

Photochromism in Anils - A Review

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Abstract: This review describes in brief the historical perspective of photochromism and photochromic behaviour of 'Anils'. This phenomenon among 'Anils' is exhibited due to the tautomerism between enol and keto form via six membered hydrogen transfer between the phenolic hydrogen and imine nitrogen and show the phenomenon of solid-state photochromism and thermochromism and photochromism in rigid glassy solutions as well. Photochromic property in 'Anils' is a characteristic of the molecule, but their chromo behaviour is not only influenced by the crystal structure of anils but also by the substituents in the salicylidene-aniline molecules by affecting the acidity of phenolic oxygen as well as the basicity of imine nitrogen that affects the enolic-character of anils. The growing interest in photochromic anils is due to the potential applications, more specifically due to the existence of anils in enolic- and keto- forms.

Keywords: Anils, photochromism, salicylidene anilines, Schiff's bases, thermochromism.

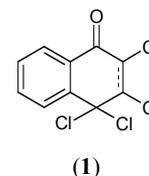
1. INTRODUCTION

One of the most active areas of photochemistry in the last century has been the study of various types of organic as well as inorganic compounds for the photochromic behaviour, a highly promising field. The phenomenon of colour change of a chemical compound on exposure to sunlight was first observed by Fritsche [1] in 1867, when he reported the decolouration of an orange coloured solution of tetracene in daylight and regeneration of the colour in the dark. Later Meer [2] in 1876 also observed a change of colour of crystalline potassium salt of dinitroethane from yellow to red in daylight and back to yellow in the dark. Markwald [3] observed the reversible colour change of 2,3,4,4-tetrachloronaphthalene-1(4H)-one (β -TCDHN **1**) by the end of 19th century.

Among the organic compounds which show photochromism include hydrazones, anils, semicarbazones, osazones, stilbene derivatives, disulfoxides, fulgides, succinic anhydrides, sydnone and spiro compounds. Even though this phenomenon is being investigated since beginning of the last century, the area of photochemistry has recently been exposed to the wealth of latest techniques, like picosecond time resolved spectroscopy, variable-temperature diffuse reflectance spectroscopy, x-ray along with other spectroscopic techniques, now available to the modern scientists to understand and explore the mechanistic aspects of the photochromic behaviour of different systems which ultimately helpful in exploring and designing the suitable applications.

In the 2nd half of last century especially since 1960 onwards lots of research work has been and is being reported on photochromism, and accumulating on different types of organic compounds, requiring critical review of each of the

class of the compounds for better understanding. The present manuscript, which covers the literature on photochromism in anils, provides a summary of the developments of photochromic behaviour of Schiff's bases (Anils), mechanistic aspects and more specifically from the potential applications point of view that may be helpful in focusing the future efforts in the area of specific application.



2. PHOTOCROMISM

Photochromism is the phenomenon of a reversible change of colour brought about by the exposure to electromagnetic radiations [4-8]. In the photochromic substances, absorption of radiations leads to a photochemically stable, with different colour from that of original, but thermodynamically metastable state "B" from which it reverts back to original state "A" by absorption of either of the light of different wavelength or of thermal energy. This phenomenon of photochromism was first recognized by Markwald in 1899 and since then has developed a lot of commercial and scientific interest during the last century. The interest in photochromic materials arises from the many potential applications, a scientist can imagine for a reversible photosensitive material. Most of the applications can be reduced to a utilization of one or more of the three defining characteristics of the photochromism:

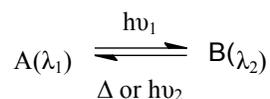
i) Light sensitivity, ii) spontaneous reversibility and iii) the colour change.

A reversible process in which a solid changes its colour when exposed to visible light and reverts back to its original

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colour when removed from it was named as “Phototropy” by Markwald [3]. With the development of the subject it has been found that the phenomenon is not only limited to visible region of the spectrum as exciting radiations, but also extends to the ultraviolet and infra-red regions of the spectrum. During the middle of the last century the term “Photochromism” [from the greek word, Phos (light) and Chroma (colour)] was suggested by Hirschberg [9] in 1950 to describe this phenomenon. Photochromism differs from thermochromism as the former is associated with electromagnetic radiations for colour change whereas the latter is associated with heat for colour change. Thus photochromism is defined as a reversible change of a single chemical species between two states having distinguishably different absorption spectra and such change being induced in at least one direction by electromagnetic radiations. Three conditions are necessary for a material to be photochromic: the state “B” should be moderately stable and it should absorb radiation in different region of the spectrum from that of “A” and the change $B \rightarrow A$ should occur either thermally or by exposure to radiations. This can be represented by the following equation [8]:



Almost all early reports of photochromism were based on the observations of the effect of the sunlight during the day and reversal during the night; the changes were readily noticeable. Only during the second half of the last century various instruments have become available to provide irradiation of the desired wavelength and intensities anywhere in the spectrum from infra-red to far ultra-violet, for measuring absorption changes anywhere in this span and to follow extensively rapid or extremely slow changes in the absorption spectra.

The concentration of the coloured form at the steady state is largely dependent on the intensity of the exciting radiation, temperature, kinetics of the reverse reaction and the influence of the solvent (nature as well as viscosity) on the reverse and forward reactions.

In a broad sense all reversible photochemical reactions which accompany the changes in the absorption spectrum of the reacting system are photochromic processes. However from the point of view of practical photochromic applications, most of them do not find many applications due to extremely short life of the coloured species, lack of photostability and their spectroscopic properties. The nature of the forward and backward reactions determines the mean lifetime of the coloured species. When the backward reaction is purely photochemical and can be induced by light which is not absorbed by the parent compound and the duration of the colour change can be controlled by changing the intensity of the light that induces the reverse reaction or by using the intermittent illumination. When the backward reaction is thermochromic, the duration of the colour change can also be controlled by the application of heat. Temperature and viscosity of the medium are the factors that influence the rate of thermally backward reaction.

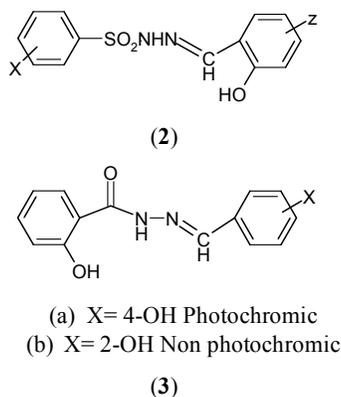
Number of colour reversals is a measure of the stability of photochromic system that can occur without suffering any appreciable loss of the photochromic efficiency. The instability is caused by the occurrence of thermal or photochemical side reactions. Low temperature, the exclusion of the light of unnecessary short wavelength and the use of rigid matrices tend to increase the stability of the photocoloured form. The processes, whether cis-trans isomerisation, tautomerism, homolytic cleavage or heterolytic cleavage are responsible for the change in the absorption spectra is immaterial, if the reversible criterion is met. Photochromism is exhibited by both organic as well as inorganic compounds. Photochromism has been appealing to many research groups because not only the colour change but also other properties such as refractive index, fluorescence, magnetic properties, electron transfer or structural features can be reversibly occurred.

