**Introduction**

**Historical Survey on Photochromism**

 Photochromism was reported for the first time by Fritzche in (1867)[1] who observed that the bleaching of an orange-colored solution of tetracene in the daylight and the regeneration of the color in the dark . Shortly after, in 1876, ter Meer [2] described the same phenomenon with potassium salt of dinitroethane (yellow in the dark; red in the daylight). Another early example was published by Phipson [3], who noted that painted gate post appeared black all day and white all night (due to a zinc pigment, probably lithopone). In 1899, Markwald studied the reversible change of color of 2,3,4,4 tetrachloronaphthalen-1(4H)-one (β-TCDHN) in the solid state [4].

He believed it was a purely physical phenomenon, naming it “phototropy”. Although used in that period, that term is not proper and should be avoided because it is akin to phototropism, which denotes biological phenomena (vide infra). However, today phototropy is understood as the light-induced interactions occurring in biological systems, including the effects of light on the nutritional systems of plants or microorganisms; whereas phototropism is the tendency of plants to turn towards the source of light[5]. Interest in photochromism was continuous but limited until the 1940–1960 period, which saw an increase of mechanistic and synthetic studies. In 1950, Hirshberg [6] suggested the term “Photochromism” [from the Greek words: photo (light) and chromism (color)] to describe the phenomenon. This is the name used today. However, it is not limited to colored compounds; it applies to systems absorbing from the far

UV to the IR, and to very rapid or very slow reactions.

**Development of the Field:**

 Photochromism expanded during the 1960s in parallel with the development of physical methods (IR, NMR, X-ray, UV, time-resolved and flash spectroscopy) and organic synthesis. Photochromic glasses became available at that period and further stimulated research. Applications, such as the photochromic micro image (PCMI) process, which showed the possibility of reducing the 1245 pages of a Bible to about 6cm2, attracted considerable interest. An important book was published in 1971by Brown [7]. A revival of activity started in the 1980s, essentially because of the development of fatigue-resistant spirooxazine and chromene derivatives. They triggered the fabrication and commercial application of photochromic ophthalmic lenses [8]. Since then, other commercial systems have been developed, and new photochromic systems have been discovered and explored. In parallel, several books have been printed (vide infra); a flow of articles in scientific journals has appeared and International Symposium on Photochromism (ISOP) have been organized for the fifth times.

**Definition of chromism**

 Chromism is a reversible change of substance’s color resulting from a process caused by some form of stimulus. Many materials are chromic, including inorganic and organic compounds and conducting polymers, the property can

result from many different mechanisms.

**Types of chromism**

There are several types of chromism .

**Thermochromism:**

 Thermochromism is the reversible color change of substance induced by temperature change. There are a large variety of substance exhibit this phenomenon. Example (bianthrones, hexacyano ferrate, and other compounds). The organic 9,9’-bixanthenylideneic colorless at 90K, yellow-green at 298 K and dark blue when melted at 592 K; This is achieved by causing conformational changes to the polymer backbone. It has been reported that region regular poly(3 hexylthiophene) P3HT reversibly changes color upon heating to 220oC due to temperature– dependent conformation changes. Other forms of thermochromism may be commercially important e.g. to give a visual indication of temperature changes. 9,9'-Bixanthenylidene, a typical thermochromic molecule, is colorless at liquid nitrogen temperature, yellow-green at room temperature and dark-blue when melted or heated in boiling mesitylene [9].

**Chirochromism and diastereoselective photochromism:**

 Generally, chirochromism is a reversible change of rotation of the plane of polarized light between two chiral diastereomers of a photochromic system (vide infra). It should be noted that the inter conversion of two enantiomers of a photochromic compound which have, by definition, identical absorption spectra in non-chiral media, does not pertain to photochromism; however, these enantiomers might exhibit different absorption spectra in chiral media, especially in solid matrices. Diastereoselective photochromism (diastereophotochromism) is a photo induced reversible change of absorption spectra between two diastereomers A and B. The diastereomeric excess (Edia) at the photostationary state (pss), from irradiation of a mixture of A and B at the wavelength λ with non-polarized light, depends on the molar absorption coefficients (ε) and the interconversion quantum yields, ΦAB (A → B) and ΦBA (B → A), according to the following equation (Fig. 1.3) [10].

The mixture (**A, B**) will result in an enrichment of **B** at λ1 and of **A** at λ2.

If A and **B** contain chiral subunits (Fig.1.3), their inter conversion will result in different effects on plane polarized light (which can be measured by circular dichroism); this reversible interconversion is referred to “chirochromism”. Enantiomerically pure, sterically overcrowded heterocycles, **a** (*cis*) and **b** (*trans*), exhibit a stereospecific photochemical isomerization of **a** to **b** and **b** to **a** (diastereophotochromism); the two diastereoisomers have been shown to be thermally stable, and no isomerization was detected at ambient temperature in the dark. The reaction is also thermally controlled (diastereothermochromism); the isomerization is accompanied by a simultaneous reversal of helicity and can be followed by circular dichroism. Such a system can be a chiroptical molecular switch [11].

