) complexes with one of the three Schiff bases, namely benzil-touldine ligand showed high fungi toxic results [337]. Schiff bases derived from 5-nitro
and 5-chloro salicylaldehyde and their complexes with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) have been studied for fungicidal activity using the growth method [303, 323, 428, 435, 447]. A series of sixteen methylated polyfluoro aromatic Schiff bases and their salts were tested as acaricides, fungicides and insecticides. Fluorination on the aldehyde part of the molecule enhanced the insecto acaricidal activity over that caused by fluorination on amine part [260]. Schiff base obtained from tris and glyoxal was studied for its pesticidal activity by Nicolae et al.,[174]. Pesticidal active phosphonium salts of C-phosphorous(III) substituted azomethines were synthesized [388].

Bactericidal and chemotherapeutical active Schiff bases were prepared from sulfapyridine [8,105]. Schiff bases with antibacterial activity derived from different aldehydes and amines were cited in the literature [13,14,77-79]. Of the seventy-three azomethines prepared by Tottistoror et al., only salicylaldehyde component possessed Schiff bases were found to contain antimicrobiological activity [63, 424, 443, 449, 450, 462]. Schiff bases having antibacterial activity were prepared and reported by various workers [218, 274, 279, 282, 297, 326, 331, 332, 361, 365, 371, 372, 387, 396, 398, 401, 403, 422, 437, 452, 459]. Various metal Schiff base complexes possessing biological activity have been reported [421, 429, 434, 442, 457, 458].

Amino acid Schiff base complexes of dimethyl dichlorosilane were prepared and studied their antibacterial activity. The data showed that the silane complexes were better inhibitors than the corresponding free ligands [199]. Antibacterial activity of Schiff bases and their metal complexes, varied from inactive to highly active, was discussed with regard to ligads and metal
Antimicrobial activity of co-ordination compounds of some 3d elements with Schiff bases was tested against strains of staphylococcus, proteus, salmonella, shigella and vaccine strains of Bacillus authraris [333]. Schiff base complexes of uranium and zirconium were examined for antibacterial activity in vitro [281]. The antimicrobial activity of two series of Schiff base derivatives of biphenyl and 2,4-diphenyl thiazole against four bacteria strains were studied using diffusion test procedure [280]. Mester et al., prepared ten Schiff bases possessing trynosomical activity [292].

Schiff bases possessing herbicidal activity were prepared by Sinha et al., [302]. Azomethines were also used as starting material and intermediates in the preparation of herbicides [256, 257]. It is found that Schiff bases have been employed as growth regulators [97]. Yangaun et al., synthesized Schiff bases having plant harmone activity [423]. D'Amico prepared six Schiff bases and found to be useful as plant growth regulators. Schiff base of aminohydroxy tetrahydronapthalene was found to possess growth regulating activity [217].

Growth regulating activity of Schiff bases on cucumbers and tomatos [259] have been studied. Some azomethine compounds used as growth stimulants were also reported [216].

Salicylaldehyde-tryptophan complex of copper(II) has been used as a tool for immobilization of protein [316, 317]. Radio labelled Schiff bases were used in brain studies and their lipophilicity and protein binding capacity have been demonstrated [212]. The role of cell-surface Schiff base forming ligands
in the inductive interaction between Class II\(^+\) antigen presenting cells (APC) and murine T cells was investigated [359]. A review with 47 references was presented on bioinorganic chemistry of metal-Schiff base chelates as vitamin B\(\delta\) analogs [83]. Azomethines with anticoagulant properties were reported in the literature [298, 362-364, 392].

Mixtures of linear poly Schiff bases of low molecular weight were synthesized from aliphatic diamines and terephthaldehyde [30]. Soluble and insoluble polymeric Schiff bases were synthesized and their Co(II), Cu(II) and Ni(II) complexes were characterized [159]. Cross linked polymers from Schiff bases have been derived and reported by Barbara and his co-workers [264]. Al-Dujali et al., synthesized liquid crystalline poly Schiff base polymers [380, 381]. Polymers of azomethine group containing (meth) acrylate esters were prepared by Ohashi et al., [411, 412] and used for second harmonic generation devices in opto-electronics.