3. ANIL

The condensation products of aldehydes and primary amines having the general formula $R-CH=N-R'$, in which R and R' are organic radicals, are known as ANILS or SCHIFF'S BASES. Senier *et al.* [10-13] at the beginning of the last century, were the first to observe reversible solid-state photochromism of anils. As mentioned by E. Richard and R. Grinter [8] in their review in 1965, more than 300 anils were examined by various workers [10-15], out of which majority of the anils were thermochromic and around 25 were observed to be photochromic and this number is still increasing with new additions. These are colourless to light yellow in the dark and become red or orange-red or brownish-red on exposure to sun-light. Time required for reversible colour change varies from anil to anil; e.g. crystals of 5-bromosalicylidene- α -naphthylamine darkens within 5 minutes exposure to sunlight [14] and requires about one hour to revert to its original colour on keeping in dark whereas in case of salicylidene- β -naphthyl-amine [13] exposure to sunlight for one hour is required to change its colour from yellow to red and takes weeks time to regain its original yellow colour on keeping in dark. These anils are susceptible to fatigue i.e. after a number of cycles of colour change some of the anils lose their photochromic activity although salicylidene-m-toluidine appears to retain its photosensitivity for at least several months [10].

Among the photochromic compounds of interest for advanced functionalized materials, salicylidene-anilines and related Schiff's Bases usually called ‘Anils’ have received particular attention due to ease of preparation, and their ability to switch between two forms, the enolic-imine and ketoamine (enaminone) isomers via intramolecular proton transfer reaction that can occur both in solutions as well as in the crystalline state. This tautomerization can be triggered either by light or heat. Proton transfer reactions in Schiff's Bases have been studied extensively both experimentally and theoretically in the last 4-5 decades [16-19]. Photochromism in salicylidene-anilines, though earlier studied by Senier *et al.* [10] and Brewster *et al.* [14], has been extensively investigated by Cohen and Coworkers [19-22] during 1960-1970. Becker *et al.* [23, 24] and Ottolenghi *et al.* [25, 26] also made useful contributions during the same period for the investigations of the mechanism involved in the photochromic

mic behaviour of anils at different temperatures and in different solvents. R. Nakagaki *et al.* [27], Sudagar Mal *et al.* [28-30], Rawat *et al.* [31] and Hadjoudis *et al.* [32-38] during 1970-1990 also studied the mechanistic aspects of the photochromic behaviour of anils by studying different types of anils. Benzene sulphonyl hydrazones (2) were found to be photochromic in crystalline state, ethanol:ether (2:1) and polymethylmethacrylate (PMMA) matrix at liquid air temperature (-170°C) [31]. Arylidene aroyl hydrazines (3) which are structurally similar to benzene sulphonyl hydrazones have not shown photochromic behavior in solid state or in PMMA matrix by irradiating with UV light which was thought due to the interaction of C=O group of one molecule with -OH group of another molecule [39]. However 4-hydroxybenzylidene salicyloyl hydrazine (3a) showed colour change in crystalline form from white to yellow on exposure to sun light in 5 minutes and revert to the original colour thermally in the dark or keeping in dark at 25°C for a week. But this did not show photochromic change in UV light (365 nm). The cycle could be repeated several times without any fatigue in the molecule. It has also been observed that when either of the OH groups was replaced or substituted by the $-\text{OCH}_3$ group, the photochromic property of the compound was lost. On the other hand 2-hydroxy benzylidene-salicyloyl hydrazine (3b) did not show observable colour change on irradiation (UV, sun light) in solid state. This observation indicated that ortho group that is able to shift its proton intramolecularly to the azomethine nitrogen is not essential for the colour change (photochromism) in arylidene aroyl hydrazines [40]. Rawat has also investigated the photochromic behaviour of N, N'- di(O-nitrobenzylidene) diamines [41], bis-N,N'-salicylideneamlines [42], N,N'-disalicylidenediamines and thermochromic property of hydroxylated polyazomethines in solid, PMMA film and solutions at different temperature [43]. The growing interest in o-hydroxy Schiff's bases has been observed lately due to their ability to form intramolecular hydrogen bonds by π -electron coupling between the acid-base centres [44-47]. Such systems are interesting both from the theoretical and the experimental point of view [45,46]. The intramolecular H-transfer reactions proceed comparatively easily in these compounds and intramolecular π -electron coupling leads to the strengthening of the hydrogen bonds in this system [48].



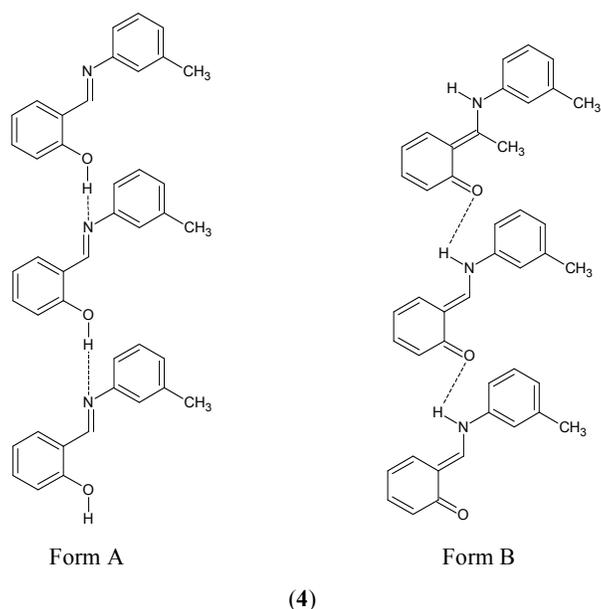
Due to their potential applications in optical communications or data storage, organic molecular switches possessing large contrasts in their nonlinear optical responses (NLO), in particular second harmonic generation, have motivated a

number of workers [21-60] in the last few decades. The large number of potential applications are reversible optical data storage, in diffraction, holography and optical communications have stimulated a great deal of experimental and theoretical work which starts to extend to the use of different photochromic systems.

4. MECHANISTIC INVESTIGATIONS

Early explanation for the mechanism of photochromic behaviour in anils involved aggregation and crystal lattice interactions [14, 15]. Salicylidene-m-toluidine changes its colour from light yellow to orange-red, an unstable form obtained in crystalline state, by irradiations with a light of 365 nm wavelength. When these photochromic crystals were dissolved in different solvents after exposure, the colour disappears immediately and the resultant solution was identical with the unexposed sample. The nature of solvents has been found critical in the case of solutions, the reversible colour change occurring only when the "Switching" conditions are favourable.

de Gaouck *et al.* [15] by their spectroscopic and dielectric studies of various anils in benzene, carbon tetrachloride and chloroform solutions detected no colour change when the solutions were irradiated with 365 nm wavelength as compared to those kept in dark. They concluded that photochromism in anils is suppressed by the presence of solvents and the colour change takes place only in the solid state. Since no crystallographic property appeared to be changed, they proposed that the colour change is due to a mutual interaction of the hydroxyl hydrogen of one molecule with the nitrogen atom of another molecule Forms A & B (4).