**Halochromism:**

 Halochromismis the reversible color change due to a change in pH of a solution. The compounds themselves are weak acids or bases and become involved in acid-base reactions. A change in pH causes a change in the ratio of ionized and non- ionized states, since these two states have different colors, the color of solution change. This change in color can be used in acid-base titrations where the color change of the halochrome corresponds to the end point of the reaction.

**Piezochromism:**

 Piezochromism is the phenomenon when the crystals undergo a major change of color due to mechanical grinding. The induced color reverts to the original color when the fractured crystal is kept in the dark or dissolved in an organic solvent .An example of a piezochromic organic compound is diphenylflavylene [12].

**Triochromism:**

 Triochromism is the phenomenon when the crystals undergo a major change of color due to mechanical grinding (as in case of piezochromic), but the induced color change doesn’t revert to original color .The crystals, prior to fracture, are in metastable state .

**1.3.1. 6. Solvatochromism:**

 Solvatochromism is the reversible color change induced by solvents. This is due to changes in polarity of various solvents. This effect charge transfer mechanisms in solvatochromic compounds, causing color changes. The effect on the polymer’s color of increasing polarity of solvent is very similar to decreasing temperature of polymer.

**Halosolvatochromism:**

 Halosolvatochromism is the reversible change in color brought on by change in ionic strength without change in the structure of the chromophore. as example is the dye, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino) phenoxide . Upon addition of salts such as KI, Ca(SCN)2 to solutions containing the dye to undergo shift in the electronic absorption spectrum that increase with change in cation density the combination of both properties is termed “halosolvatochromism” [14].

**Ionochromism and acidichromism:**

 Ionochromism and acidichromismis the reversible color change caused by the addition of ions. It can occur in addition to photochromism and can trigger an alteration in conductivity. When ionochromism does occur alongside photochromism, both the relaxed and excited states can undergo ionochromism , i.e. in the photochromism reaction A  B, A can react to form AM+ and B can react to form BM+.

**Electrochromism:**

 Electrochromism is potentially the most commercially useful form of chromism. Electrochromic materials have been known since 1968. Three classes of electrochromic materials are known. These are metal oxide films, molecular dyes and conducting polymers. They have a number of potential uses, including displays, smart mirrors and windows, active optical filters and computer data storage. The key properties of electrochromic materials are their switching times, the contrast ratio, coloration efficiency. The coloration efficiency (CE) is the change in optical density per unit area of the electrode (QD) for given wavelength.

**Gated photochromism:**

 Gated photochromism is a special type of photochromism in which one or both forms of the photochromic system are transformed (chemically or electrochemically) reversibly into a non-photochromic form. The photochromic process is controlled like the flow through a gate. The opening or closing of the gate may depend on external stimuli such as protonation, oxido-reduction, solvation, and temperature. Gated photochromism is illustrated with the following example [15]. The conrotatory photocyclization of diarylethene **3** proceeds only from the antiparallel form (**3a**) in ethanol. The cyclization is completely inhibited in cyclohexane or decalin, where the parallel form (**3b**) is maintained by H-bond formation. Heating at 100 °C (or adding EtOH) disrupts the intra molecular H-bonds and allows the photochromic reaction to occur between **3a** and **3c** (Fig.1.7).

**Definition of Photochromism:**

 Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra .

The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally.

**Classification of photochromic systems**

 Photochromic systems involve very different structural or bond changes. They can be roughly divided in to six known classes based on the following simple reactions or processes [18,19].

**Photochromism based on *cis –trans* – isomerization.**

 The photochemical excitation of double bond system in olefins, azomethines or azo compounds often leads to reversible *cis* –*trans* isomerization. *Cis*- and *trans*- isomers can be differentiated by their absorption intensities and wavelengths. The change in wavelength is especially great in conjugated systems. For example the purple–red *trans*–form of both thioindigo **(3)** and indigo **(5)** can be photochemically transformed into the corresponding yellow *cis*–form **(4)** and **(6)**, respectively, which undergoes a slow thermal reverse isomerization [19-21].

**Photochromism based on tautomerism.**

 Usually tautomerism is isomerism in which the isomers are in equilibrium under ordinary laboratory conditions. Photochromic tautomerism includes mainly hydrogen transfer (phototropic) tautomerism and valence tautomerism. For example (Fig. 1.10), on exposure of crystalline anils of salicylaldehyde to light, a displacement of the absorption maximum from the UV-to the visible region takes place. This can be reversed through solvation in organic solvents [22]. Flash –photolysis experiments showed that this results from an interamolecular proton

migration which also takes place in the dissolved state [23-25].