Mixtures of azomethines and diazomethine pigments were used for PVC, printing inks and coatings with good migration resistance [90, 128]. Azomethines and their metal complexes with Cu(II), Ni(II), Zn(II) and Co(II) reported by Hunger were used as pigments [134]. The Schiff base derived from salicylaldehyde and dianimomalenitrile and its metal complexes were used as pigments [128, 265]. Some azomethine transitional metal chelates useful as pigments for plastics were also cited in the literature [78]. Theodor [99] synthesized fast greenish yellow to bluish red diazomethine pigments. Azomethine – metal complexed pigments from bibenzyl series have been prepared [382].
Paints containing drying oils with conjugated double bonds and Schiff bases were reported [34]. Property of Schiff bases increasing the drying rate of paints was cited in the literature [33]. Schiff base compounds useful for electrophoretic coating [293] and corrosion inhibitors [306, 420] were also reported.

Polyazomethine dyes were synthesized by Streel and Reindl [43]. Azomethines were used for dyeing and printing of fibrous material from polymers or copolymers of acrylonitrile or dicyanoethylene [28]. Schiff base metal complexes containing azo groups have been prepared and used as dyes for cotton, polyester, wool and leather [208, 210]. Chromium Schiff base complexes have been used as fast brown dye for wool and leather [209]. Metal chelates of Group IV elements with Schiff base ligands have been synthesized and reported as coloring material for fesins [290]. Complexes of o-phenylenediamine bis(salicylaldimine) with Fe(III), Ni(II), Cu(II) have been employed in textile dyeing [309]. Yogihara et al., prepared Schiff base compounds useful as intermediates for drugs, agro chemicals, porphyrins and dyes [352, 390]. Bis(hydroxy benzylidene amino) benzene sulfonamide derivatives of metal complexes were used for mass dyeing of polyester fibres [211]. Schiff bases were also used to promote the light-fastness of synthetic threads, fibres and foils [41]. Complexes of azomethines useful for improving the light-fastness of dyed leathers were synthesized [250]. Schiff bases as luminiscent dyes for solar collectors were also reported [379].
The copper complexes of Schiff bases derived from phenolic aldehydes with aliphatic diamines were used as good light stabilizers for dyed and undyed polyamide fibres [350].

In photography, a yellow Schiff base was used in irreversibly dischargeable photographic filter and antihelation layers as filtering agents [24]. Zgiercki, and Grabowska prepared Aromatic Schiff bases exhibiting photochromium [460]. Anils formed yellow styryl dyes particularly useful for colour correction masks for the cyan layer of colour layer of colour film [27]. Inaba and his researchers doped silver halid photographic materials with metal Schiff base complexes [463]. Photographic developers incorporating azomethine group were also described [15]. Certain Schiff bases of dialdehyde and diamino compound, when mixed with gelatin were used as colour filter in making colour films [16]. Schiff bases prepared by Mariko and Sadao showed good miscibility in various resins, have good solubility and were used in the charge transferring layer of electro-photographic photoreceptors [253]. Substituted azomethines were also employed in the coating of electrophotographic paper [44]. Some cationic technetium complexes of Schiff base ligands were studied as myocarial imaging agents [255].

Schiff base compounds useful as aroma and taste enhancers in perfumes, cosmetics, food stuffs, chewing gums and beverages were prepared [310, 321, 322]. Schiff bases derived from amines and organoleptically acceptable aldehydes were employed as deodorants for
removing aldehyde associated off flavour in fats, oils [351] and odourous air from refrigerators or raw garbage [319, 392].