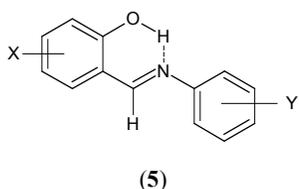
They considered the whole solid to be a "hybrid" between the states represented by "A" and "B", in which the molecules are imagined to be oriented as given in the diagram; Forms "A" would be yellow and Form "B" would be coloured red to orange-yellow. Modern nomenclature would designate "A" and "B" as tautomers and not as hybrids. Form "B", the coloured form, is a distinct species different

from the form "A". In the crystalline form the molecules are either "A" or "B" but not hybrid. If the hydroxyl hydrogen is blocked by methylation it is found that the photochromic property is destroyed, a result which would be expected according to this theory.

Although the solid state studies are more important with regard to the applications, significant evidence for the molecular nature of photochromism in anils comes from the solution studies [16-43]. Most of the information available regarding anil systems is due to the investigations by Cohen *et al.* [16-22] first showed the presence of *o*-hydroxyl group is a structural requirement for the photochromism in anils.

They further reported [16] that the rigid glassy solutions of salicylideneanilines are photochromic at low temperatures with the development of a new absorption band around 480 nm after irradiation with 365nm wavelength (the absorption maxima of "Anils" is around 365 nm).

It was also observed [17-20] that photochromism in anils is a topochemically dominated phenomenon in crystalline state, because they fail to find any correlation of the photochromic activity with the chemical nature of the ring substituents X and Y (5), and suggested that packing arrangement in the crystalline state is of more importance as polymorphic forms of a given anil which differs markedly in the light sensitivity. Chemically very similar 4-chloro and 4-bromo-anils, the latter is photochromic but former is not. They concluded that in the crystalline anils, thermochromy and photochromy are mutually exclusive properties and neither of them could be obtained in the absence of ortho-hydroxyl group and proposed that the structure effect is two fold:



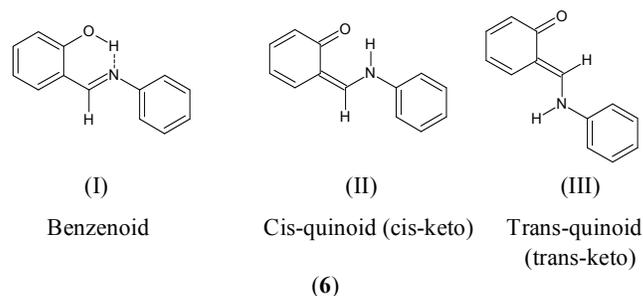
- i) It enables the photochemical cis-trans isomerization to occur in the photochromic crystals but not in the thermochromic crystals;
- ii) cis-quinoid species produced in the case of thermochromic crystals are stabilized by crystal structure.

They further classified the crystalline anils into two types:

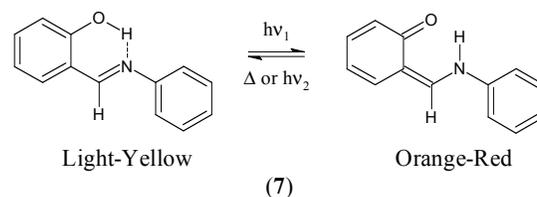
- i) α -type: which are photochromic, pale yellow at all temperatures but not thermochromic.
- ii) β -type: which are not photochromic but thermochromic (i.e. their colour darken with the increase of temperature and becomes lighter on decreasing the temperature and proposed the structures (6) for this behavior.

By x-ray diffraction studies it was suggested [22] that in the crystals of thermochromic anils, the molecules are essentially planar and packed plane-to-plane at about 3.4\AA spacing while displaced relative to one another along the length of the molecules providing stabilization of cis-quinoid through dipole-dipole interactions. Thus it is assumed to be responsible for the lack of photochromic behaviour by pre-

venting cis-trans isomerization. In photochromic crystals the structure is sufficiently open to allow cis-trans isomerization while packing is not of the right type for dipole-dipole interaction to lead to the stabilization of the cis-quinoid.



Further in the investigations of photochromic behaviour of anils (5-bromo-, 5-methyl-, 5-nitro-, 3,5-dinitrosalicylideneanilines, salicylidene-(*p*-nitro)aniline, and salicylidene-(*p*-methoxy)aniline) in rigid glassy solutions at low temperatures, it was concluded [20] that photochromy is a property of an isolated anil molecule in an arbitrary rigid matrix. They proposed that a six-member ring hydrogen transfer phototautomerism occurs to form a coloured quinoid structure and the action of light upon anils causes a proton transfer to form a keto-anil in rigid glassy solutions as below (7).



In crystals they suggested that trans-keto (III) anil may be a photoproduct and cis-keto (II) form may responsible for the thermochromic behavior (6).

Becker and Richey [23] concluded from their investigations of the photochromic behaviour of anils in 3-methylpentane (a nonpolar and non-hydrogen bonding solvent) at 77°K that most of the anils of salicylaldehydes exist in the enolic form and addition of small quantity of an organic acid results in the conversion of some enol form to cis-keto form (II) as the temperature of solution is lowered to 77°K. The irradiation of enol form causes photocolouration with the formation of trans-keto anil (III) (6). Their information was based mostly on the absorption, emission and excitation spectra of anils at low temperatures in rigid glassy solutions, as the photoproduct (coloured species) has well defined characteristic band with absorption maxima around 480nm which is neither observed in the spectra of enol form nor in the spectra of cis-keto form having absorption maxima around 440 nm (obtained by the addition of a small quantity of organic acid to the enol form).

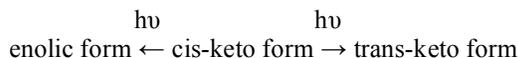
They further observed that on warming the photocoloured (orange-red coloured) product in rigid glassy solutions (obtained after excitation with 365 nm wavelength of the enolic form) to the softening point (by 10-15°C) gave the similar absorption, emission and excitation spectra as were obtained in case of cis-keto form (II) produced by the addition of small quantity of organic acid to the enolic form.

No photocoloration or photo eradication was observed from the cis-keto form obtained by the addition of small quantity of organic acid to the enolic form or from the yellow coloured species obtained by warming the photochromic product (in rigid glassy solutions) to the softening point and again recooling to 77°K.

All these informations account for the formation of cis-keto product by thermal process from the photocolorated product. Further the cis-keto form on warming to room temperature changes to the enolic form is supported by spectral studies. Thus the reverse process from the photocolorated product to enolic form is as follows:

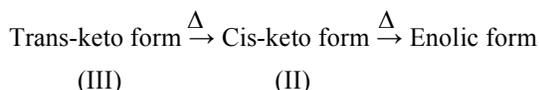


Since Becker *et al.* [23] observed no photocoloration or photoerasure of the cis-keto form obtained by either of two ways mentioned above, therefore, they proposed that neither cis-keto form can be obtained nor it can be converted to either photoproduct or enolic form photochemically. Thus they commented that the following reactions are not photochemically feasible.