This color shift originates from the transformation of the benzenoid system (End-form) into a *O*–quinod system (*Cis-form*) and (*Trans-form*) respectively

**1.5.3. Photochromism based on photo–redox reactions (electron transfer reactions):**

 The photochromic mechanisms of redox –photochromics are usually difficult to determine as they are multicomponent systems. Relatively well known is the system methylene blue / iron sulphate [26].

A photochemically excited methylene blue molecule M+\* probably reacts via a single electron transfer (SET) with Fe2+, which is oxidized to Fe3+. The methylene blue radical M**٠** produced disproportionates to give the colorless leucobase M**.**and dye molecule M+. The leucobase M**-**is then reoxidized thermally through Fe3+ to the dye molecule M+ through several intermediate steps yet unknown (Fig 1.11). Nanasaw [27] has reported studies on new photochromic viologens based on electron transfer. The colorless viologens composed of diquaternary salts of 4, 4**\** -bipyridine **(7)**, 2,2**\**-bipyridine, 1,10 phenanthroline turn into a violet-blue radical-cation **(8)** by one electron reduction [28-34], and are further reduced to the yellowish quinonoid **(10)** via the biradical **(9)**.

* + 1. **Photochromism based on dissociation**

 Hemolytic and heterolytic dissociation processes play the dominant role in the field of reactions responsible for the photochromic properties of chemical individuals [35-42].

**Homolytic dissocation processes**

 Imidazole **(11)** under oxidative condition form dimers **(13)** which are photochromic both in the crystalline states and in solution. A long–live intermediate **(12)** was assumed to be responsible for the observed purple color [36,43-45] and the radical nature was proved by ESR methods.

**Heterolytic dissociation processes.**

 Triarylmethanes readily undergo photolytic cleavage in solution when exposed to light of suitable wavelength. These systems are characterized by good to excellent quantum yields, high extinctions and great differences between the absorption maxima of leuco and colored products. Depending on structure and reaction conditions, either hemolytic or heterolytic cleavage may occur leading to colored fragments and the color normally fades in the dark by a thermally induced recombination process [37-46]. An alcoholic solution of malachite green leucocyanide has been shown to become deeply colored when exposed to ultraviolet light and discharge in the dark [47-50]. Lifschitz and his coworker [49] proposed the following equation for the photolysis and dark reaction of malachite green leuco-cyanide in absolute alcohol.

**Photochromism based on triplet–triplet Absorption.**

 Photochromic compounds based on triplet–triplet absorption is the easiest photochromic system which consists of molecules stable in ground states and metastable in excited state [51-54]. When light is absorbed by an organic substance dissolved in a rigid solvent, various processes might occur. The phenomenon of phosphorescence has been studies extensively with the mineral phosphorus, with dyes absorbed on various materials. Fluorescein **(14)** in boric acid matrix and picens in polymer layers are very good examples for such type of photochromism.

**Photochromism based on pericyclic reactions ( valance isomerization and electrocyclic reactions):**

 Pericyclic reactions are among the most important processes that allow for the design and construction of photochromic system and most of the photochromic systems belong to the group of valence isomerizations and electrocycliztion reactions.

**Photocycloaddition.**

**Intramolecular (2+2) photocycloaddition**

 According to Woodward–Hoffmann rules, the concerted (2+2) photo-cycloaddition is “allowed” in the excited state [55-58]. The same is true for photo dissociation. Other approaches by Dewar [59] and Zimmerman [60] indicate that the reactions involving (4n) electrons are favored in the excited state without any symmetry requirement. These reactions involve the singlet state (S1). Phenantherene and its derivatives **(15)** absorb light in the near UV region (Fig 1.15) (max=360nm); with activated olefins, the from cycloadducts **(16a)** and **(16b)** absorbing at higher energies (biphenyl chromophores) than addends [61,62].

**Intermolecular (4+4) photocycloaddition**

 The (4 s +4s) photocycloaddition and (2s+2s) cycloaddition constitute an important group of photochemical reactions. They can be formally depicted by the equation below

**Intramolecular (4+4) photocycloaddition**

 The linkage of two chromophores (A) and (B) by a non-absorbing and flexible chain can be of great value for generating photochromic systems which are concentration independent. According to its nature, the chain is also able to increase the solubility of these materials in various media. Indeed, the intrinsic folding rate of the chain should be in the range of the decay rate of the excited chromophore and the preferred conformations should be compatible with the geometry imposed on the intramolecular encounter complex, and, subsequently,

on the intermediate transition state [64]

 Irradiation of the yellow colored 9,9**\** -linked bisanthracene derivatives (< 400 nm) is usually accompanied, as observed for the intermolecular process, by a blue shift of the absorption spectrum of the starting materials (< 300 nm) owing to the saturation of the anthracene central ring in the photoproduct. Particular emphasis was given to use of short chains (Z bearing 1 to 4 atoms) in which a minimum of conformational transitions should be necessary for reaching the

encounter complex [64-67].