Aromatic polyazomethines were used in the manufacture of filaments [251]. Dicarboxyiic acid azomethines were reported and used in the preparation of high glass-temperature materials from epoxy resins [258]. Heat and fire resistant polyazomethines have also been prepared [308, 320, 349, 393]. Rajan carried out studies on the application of Schiff bases for high temperature lubrication [386]. Heat resistant polyazomethines with good electrical properties and useful for manufacturing printed circuit boards were prepared by Kihara et al., [391]. The polymeric Schiff bases synthesized were found to possess semiconducting properties [73]. A review with seven references on organic semiconductors prepared from polymeric Schiff bases was discussed [204]. Yasuo et al., prepared six thermostable and semiconducting polyazomethines by polycondensation of diamines with dialdehydes [356]. Nishikawa et al., prepared Schiff base type epoxy compounds with excellent heat resistance, mechanical strength and optical characteristics and were used for laminates, coatings and semiconductor sealants [354, 355, 416]. Schiff bases were also used in the preparation of automobile – antiglare mirrors [252]. Anils derived from heterocyclic carbonyl compounds with 2,6-diethylamine were used as rubber antioxidants [205]. Modified rubber compositions with improved green strength and cured properties and useful for tires, were manufactured by treating unsaturated rubbers with Schiff bases in the presence of a Friedel-Crafts catalyst and then adding carbon black [307].
Schiff bases were used as catalysts in accelerating the formation of the factice [21, 80, 100]. Mn(II) Schiff base complexes were used as catalyst in laser flash photolysis [464]. Organic compound containing an azomethine group was used as a catalyst for the polymerization of H₂CO in an inert medium [47]. The catalytic and oxidative activities of azomethines and their corresponding copper, nickel chelates were discussed by Aptekar et al., [68]. Rhodium-salicylidene complexes and nickel-azomethine complexes used as catalysts for isomerization and dimerization of α-olefins respectively were reported [80, 100]. The liquid phase oxidation of 2,3,6-trimethyl-phenol to 2,3,6-trimethyl-p-quinone with molecular oxygen catalyzed by metal-Schiff base complexes was performed in various solvents by Mizukami et al., [202]. Titanium(IV)-Schiff base complexes were employed as catalysts in the oxidation of thianisole [268]. Optically active quadridentate Schiff bases and their titanium(IV) complexes were prepared by Coari et al., and employed as catalyst in the asymmetric oxidation of methyl phenyl sulphide with organic hydroperoxides [402]. Ring opening reactions of epoxides with trimethylsilyl cyanide catalyzed by titanium alkoxide-Schiff base complexes were studied by Hayashi et al., [419]. Catalytic dehydrogenation of hydrozones to diazo compounds was carried out with cobalt-Schiff base complex-oxygen system [266]. Catalytic efficiency of cobalt(II) complexes of tetra- and quinque dentate Schiff base ligands had been tested towards the oxidation of 2,6-di-tert-butyl phenol by molecular oxygen [287, 318]. In the oxidation of 3,5-di-tert-butyl catechol to 3,5-di-tert-butyl quinone, complexes of UO₂(II), Cu(II) and Ni(II) with compartmental Schiff bases were used [241]. Srinivas et al., prepared Ni(II) and Co(II) complexes which are less active than their Cu(II)
analogs and used as catalysts in the oxidation of 3,5-di-tert-butyl catechol by 
\( \text{O}_2 \) [400]. The mechanism of oxygen binding by cobalt(II) complexes with 
bidentate Schiff bases was considered by Vogt et al., [203]. Palladium 
complexes of Schiff bases derived from heterocyclic aldehydes were used as 
catalysts for the hydrogenation and isomerization of allyl benzene in methanol 
in presence of \( \text{NaBH}_4 \) [289]. Stable peroxo Schiff base complexes of thorium 
[341] and zirconium [342] were tested for their catalytic activity. 
Bis(salicylidene)-1,2-diaminocyclohexane-Mn(III) complex was synthesized 
and its catalytic property was studied [348]. Cobalt-Schiff base complexes 
were used as metal complex carriers of oxygen [203, 345].