Nitrosalicylideneanilines investigated by them [23] in 3-methylpentane showed the formation of cis-keto form on cooling to 77°K without the addition of organic acid. Irradiation of all these nitrosalicylideneanilines in 3-methylpentane at 77°K did not show photocoloration even when irradiated throughout the entire range of the absorption, which is most likely the result of the increased acidity of the hydroxyl hydrogen due to the nitro group present in the salicylidene ring, resulting in strongly intramolecularly hydrogen bonded molecule to the extent that proton is nearly equal distant from oxygen and nitrogen atoms and excitation essentially causes no significant difference in its location. This situation results in a energy barrier too high to be crossed over by light absorption and thus no trans-keto form is produced. Thus all these observations provide strong evidence that the molecular species formed upon irradiation is trans-keto anil that on reverse reaction isomerizes to the cis-keto anil, which further undergoes proton transfer to produce enolic form.

Taking into consideration all these observations they postulated that photocolorated product is trans-keto form (III) produced photolytically from the enol by means of a concerted reaction which involves an intramolecular proton transfer with extensive electron redistribution accompanied by rotation about the ring carbon –imine carbon bond finally resulting in the trans-keto form. The cis-keto form (II) is produced in the thermal back reaction from the trans-keto form (III) as follows:



Ottolenghi and Mc Clure [27] by flash photolysis techniques confirmed the formation of “Trans-keto”, a photoproduct, and suggested the following reaction sequence for the photochromic behaviour in anils.



Where 'E' is the enolic form and E* is the excited enolic form, 'X' is an intermediate produced during the formation of 'Q' a photocolorated product. 'X' does not last long enough to be observed by flash techniques but it is an intermediate during the formation of a photoproduct 'Q'. Its formation does not involve large distortions of the geometry of the molecule as this step is not affected by rigid matrix. Also its formation from 'E*' is affected by deuterium substitution in place of the proton of the hydroxyl group. They suggested that 'X' is a state in which the proton in the O-H---N bond has moved out of its ground state equilibrium closer to the imine-nitrogen in the asymmetric potential surface along the O-N coordinate, possibly a quinone with an intramolecular hydrogen bond (6(II) Fig. 1).

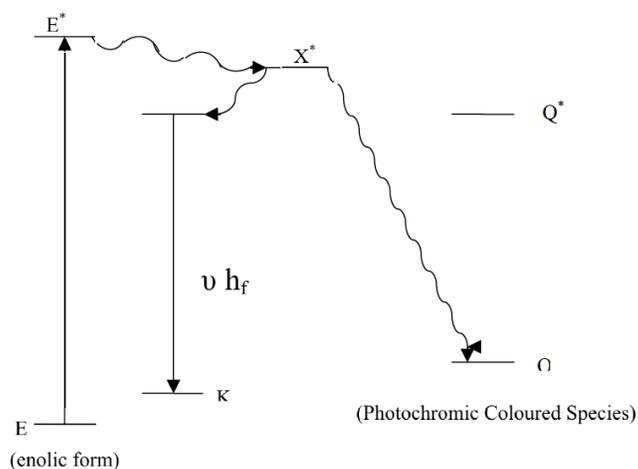


Fig. (1). Schematic Energy level diagram for the photochromic coloured species.

They also observed that unlike $E^* \rightarrow X$, the process $X \rightarrow Q$ exhibits no isotopic effect and is inhibited by the rigid matrix. Hence they concluded that the formation of 'Q' from 'X' involves a change in the geometry of the molecule by cis-trans isomerization around the bond between the ring carbon atom and that in the C-N bridge. This will lead from the hydrogen bonded imine ('X') to a form where oxygen and hydrogen are geometrically separated, that it does not favour the reestablishment of the hydrogen bond (6(III)).

Thus the relative stability of the photoproduct species 'Q' in the rigid matrix can be easily understood bearing in mind that the backward reaction to hydroxyl form will involve a reverse trans to cis isomerization. They postulated that the reaction pathway which leads from anil molecule 'A' to the photoproduct 'Q' involves three principal steps:

- i) the lowest $n\pi^*$ singlet is populated.
- ii) transfer of proton along the O-H---N coordinate to form the hydrogen bonded quinone 'X' (6(II)), and
- iii) cleavage of O-H bond and oxygen-nitrogen separation are both caused by the cis \rightarrow trans isomerization.

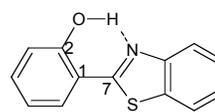
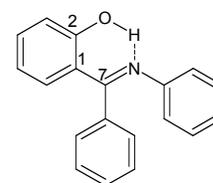
Both the processes of production of the photocolorated species and photoeradication, involves crossing a potential

energy barrier which contains a viscosity component in addition to thermal component, support the earlier suggestions [16] that the formation of a photocoloured product involves large distortions in the geometry of the molecule. The observations that high viscosity hinders the formation of photocoloured species indicate that its formation involves a change in the molecular geometry from that of an essentially planar form. Moreover the existence of this viscosity effect explains why in thermal back reaction, “photocoloured species” change in to “cis-keto species”, the colour changes from orange to red/red to yellow as the rigid glasses begins to soften even though the temperature increase is only 10–15°C above that of liquid nitrogen temperature. This yellow colour attributed to the cis-keto form by spectral studies and concluded that the viscosity effect provide strong evidence that “cis-keto”, the photocoloured species, is a non-equilibrium form of the cis-keto tautomer [24].

By inclusion in the channel of a porous coordination network, an otherwise thermochromic salicylideneaniline derivative becomes photochromic because its intrinsic planar conformation is transformed into a nonplanar one. The photochromic properties of the nonplanar guest molecule can be tuned by changing the co-included solvent in the channel [61].

It was also suggested that the absence of photochromism among nitrosalicylidene anilines is due to the increase in height of potential energy barrier between the excited cis-keto and the photocoloured species which is the result of stronger internal hydrogen bonding as compared with other salicylideneanilines, that in turn is due to the nature and the position of the nitro group in the salicylidene ring which makes the phenolic proton less basic (i.e. more acidic) in the ground state thereby facilitating proton transfer to imine nitrogen to form cis-keto tautomer. The height of potential energy barrier is such that the rate constant for crossing between the excited cis-keto and the photocoloured species, “cis-keto” form cannot compete with that of fluorescence and no photocolouration is observed [24].

Potashnik and Ottolenghi [26] based on their investigations suggested trans-keto species to be photochromic product in contradiction to “cis-keto”, a suggestion of Becker *et al.* [23,24] by running flash photolysis experiments over a wide range of solvents and temperatures. They postulated that photochromism in the anil system does not consist of a simple light induced shift in the dark equilibrium between the enol and keto but it involves the formation of a new quinoid isomer **6 (III)**. They concluded by comparing the photochemical effect in fluid solvents and in most crystals [27] that the formation of **6 (III)** from **6 (I)** is inhibited by rigid ring structure, thereby causing a considerable rearrangement in the molecular geometry, which may involve cis-trans isomerization either around the $-C_1-C_7-$ bond (which is predominantly double in a quinoid structure) or as suggested in case of similar (azo) systems around the predominantly single C_7-N bond. From their experimental observations they favoured the first alternative because 2-(O-hydroxyphenyl)benzothiazole (**8**) in which rotation around C_7-N bond is prevented by the rigid ring structure is still photochromic whereas 7-phenylsalicylidene-aniline (**9**) in which rotation around C_1-C_7 bond is sterically inhibited does not exhibit the photoproduct.