**1.5.8. Electrocyclization reaction**

 Electrocyclic reactions are the basis of many photochromic systems. It involves the formation of -bond between the termini of a fully conjugated neutral or ionic -system or its reverse process. An examples of electrocyclization processes in 4n- or 4n+2 systems (n= 0, 1) are shown in the scheme below (Fig. 1.18).

**The different types of electrocyclization processes are classified as follows:**

 **1.5.9.1. 4n systems based on 1,3–electrocyclization**

 Important photochromic heterocycles based on 1,3–electrocyclization (4–electrons) and opened ring forms iso–electronic with the cyclopropyl and allyl anion, respectively, are given. Substituted cyclobutene–butadiene interconversion

has not given rise to important photochromic systems (Fig. 1.19) [68].

 Oxiranes, for example, have been shown that room temperature photolysis of aryloxiranes (incorporating **(17)**) causes cyclo-elimination to give arylcarbenes **(19)** and carbonyl compounds **(18)** [69-72].

 Photolysis of **(20)** in rigid glasses produces highly colored intermediates [73], attributed to C-C bond cleavage with formation of carbonyl ylides **(21)** (Fig. 1.21).

 Ullman and his co-worker reported that, stable ylides have been generated also from substrates **(22)** incorporating aryl-substituted cyclopentadienone or indenone oxides. As shown in

 The photochromism of arylaziridines was discovered some time ago by Cromwell and coworkers [74]. Padwa and Hamilton [75] investigated the photochromism of glasses solution at 77ºCin the arylaziridine system **(26-28)**. On warming slowly the colors fade away and the aziridine is regenerated.

 All attempts to obtain colored species by carrying out the irradiation in the solution failed. Another class of photochromic aziridines based on 1,3–electrocyclization was investigated by Lown and Matsumoto [76] as well as

Padwa and Vega [77]

 **1.5.9.2. 4n+2 systems based on1.5 –electrocyclization.**

 The photochromism of dihydroindolizines (THIs) and tetrehydroindolizines (THIs)–new classes of photochromic molecules which are based on 1,5–electrocycliztion–were discovered in 1979 by Dürr [79,84]. The characteristic structural feature of the dihydroindolizines –based molecules is a five–membered ring , typically a cyclopentene anion. The substitution of one carbon atom in this molecule by a heteroatom generates heterocyclic five–membered rings [95-101].These can undergo a ring opening to zwitterionic species or neutral heteropentadienes. The process can be induced photochemically. This system can in principle be the essential structural unit of many photochromic systems, such

as those shown in [95-100]

 Type-1 systems (heteroatomic at position 1) possess a formally charge–free resonance formula such as **(30a)**. The cyclic structure can be represented only by the charged formulas **(29a, b)**. This is the reason why the more stable species in this case is the open–ring form **(30)**. In the type -2 systems the heteroatom is at position 2 allowing a uncharged resonance formula **(31a)** for the cyclic molecule to be drawn, thus favoring the latter. In the type -3 systems only the open ring **(33b)** can be written in a non polar form, which becomes here the most probable structure in the equilibrium shown. To the best of our knowledge, photochromic examples for type-1 systems have not been described so far. With type-3 systems, reversibility is not clear. However, type -2 and the mixed systems; type -1,2; type-2,3; and type-1, 2,3 possess photochromic properties when substituted properly. The categoriesof1,5–electrocyclization in new photochromic systems are described in the table below (Fig. 1.26).

**Synthesis of photochromic molecules based on 1, 5 electro cyclization reaction:**

 Viewing photochromic systems on the basis of a 1,5–electrocycliztion and its reverse, molecules must be envisaged in which the open ring as well as the cyclic structure have similar energy content. This is the challenge in synthesizing molecules with tailor–made photochromic properties in connection with easy access to these molecules.

 **Type -2 systems**

 are the basis of a new type of very potent photochromic compounds. Several routes to this type of system have been developed recently. Incorporation of a Δ2 Pyrroline ring into more complex molecules has led to a very efficient new class of photochromic compounds [78-94] including dihydroindolizines, tetrehydroindolizines and hexahydroindolizines.

**Dihydroindolizines**

 Dihydroindolizines can be obtained through the following routes:

 **Cyclopropene route**

 Reactions of the easily obtainable spirocyclopropenes **(37)** [104] with aza–heterocycles or azines such as pyridines, pyridizines, quinolines, isoquinolines, azaphenanthrenes, and other bases afford spiro (1,8a) dihydroindolizines **(35)**in good yield (50-84%). The intermediate in this synthesis is the color betaine

**(36b)**.Typical DHIs have been made via route (Fig. 1.27) [78-94,102-105].

 **Pyrazole route**

 In some cases i.e; with strongly electron–attracting groups such as CN or CF3, the cyclopropene route cannot be used. An alternative synthesis has been developed in which spiropyrazoles are photolyzed directly in an azine-solvent mixture. Intermediate in this process are the vinyldiazoalkanes **(40)** and carbens

 **(41)** [106-112]. Overall yields are between 40 and 70% (Fig. 1.28).

 **1.5.10. 2. Retro -1,5–electrocyclization route.**

 Routes 1 and 2 give access only to DHI **(35)** bearing identical substitutents R1or mixture of region isomers. However, it was shown that properties of DHI **(35)** are strongly dependent on the substitution pattern of the double bond 2,3. Therefore, two additional routes (3,4) were devised. Route 3 starts with diazoalkane **(41)**, which is formed **(42)** via pyrzole **(39)**. The vinyldiazoalkane **(41)** is converted to **(35)** in the same way as in the pyrazole route (Fig. 1.29) [107-115].