Du, Wen et al., carried out the catalytic oxidation of phenols by cobalt-
Schiff base complexes [347]. Epoxidatin of olefins catalysed by mono- and bi-
nuclear Schiff base complexes was reported and the catalytic activity was 
correlated with the structure of the ligand, the redox potential of the metal ion 
and the binuclear character of the complex [344, 346, 377]. Reductive 
carbonylation of nitrobenzene to phenyl urethane catalyzed by ruthenium(III)-
Schiff base complex was reported by Khan et al., [343]. Schiff base complex 
of ruthenium(III), useful as catalytic organic oxidant was prepared [410]. 
Epoxidation of alkenes with iodosylbenzene using mono- and binuclear 
ruthenium(III)- Schiff base complex catalysts is studied by Upadhyay et 
al.,[417].

In addition to the above mentioned applications, Schiff bases have 
been employed in preparative uses (e.g. heterocyclic compounds) [358] for 
the identification, detection and determination of aldehydes or ketones, for the
purification of carbonyl or amino compounds (amino acids in protein hydrolysates) [7], or for the protection of these groups during complex or sensitive reactions (e.g. amino acids during peptide synthesis) [52]. Primary amines were determined by Fluorescent high performance liquid chromatography and chemiluminescence flow injection methods after converting them as Schiff bases [383, 404, 405]. The condensed product of salicylaldehyde with o-amino phenol was used as a gravimetric reagent for copper(II) [98]. Metallic impurities, such as copper from petroleum products were removed using Schiff bases [32]. In bioprosthetic tissue, residual aldehyde levels, which when high may cause implantation problems such as inflammation and other adverse reactions, were reduced in the form of Schiff base by contacting the tissue with a rinsing solution containing a primary amine [305].
Chapter - I

SECTION (ii): SYNTHESIS AND CHARACTERIZATION OF PARA BROMO ACETOGENONE - TRIS [PBAT]
**Synthesis**

Equimolar concentrations of Para Bromo Acetophenone and Tris (hydroxy methyl) methylamine [TRIS] were dissolved in methanol and were taken in a reflux flask. To it 20ml of excess methanol was added and refluxed for one hour. The refluxed solution was kept for over night. Colourless crystalline needles were obtained. The compound was recrystalised in hot methanol. The M.P of the substance was 152° – 155°C.

**Characterization of the ligand**

**IR Studies**

Infra red spectrum for the compound was recorded in nujal medium by perkin elmer IR Instrument. Peak at 1631 indicated the existing of–C=N-group in the compound. Peaks at 1585, 1545, 1500, 1458 Cm⁻¹ [C-O stretching]. Peak at 594-500cm⁻¹ (Aromatic C=C Vibrations) and 1230 –1210 Cm⁻¹ indicated presence of bromide in the structure. In view of the above data it was believed that condensation reaction was taken place between Primary amine (Tris) and Carbonyl group (para bromo Acetophenone) resulting the expected Azomethine compound. This was further substantiated by chemical reactions carried out for – NH₂ and >C=O groups. The other groups in the compound remain unaffected during condensation reaction. The elemental analysis, IR data are tabulated in Table 1.
Fig. 1: Infrared Spectrum of Para Bromo Acetophenone Tris (PBAT) Schiff base in KBr Pellet.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Colour</th>
<th>M.P°C</th>
<th>Elemental analysis</th>
<th>Yield</th>
<th>IR absorption cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parabromo Acetophenone Tris (PBAT)</td>
<td>C₁₂H₁₆O₂NBr</td>
<td>White</td>
<td>152-155</td>
<td>Carbon %</td>
<td>78%</td>
<td>1631</td>
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<td></td>
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<td>Hydrogen %</td>
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