**(8)****(9)**

Taking into consideration all these experimental observations, they [26] proposed trans-keto structure **6 (III)** for photoproduct.

R. Nakagaki *et al.* [27] also supported the suggestions of Ottolenghi *et al.* [25] by their investigations of photochromic behaviour of anils that the trans-keto form is the structure for the photocoloured species, Q. They showed the existence of the precursor of the photochromic coloured species using the picosecond time-resolved spectroscopic technique by measuring the rise time of the photochromic transient absorption in solvents of different viscosities which increases with the increase of viscosity. Which means that the enolimine in the excited singlet state passes over the energy barrier sensitive to the viscosity in the course of transformation into the photochromic coloured species, in other words that in the photochromic phenomenon of anils the hydrogen transfer in the excited state is followed by a geometrical change in the whole molecular framework of the molecule and proposed the following energy level diagram for the phenomenon (Fig. 1).

Effect of the substituents on the photochromic behaviour of anils has been investigated by various workers [16, 24]. Cohen *et al.* [16] observed that the substituents in the salicylidene part of the anil molecule do affect the photochromic behaviour of anils by affecting the basicity of hydroxyl oxygen that affects the strength of hydrogen bond whereas the substituents in the aniline part of the anil molecule has no effect on the photochromic behavior, as anils of p-methoxyaniline and p-nitroaniline are both photochromic indicating that the electron density of the lone pair of electron on imine nitrogen atom responsible for H-bonding is not affected by the nature of substituents in the aniline part of the anil molecule and confirm the earlier observations that the lone pair of electron on the imine nitrogen is not overlapping with the π -electrons of the aniline ring as the N-phenyl ring has rotated out of the plane of the rest of the salicylidene aniline molecule to such an extent (certainly less than 90°) that the substituents in the aniline ring has no effect on the basicity of imine nitrogen and hence the photochromic behaviour of anils.

Steric effect of the C_7 -phenyl group for the lack of photochromic behaviour in C_7 -phenylsalicylideneaniline as proposed by Potashnik and Ottolenghi [26] does not seem to be the only reason for the lack of photochromic behaviour.

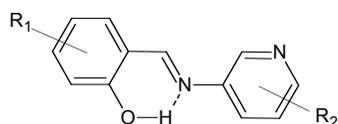
Mal *et al.* [30] also studied the photochromic behavior of C_7 -substituted anils and found that all these C_7 -substituted anils were not photochromic both at liquid air (-180°C) as well as at dry ice-acetone (-75°C) temperatures. If the steric hinderance due to the C_7 -phenyl group was the only reason for the absence of photochromic behaviour in 7-phenylsalicylideneaniline as proposed by Ottolenghi *et al.*

[27], then the anils having $-\text{CH}_3$ or $-\text{CH}_2$ -Phenyl group at C_7 -position should have yielded photochromic coloured species on exposure to 365nm wavelength in rigid glassy solutions. It appears that +I effect (inductive) of these groups might have been the dominating factor that causes the increased electron density on imine nitrogen thereby increasing the strength of hydrogen bonding and shifting the hydroxyl proton more closer to imine nitrogen along the $-\text{O}-\text{H}\cdots\text{N}$ coordinate i.e. increasing the cis-keto character in the ground state of the anil molecule which increases the height of energy barrier between the excited cis-keto and trans-keto forms. The same is also substantiated by the pmr values of phenolic protons of anils with C_7 -methyl and C_7 -benzyl and C_7 -phenyl groups which increase basicity of the imine nitrogen. PMR signals of the hydroxyl protons of these anils are shifted downfield by $>1.1 \delta$ (approx) as compared to those of simple salicylideneanilines indicating that +I effect cannot be ignored and seems to be a dominating factor in this case. Chemical shift values [29] of the hydroxyl proton in the PMR spectra of these anils (tabulated in Table 1) support the above observations.

Table 1. Chemical shift values of the hydroxyl proton in the PMR spectra of Anils.

| C_7 -group | Photochromic behaviour | Chemical shift values of hydroxyl proton in PMR spectra (δ) |
|---------------------|------------------------|--|
| $-\text{CH}_3$ | -ve | 14.1 |
| $-\text{CH}_2$ -Ph | -ve | 13.90 |
| -Ph | -ve | 13.85 |
| -H | +ve | 12.73 |

Various substituted salicylidene-(m-amino)pyridins (**10**) have been examined [33]. These anils are observed to be weakly thermochromic due to non polarity of amine- pyridine ring (aminopyridine part is rotated by $\approx 15^\circ$ w.r.t. the salicylidene part) thus explaining weak thermochromism. Crystal structures of these salicylidene-(m-amino)- pyridines permit only cis-trans isomerization so no photochromism was observed.



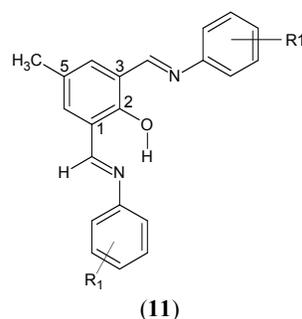
Where $\text{R}_1 = \text{R}_2 = \text{H}$
 $\text{R}_1 = 5\text{-MeO}$, $\text{R}_2 = \text{H}$

(10)

Dianils of 2-hydroxy (5-methyl)isophthalaldehyde (**11**) were observed to exhibit remarkable thermochromic behaviour as observed by E. Hadjoudis *et al.* [32], due to its structural characteristics, with strong contribution of the quinoid form in the ground state at room temperature.

Mal *et al.* [30] investigated the effect of substituents in aniline ring on photochromic behaviour of anils by studying the substituted salicylidene-(o-, m-or p-benzoyl)anilines and observed that the benzoyl group ($-\text{CO}-\text{C}_6\text{H}_5$) at ortho, meta,

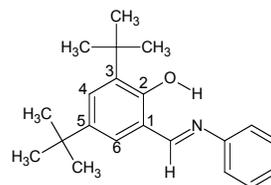
or para-positions to the imine nitrogen in the aniline ring affect the photochromic behaviour of anils but to a different extent as it is evident from the absorption spectra of these anils after irradiation with 365 nm wave length in rigid glassy solutions at -180°C at the same concentrations ($3.98 \times 10^{-5} \text{M}$). A well resolved band at 480nm with higher intensity for m-isomer than for o-isomer and least for p-isomer were observed. At -75°C in rigid glassy solutions only o-isomer showed photochromic behaviour which also faded away after 25-30 mins, whereas no photochromic behavior for m- & p-isomers was observed. Lack of photochromic behavior in m- & p-isomers at -75°C may be due to the temperature limits as suggested by Cohen *et al.* [19]. Parallel observations for N-(5-methylsalicylidene)-(o-, m-, or p-benzoyl)-anilines were also noted. Surprisingly no photochromic results could be observed for N-(5-bromosalicylidene)-(o-,m-,or p-benzoyl) anilines contrary to the expectations which needed further investigations.