**Diazo–Route**

 Diazo–Rote uses a classical entry via the fulvene **(43)** into the diazoalkane series **(41)**. Identical conversions via **(37)** lead to the DHI **(35)** in 30-50% yield (Fig 1.30). Recently, new compounds of type **(35)** belonging to molecules with supra molecular properties have been prepared [94-103]

**1.5.11. Tetrahydro–and hexahydroindolizines:**

 Tetra–or hexahydroindolizines (THI and HHI) (type-2systems) were also synthesized using either of the formation routes. Reacting **(37)** with dihydroisoquinoline **(44)** in ether–methylene chloride solution gave the tetrahydroindolizines **(45)** in good yield (Fig1.31) [116]. The catalytic hydrogenation of **(45)** afforded the hexahydroindolizine **(46)** [117-139]. UV or visible light converts spirotetrahydroindolizine **(35)** into deep blue–green betaines **(47)** [123-128].

 The colored species obtained from THIs **(45)** can exist in two conformers, **(47a, 47b)** of which we favour **(47b)** (Fig 1.32). The trans form is the most stable one. HHIs **(46)** show photochromism as well. The process responsible for photochromism is no longer 1,5-electrocyclization and its reverse reaction but rather, a simple bond breaking to a zwitterionic structure [127,128].

**Biphotochromic systems**

 Applying one of the above four synthetic routes in combination with the same or a second approach, can lead to biphotochromic systems [129-132]. In principle, these are symmetrical systems such DHI-DHI and unsymmetrical systems such as DHIa- DHIb : HDI, photochromic systems are possible. In addition of spirene **(37)** to 1,3–or 1, 4 –diazines gives the potential photochromic bisadducts. The reaction of **(37)** with the bisazine affords the photochromic 1:1 adduct **(35)** and biphotochromic 2:1 adduct **(48)** (Fig 1.33), depending on reaction. By controlling the molar ratio of **(37)** to biazine, or reacting **(35)** with **(37)**, symmetrical and unsymmetrical bi photochromic DHI compound **(48)** are accessible selectively (allover yields 40-70%) [129-132].

 A typical system for an unsymmrtrical photochromic compound is molecule **(50)** . It is prepared by reaction of **(37)** with pyridosalicylidenanil [132]. Recently [133] unsymmetrical biphotochromic molecules [129], combining spiroxazine and spirodihydro–indolizine structure have been prepared [133].

**Photochromic systems based on pentadienyl anion with two heteroatoms**

Substitution of two carbons in position 2,3 of the pentadienyl anion creats a type 2,3 system. Such as dihydropyrazolopyridines (DHPP) [134-136]. The dipolar cycloaddition reaction, can also be used to prepare spirohetrocyclic compounds of 2,3 type. If a suitable substituted dibenzopentafulvene is reacted with pyridine the pyrazolo-pyridine **(58)** is formed in a high yield.

 After irradiation of **(58)** the colored species **(57)** is formed which undergo a thermal 1,5–electrocyclization to give **(58)** again (Fig. 1.36). In unsymmetrical molecules, region selective ring closure may occur.

**Phtochromic systems based on pentadienyl anion with three hetroatoms:**

 The resulting heterocycle is a triazoline ring. Photochromic molecule **(59)** containing these structural elements have been synthesized [135,136].

The UV/VIS spectra of **(59, 60)** show absorption maxima at 400 and 586 nm (in CH2Cl2), respectively, and half–life time, t**½,** of the colored species **(60)** is 60 sec. fluorescence is observed at 614 nm, with a rather low quantum yield of Φf = 7.6\*10-3, showing a value similar to those observed for DHI **(35)** and DHPP **(58)**.The photochemistry of this new photochromic system has not been studies extensively.

**Supramolecular photochromic systems, environmental effects and applications.**

 The properties of photochromic molecules such as DHI **(35)** and related compounds are dependent not only on structure but to a large extent also on their environment. Clear differences are to be expected if solution or solid phases of photochromic molecules are compared, i.e. (I) containing supramolecular anchor groups, (ii) in liquid crystalline phases, or (iii) polymer–containing photochromic systems. It is necessary to use the appropriate spectral methods for the detection of different properties. In addition to normal methods, photoacoustic spectroscopy (PAS), polarized light, and others may be applied.