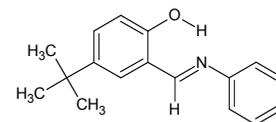
(11)

Rawat *et al.* [31] observed that the anils of benzenesulfonylhydrazine, and p-toluenesulfonylhydrazine with salicylaldehydes are photochromic on exposure to 365 nm wavelength with the appearance of a characteristic absorption band of photochromic anils around 480 nm wavelength, in rigid glassy solutions of ethanol-ether (2:1) and in polymethylmethacrylate (PMMA) films at -180°C indicating that the rotation of these anil molecules around $-\text{C}_1-\text{C}_7$ bond is not hampered in the rigid polymeric matrix. Electron withdrawing substituents in salicylidene ring affected the formation of photo-coloured species where as substituents present in the benzene sulphonyl ring did not have significant effect.

Kawato *et al.* [62] made interesting observations that N-(3,5-di-tert-butyl)salicylidene- aniline (**12**) and N-(5-tertiary-butyl)salicylidene- aniline (**13**) gives more stable photochromic product as compared to salicylideneaniline due to the increase in free space in the crystal packing owing to bulky tertiary butyl groups in the salicylidene part of the anil molecule.



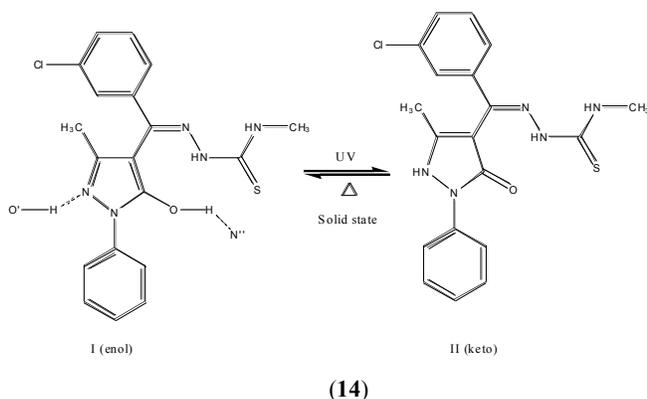
(12)



(13)

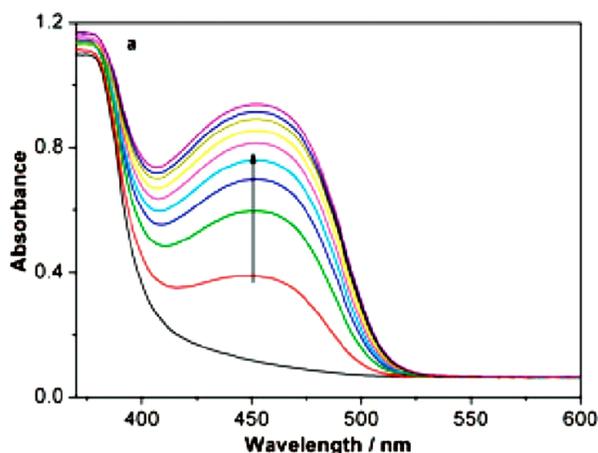
Photochromic behavior in crystalline state was observed in thiosemicarbazones of 4-acylhydroxy pyrazoles with

thiosemicarbazide when irradiated with 365 nm light. The mechanism of photoreaction is given in structure **14** [63]. Compound I showed an interesting photochromic transformation from white to yellow upon UV irradiation. The white crystalline powder (enol form I) changed gradually in to yellow (keto form II) under irradiation of 365 nm. Fig. (2a) and (2b) illustrate the absorption and fluorescence spectral change of I upon irradiation with 365 nm light at different times. New band around 400-550 nm in Fig. (2a) denotes the photochromic product in solid state. The photochromic process of the compound is similar to those of other analogous compounds such as 7-hydroxyquinolines and 2-hydroxypyridine [63, 64] but different from those of Schiff base compounds.



H. Koshima *et al.* [65] observed that platelike microcrystals of N-3,5-di-tert-butylsalicylidene-3-nitroaniline (**15**) can be repeatedly bend and straighten upon alternate irradiation with UV and visible light. They have given the mechanism of bending before and after photo irradiation by X-ray crystallographic analysis [65].

J. Harada *et al.* [66] measured variable temperature diffuse reflectance and fluorescence spectra of the crystalline powders of salicylidene anilines. They also determined their fluorescence quantum yields and concluded that the temperature-induced shift of the tautomeric equilibrium is not the main cause of the thermochromic colour change of the thermochromic crystals and that the thermochromism can be explained only by taking account of the temperature induced change of fluorescence.



Substituted salicylidene-(2-amino)-pyridines (**16**) showed thermochromic behavior in the crystalline state are also having planar structures as observed by X-ray crystallographic studies [67] due to interlocking of H₇-proton and 2-aminopyridine nitrogen.

Further, x-ray crystallographic studies showed the non planer structure of salicylidene-(4-amino)pyridine has shown both photochromic and thermochromic behavior. X-ray analysis studies of structural change in photochromic salicylidene aniline crystal was carried out to validate the trans-keto form of photo product [68].

Photochromic and thermochromic properties of various schiff's bases of salicylaldehyde with benzylamine and thioenylamine were investigated [32,33] in crystalline state at various temperatures and this class of compounds showed that planarity or non-planarity of the anil molecule is not the determining factor for thermochromic or photochromic behaviour respectively. The nature of the substituents in the salicylidene imino part of the N-salicylidene-benzylamines leads to the hypothesis that the electron density of the lone pair of electron on imino nitrogen is the determining factor for their chromo- behaviour. If the electron density is high the compound is thermochromic, if low, it is photochromic. The role of the planarity or non-planarity of the molecule is important only so far as it affects the electron density on nitrogen. The same observations have also been confirmed by Fujwara *et al.* [69] In the case of anils (**17**) & (**18**), the electron density on imine nitrogen is not decreased in the non-planar molecule because the aromatic group has been isolated by methylene group. It follows therefore, that the anils of aliphatic amines should exhibit thermochromism irrespective of the molecule packing and they may exhibit photochromism simultaneously, if the molecular packing permit cis-to-trans isomerization for the formation of photo-product. Same has been corroborated by the results of Carles *et al.* [70] in cases of N-salicylidene-methylamine (**19**) and N-salicylidene-2-propylamine (**20**) that are photochromic and thermochromic, respectively.

Hadjoudis *et al.* [71] also investigated the photochromic and thermochromic properties of solid trans-N,N'-bis(salicylidene)-1,2-cyclohexanediamine (**21**), trans-N,N'-bis(3,5-di-chlorosalicylidene)-1,2-cyclohexanediamine (**22**), trans-N,N'-bis(3,5-di-tert.butyl-salicylidene)-1,2-cyclohexane-

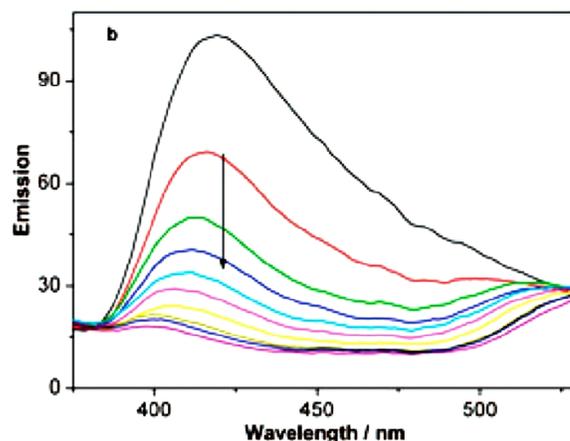


Fig. (2). (a) Absorption and (b) fluorescence emission spectra.

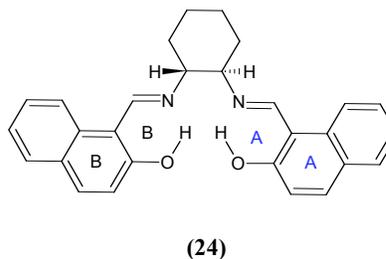
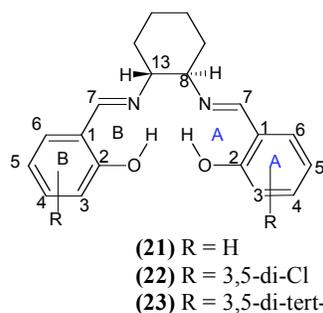
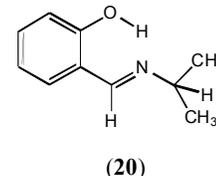
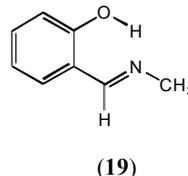
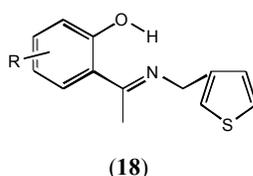
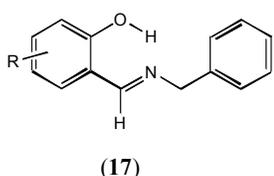
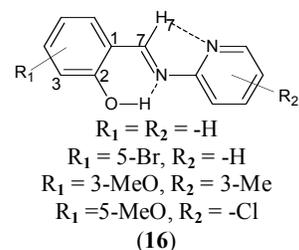
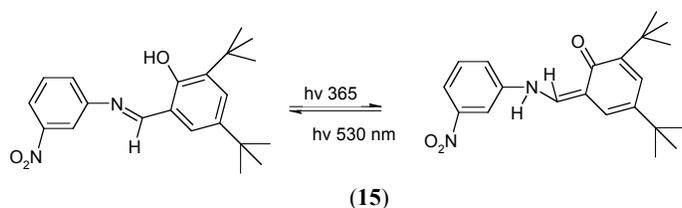


Table 2. Photochromic and thermo- chromic behaviours of the Schiff's bases anils.

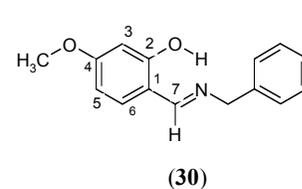
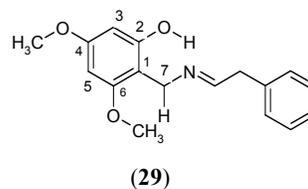
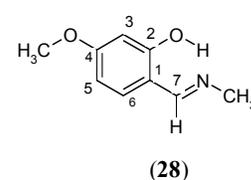
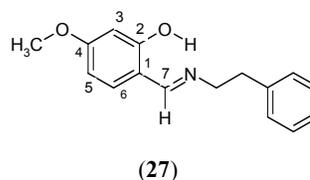
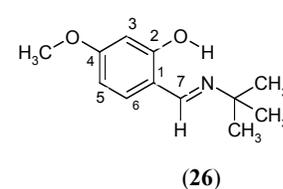
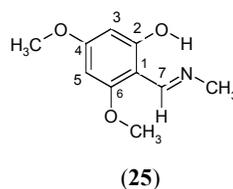
| 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 34 |
|-----|-----|-----|------|-----|----|----|-----|-----|-----|-----|
| P/T | P/T | P/T | ---- | P/T | P | T | P/T | P/T | P/T | P/T |

where P = Photochromic ; T = Thermo chromic

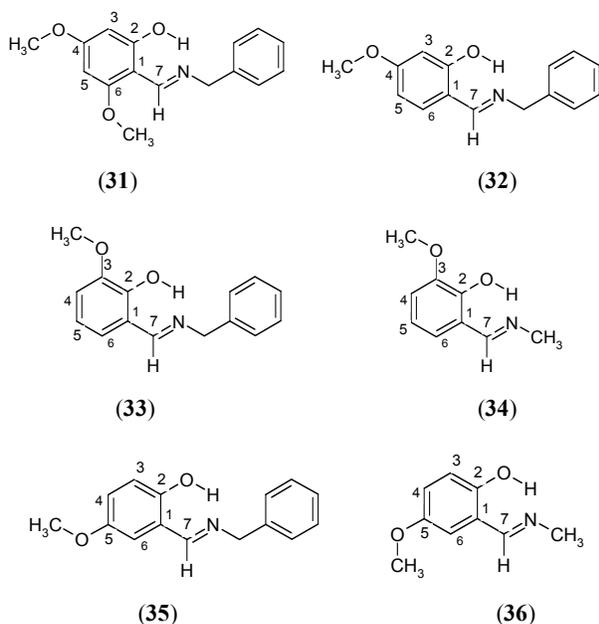
diamine (**23**), and trans-N,N'-bis(2-hydroxynaphthylidene)-1,2-cyclohexane-diamine (**24**) in crystalline state at various temperatures and found them thermodynamic. The role of crystal structure in this case is important only in so far as it affects the electron density on imine nitrogen atom. Photochromism, however, is structure dependent and requires space for generation of the photoproduct that involves cis-trans isomerization in excited state. Anils (**21**) to (**24**) are thermo chromic, whereas (**21**) and (**23**) are additionally photochromic also. Crystal structure determination of (**22**) & (**24**) show very clearly that cis-to-trans keto isomerization of the photoproduct is impossible due to the very dense packing, thus explaining the absence of photochromism. On the other hand the packing of (**21** & **23**) is quite open and permits photochromism.

N-(4-hydroxysalicylidene)-amino-4-(methylbenzoate) and N-(3,5-di-tert-butylsalicylidene)-4-aminopyridine in the crystalline state have been reported photochromic [72].