 **Supramolecular systems.**

 Linking a suitable chain or ring to a dihydroindolizine generates photochromic systems of type A, B and C (Fig. 1.38).

These molecules are set up for supramolecular interaction with inorganic (salts) or organic guests. This concept has been applied to mono–or biphotochromic dihydroindolizines **(48)** [136-139]. A model calculation for type molecules using the force–field method CHARMm (Chemistry in Harvard Molecular Modlling) showed a linear arrangement of the poly(ethylene glycol) chain for compound **(61)** (Fig. 1.39).

 A very interesting effect is seen for the type B, the 19-N-oxa-6-crown in DHI **(62a)** is obviously protonated in methanol solution. In the presence of triethanolamine / MeOH, the base binds the proton and the free crown DHI **(62a)** is present in solution. Adding Li+, Na+, or K+ shows a strong hyperchromic effect and a slight bathochromic shift on the UV spectra. Dramatic changes have been seen in the half–life, *t*1/2. Li + shows the strongest decrease of, *t*1/2, by a factor of about **106.** These supramolecular assemblies can be clearly regarded as molecular switches, where in the supramolecular assembly the half–life of the colored form is clearly affected. Here the stronger or weaker binding of a salt can be felt in the reactivity, i.e; in the changes of Kr = 1/t1/2 of the electrocyclic process. Similar results were obtained for compounds of type C, as demonstrated [135] by the decrease of t1/2 in the presence of K+ or Ba+2. This indicates that the reaction rate can be reduced by supramolecular structure of K+orBa+2 and **(62b)** .

**Families of Organic Photochromic Compounds:**

**. Spiropyrans**

 “Spiropyrans” refers in general to a (substituted) 2*H*-pyran having a second ring system, usually (but not necessarily) heterocyclic, attached to the 2-carbon atom of the pyran in a spiro manner as shown in structure 1; i.e., a carbon atom is common to both rings. Compounds in which the second ring system is merely a saturated carbocycle such as cyclohexyl or adamantyl are better considered simply as 2,2-dialkylpyrans (Fig 1.41)

 The “pyran” portion of “spiropyran” usually refers to 2*H*-1-*benzo*pyran, as well as to its literal meaning of a single ring. The Russian literature often uses the less ambiguous (and therefore preferable) “spirochromene,” incorporating the common name for [2*H*]-1-benzopyran. A very wide variety of possible spiropyran ring systems is implied by the above definition, and a considerable number of these systems have been prepared and examined for use in various practical applications. The spiropyrans, their photochromism, and their applications have been extensively reviewed [140,141]. Little is said about spiropyrans or the many other known ring systems. Azaheterocyclic spiropyrans having benzothiazoline, benzoxazoline, thiazolidine,thiazine, oxazoline, oxazine, pyrrolidine, and piperidine moieties, which have beenextensively studied by Guglielmetti *et. al,* A spiropyran can be synthesized in several different ways. As indicated below .

**Spirooxazines.**

 Photochromism of spirooxazines implies the heterolytic or homolytic cleavage and reformation of the carbon–oxygen single bond of the oxazine ring, as seen in the equation. The first photochromic spirooxazine compounds synthesized (1970) belonged to the spiroindolinonaphthoxazine ring system. Both Ono and Osada [142] and Arnold and Vollmer [143] disclosed indolinospironaphthoxazines derived from 1-nitroso-2-naphthol. The synthesis of 1,3,3-trimethylspiro[indoline-2,3’-[3*H*]naphth[2,1*b* ][1,4]oxazine]. In liquid or solid solution, the parent indolinospiro- naphthoxazine (NISO) turnsblue upon irradiation with UV light and rapidly fades back to colorless when the activating radiation is removed. Only UV-A light (315–380nm) is required for activation. It is generally recognized that the blue color is caused by the formation of the ring-opened merocyanine structure, which absorbs in the region of 600 nm. There was essentially no activity in this area between the disclosure of Ono and Osada [142]

or Arnold and Vollmer [143]and the U.S. patent issued to Hovey et.al [144]. During the 1980s there was a rapid acceleration of research and publications on spirooxazines.

**Benzo and Naphthopyrans(Chromenes)**

 The benzo and naphthopyrans have the general structures (**63-66**) shown in following (Fig 1.45). In which R³ and R4 are notcombined to form a spiro heterocyclic group. The benzo or naphtho portions of (**63-66)** often contain additional substituents, while on the other hand, R¹ and R² are usually hydrogen.