Eleven new schiff's bases of methoxy substituted salicylaldehydes with aliphatic and aromatic amines have been examined by x-ray crystallographic and spectroscopic techniques by Chatziefthimiou *et al.* [49] to investigate the effect of substituted positions on the keto-enol equilibrium in the crystalline state and photochromic as well as thermo- chromic behaviours of the molecules (the results are tabulated in Table 2) (**25-36**):



X-ray crystallographic studies in thermodynamic N-salicylidene-azine by G. Arcovito *et al.* [73] have observed close packing plane-to-plane stacking at a distance of 3.4 Å and A. Destro *et al.* [74] have observed the N-phenyl ring of the salicylidene-anils nonplanar by an angle of 40°.



Photodynamics of salicylidene aniline and N-(2-methoxybenzylidene)aniline are studied by steady state and transient optical spectroscopy in solution and gas phase at different excitation wavelengths (266, 355 and 390 nm). Two competitive processes are observed from the enol excited state. On one hand a rotation formed and on the other hand an excited state intramolecular proton transfer followed by a cis–trans isomerisation to get the trans-keto photochromic product [75].

Sliwa *et al.* have studied by time resolve spectroscopy that when aniline molecules excited in capsulated state then the deactivation occur either to solvated state or to a crystalline photochromic state [76].

M. Sliwa *et al.* [77] have observed photochromic behavior of N-(3,5-di-tert-butylsalicylidene)-4-aminopyridine in both solution and crystalline state whereas N-(3,5-di-tert-butylsalicylidene)-2-aminopyridine is photochromic in solution like anils but exclusively thermochromic in crystalline state.

Acid-base co-crystallization has been used to control the photochromic reactivities of salicylidene aniline derivatives in co-crystals [78]. The weak photochromic compound N-salicylidene-3-carboxyaniline becomes non-photochromic or strongly photochromic in the co-crystals with 2-aminopyridine, guanylthiourea, cystosine, 4,4'-bipyridyl, anhydrous piperazine, 1,3-di-O-tolylguanidine and dibenzylamine and non photochromic compound N-salicylidene-4-carboxyaniline becomes photochromic in the co crystal dibenzylamine. The change in the photochromic properties of these compounds is because of the conformational changes induced in the salicylidene aniline moieties in the crystal structure. The life duration of the coloured species formed in the photochromic reaction is also affected by the changes in the environment around the molecule in the crystal.

5. OUTLOOK

The phenomenon of photochromism is usually defined as a reversible photo- induced transformation between two mo-

lecular states whose absorption spectra are significantly different. Besides this colour change, which is the visible evidence of photochromism, there are many other molecular as well as bulk properties that also change along with this transformation like refractive index, dielectric constant, fluorescence, magnetic properties, electron transfer or structural features etc which can be reversibly modified. Anils have received particular attention due to their ability to switch between two forms, the enol-imine and keto-amine tautomers via intramolecular proton transfer that can take place both in the crystalline state as well as in rigid glassy solutions. So applications such as molecular switches and sensors are being explored. The associated photochromism and thermochromism makes salicylidene-aniline type anils as intelligent materials due to their capability of switching between two forms, which can be used as molecular switches and memory devices. With the successful use of organic dyes as memory media in CD-R (Compact disc recordable) systems, photochromic materials are also anticipated as a promising candidate for erasable memory media in future. So depending upon the anticipated change in different types of anils, various scientists [5-7,52-63] have made significant effort to unravel the different possible applications of the photochromic anils that are briefly discussed here.

K. Nakatani *et al.* [53] carried out useful studies on reversible photo switching of second order non-linear optical responses in organic photochromic crystals of Schiff's bases. Sliwa M. *et al.* [57] carried out extensive studies of design, synthesis, structural and non-linear optical properties of salicylidene-2-amino- & 4-aminopyridines Sliwa, M. (57, 72) further studied the non linear optical properties (NLO) of N-(4-hydroxy)salicylidene-amino-4-(methylbenzoate), and N-(3,5-di-tert-butylsalicylidene)-4-aminopyridine.

A. Plaquet *et al.* [58] also reported about the investigation on the second order nonlinear optical responses in the keto-enol equilibrium of the anil derivatives, in particular second harmonic generation with focus on potential applications in optical communications, data storage and organic molecular switches.

Delaire *et al.* [52] reviewed the studies of Linear and Non-Linear optical properties of photochromic molecules and materials related to Schiff's Bases. Guillaume *et al.* [54] have reported the Second-Order Nonlinear optical responses in keto-enol equilibrium of various types of substituted salicylidene-anilines in view of designing the compounds with a contrast of second order nonlinear optical properties.

E. Bogdon *et al.* [59] have reported the effects of solvents on the Second-Order Nonlinear Optical Responses in the keto-enol equilibrium of a 2-hydroxy-1-naphthaldehyde derivatives. Sworakowski *et al.* [55] studied reversible mobility switching in molecular materials controlled by photochromic reactions.

CONCLUSION

To summarize the above observations of different research groups it is established that the presence of o-hydroxyl group in salicylidene anilines is essentially a structural requirement for the photochromic and thermochromic behaviour in anils and it is strongly felt that planarity or non-

planarity of the anil molecule is not the determining factor for thermochromic or photochromic behaviour in anils, but the electron density on hydroxyl oxygen as well as on the imine nitrogen atom is what determine their chromobehaviour. For thermochromic behaviour, the enolic form of the anil molecule has more cis-keto character i.e. the hydroxyl proton is more closer to imine nitrogen, which on heating changes to cis-keto forms having absorption band at 440 nm, and for photochromic behaviour the enolic form on excitation with UV radiation converts to enolic form (excited form, in which hydroxyl proton is still close to hydroxyl oxygen) in which transfer of hydroxyl proton to imine nitrogen takes place along with cis-to-trans isomerization to give a trans-keto form, a photocoloured form, with an absorption band at 480 nm which is different from that of cis-keto form having absorption band at 440 nm wavelength. In crystalline state, thermochromic anils have close packing plane-to-plane stacking at a distance of 3.4 Å and in case of photochromic anils in crystalline state, a nonplanar structure with N-phenyl ring rotated by about 50° w.r.t. salicylidene part of anil molecule that has sufficient open space for cis-to-trans isomerization to take place. The role of planarity or non-planarity of anil molecule is important only so far as it affects the electron density on imine nitrogen. Photochromy is a property of an isolated anil molecule in an arbitrary rigid matrix and photocolouration involves the six membered ring hydroxyl hydrogen transfer photo tautomerization (cis-to-trans) to form a coloured quinoid structure which is sensitive to the viscosity component of the medium (matrix). Thus both the process of formation of photocoloured species and photo eradication (as in the case of paraffin oil) involve crossing a potential energy barrier which contains a viscosity component in addition to the thermal component is suggestive of the fact that the formation of a photocoloured species involves transfer of hydroxyl proton to imine nitrogen along with the large change (distortions) in the molecular geometry from that of an essentially planar form. Also the substituents in the salicylidene ring as well as in the aniline ring at different positions (o-,m-,or p-) of the anil molecule have significant effect on the photochromic behaviour by way of affecting the basicities of hydroxyl oxygen as well as that of imine nitrogen.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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