 Until the past decade, the photochromism of benzo and naphthopyrans had gone largely unstudied, although their chemistry, including preparations, properties, and reactions, have been thoroughly explored [145,146]. Bertelson[147] and Laarhoven [148] briefly reviewed the photochromism of benzo and naphthopyrans as a part of their more comprehensive reports, respectively, on spiropyrans and related compounds and 4n+2 systems: molecules derived from Z-hexa-1,3,5-triene/cyclohexa-1,3-diene. The lack of interest until recently in the photochromism of benzo and naphthopyrans is due in part to the limited, and in some cases, misinformation found in the early literature. A case in point are the early publications dealing with 3,3-diphenyl-3 *H*-naphtho[2,1-*b*]pyran (**67**). In 1940 Wizinger and Wenning [149] reportedthe first preparation of this compound which, unknown to them, yieldeda two-to-one adduct (**68**) of diphenylethylene and 2-hydroxy-1-naphthaldehyde. This mistake was corrected by Livingston et.al [150] in 1960 when the adduct was correctly identified, but not before Hirshberg and Fischer [151] reported that the Wizinger product, which he believed to be **67** ,was not photochromic.

**Fulgides and Fulgimides.**

 The name “fulgides” (from the Latin fulgere, to glisten) was given by their first investigator, Stobbe, because they were isolated as fine glittering crystals. Their photochromic properties have been studied extensively by Heller [152].

The fulgide family constitutes an important type of photochromic compounds and several reviews [153,155] have been published. Stobbe [156] first discovered the Photochromism of some phenyl-substituted bismethylene succinic anhydrides in the solid state and named as fulgides. The general formula for fulgides is shown for compound **(69)** (Fig. 1.48).

Fulgides are generally synthesized by a Stobbe condensation of aryl aldehyde or ketone with a substituted methylene succinate, followed by hydrolysis and dehydration processes as shown (Fig 1.49).

The first compound of the fulgide family developed by Heller et.al [155] was a succinimide which was called a fulgimide. The general formula is shown in compound **(70).** Isofulgimides were also introduced by Heller et.al [157] in 1993. An isofulgimide is a fulgide derivative in which one of the oxygens in the carbonyl group of the anhydride ring of the fulgide is replaced by a substituted imino, as shown in compounds **(71)**and **(72).** In the same year, Heller et. al [155] reported a new kind of photochromic compound – dicyanomethylene derivatives of fulgide. According to the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), they should be named as 5-dicyanomethylene tetrahydrofuran-2-one derivatives, as shown in formula **8 (73).** Fulgenolide and fulgenate having the general formula found in structure **(74-76)** (Fig. 1.50) have also been published by Heller and Szewczyk [157] and Yokoyama et. al [158,159].

**Diarylethenes and related compounds***.*

 Stilbene is well known to undergo a *trans-cis* photoisomerization upon irradiation with UV light. In addition to this isomerization, stilbene shows a photocyclization reaction to produce dihydrophenanthrene .

Although in the presence of air the dihydrophenanthrene irriversibly converts to phenanthrene by hydrogen elimination with oxygen, it thermally returns to the initial stilbene in the absence of oxygen. When methyl groups are substituted at 2- and 6-positions of the phenyl rings, the compound undergoes a reversible photocyclization reaction, even in the presence of oxygen [160,161] Both isomers, open-ring and dihydro-type closed-ring forms, became thermally stable and cyclization/ring-opening reactions could be repeated many times while retaining adequate photochromic performance.

**Spirodihydroindolizines.**

 The photochromism of dihydroindolizines (DHIs) (a new class of photochromic molecules) was discovered only in 1979 by Dürr [162,163] These molecules are among the few new photochromes discovered in the past 40 years [3]. Their synthetic access has been exploited in detail and their photochemical and photophysical parameters have been studied in a broad sense [162-168]. The potential applications are vast and compare favorably with those of the known photochromes [169]. The chemistry and photochemistry of the DHIs have been described previously in several surveys [165-168]. This review will serve as a short introduction to the field. It will as well include typical preparation modes for the class of dihydroindolizines as well as their azahomologs, typical five-membered heterocycles. A new class of photochromics derived from these photochromic heterocycles (DHIs) that allows for supramolecular interactions is presented. Some typical applications that are close to commercially useful systems are discussed. The characteristic structural feature of the dihydroindolizines-based molecules is a five-membered ring, typically a cyclopentene anion. The substitution of the carbanion in this molecule by a heteroatom generates heterocyclic five-membered rings [170-172]. These can undergo a ring opening to zwitterionic species or neutral heteropentadienes. The process can be induced photochemically and is reversed either thermally or photochemically. Thus a new photochromic system based on a five-atom, six-electron (4n + 2)  system is created. This system can in principle be the essential structuralunit of many photochromic systems, such as those shown in.

 Type-1 systems (heteroatom in position 1) possess a formally charge-freeresonance formula such as **30a.** The cyclic structure can be represented only by the charged formulas **29a, b.** This is the reason the more stable species in this case is the open-ring form **(30).** In Type-2 systems the heteroatom is in position 2 allowing a uncharged resonance formula **31a** for the cyclic molecule to be drawn, thus favoring the latter. In Type-3systems only the open-ring **34b** can be written in a non polar form, which becomes here the most probable structure in the equilibrium shown. To our knowledge, photochromic examples for Type 1 systems have not been described so far. With Type-3 systems, reversibility is not clear. However, Type-2 and the mixed systems, Type-1,2; Type-2,3; and Type-1, 2, possess photochromic properties When substituted properly.

**Polycyclic quinones (periaryloxyquinones).**

 Photochromic quinones are a class of organic photochromic compounds that have become known as photochromic substances quite recently compared with other compounds [177]. They were discovered during the synthesis and studies of the properties of anthraquinone derivatives [178-180]. It turned out those anthraquinone derivatives with an aryloxy group at the peri-position relative to the carbonyl group change color reversibly in the presence of UV light. In succeeding years, various photochromic quinones have been synthesized. The properties of these compounds have been analyzed in books [177,181] and many papers [182-186]. At present, the photochromism of quinones is explained by the reversible photoinduced para-Ana-quinoid transformations due to photochemical migration of different hydrogen, aryl, and acyl groups [184].

**1.7. 8. Perimidinespirocyclohexadienones.**

 Valence and prototropic tautomeric reactions are among the most important mechanisms that govern transformations of a broad variety of photochromic organic systems [187,188]. Until recently, no examples of photochromic compounds have been reported whose photochromic behavior was due to a combination of these two tautomeric reactions. Such a combination, which is characteristic of ring-chain tautomerism [189,190] has been implemented in the photochromic and thermochromic rearrangements of a novel type of heterocyclic photochromes, derivatives of 2,3-dihydro-2-spiro-4'-(2',6'-di-*ter*t-butylcyclohexadien-2',5'-one)perimidine **77a** and its analogs [190]. The mechanism of the photochromic reaction involves cleavage of a C–N bond in the first singlet excited state of **(77a)** followed by the conformational rearrangement of the thus formed zwitterionic (biradical) intermediate **(78)** that precedes the final step of the intramolecular proton transfer (Fig. 1.59).

**Photochromism by Electron Transfer: ‘Photochromic Viologens.**

 Photochromic compounds functioning by an oxidation–reduction mechanism (electron transfer), especially a photoreduction mechanism, are known in inorganic materials such as silver halides, which are utilized in eyewear lenses. Although the number of organic photochromic compounds operating via electron transfer is fewer than those by isomerization, heterolytic (or homolytic) cleavage, and pericyclicreactions, several classes of compounds have been reported, such as thiazines [191], viologens [192], and polycyclic quinines [193].

**1.8.1.Photochromic systems in polymers:**

 Photochromic molecules may be dissolved in, adsorbed on, or bound to a suitable polymer. Depending on these three different environments, their properties may be changed in a variety of ways.

**Application of photochromic materials:**

**Application of photochromic materials based on 1,3–electrocyclization**

* Windshields or glass panes which darken on being exposed to glare.
* Sunglasses.
* Switching devices which excisting in two states; one state characterized by absorption of certain radiation over a wavelength range and the other state by high transparency.

**Application of photochromic materials based on 1,5– electrocyclization**

Application directly dependent upon the color change caused by the molecular and electronic structure of the two species (A, B) and their corresponding absorption or emission spectra. e.g.

1. Variable–transmission optical materials such as the photochromic ophthalmic lenses or camera filters.
2. Fluid flow visualization.
3. Optical information storage.
4. Novelty items (toys, T-shirts, etc.)
5. Authentication systems (security printing inks).
6. Cosmetics.

Application dependent upon changes in the physical or chemical properties, along with the more easily observed color change during the photochromic reaction; Examples of such properties are conductivity, refractive index, electrical moment, dielectric constant, chelate formation, ion dissociation, phase transition, solubility, and viscosity.

 Certain physical changes that occur when the photochromic entity is chemically attached to the macromolecular backbone of polymers are of special interest. Some examples of potential application utilizing the physical or chemical changes that accompany the observed shift in the absorption maxima are:

1. Optoelectronic systems (semi–conductor modulated by photochromic pigments ),
2. Reversible holographic systems.
3. Optical switches.
4. Optical information storage.
5. Photochemically switchable enzymatic systems.
6. Non–linearoptical devices.

Of all these potential application, a few have commercially been successfully (polymer–bases photochromic eyewear, novelty items and security printing inks) demonstrated to be useful (fluid flow visualization). Several others have shown considerable promise and may very well be utilized in commercial products in future.

**Obviously, photochromism is an open era for extensive studies and wide application.**

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 **Abstract**

The presented research work dealing with an important phenomena of photochemistry which is photochromism. The photochromic materials have been found to have many sounding and interesting applications. To follow-up such kind of application the present work has been done. In this work two family of thermally reversible and thermally irreversible photochromic materials have been synthesized and characterized using both spectroscopic and analytical tools. In the thermally reversible photochromic part (part A), six photochromic materials based DHI have been prepared via both chemical and photochemical reactions and their photochromic behavior in both solution and thin film has been studies. The most pronouncing properties is the structure- photochromic properties relationship which will led to tune the chemical structure of the DHI skeleton towards many applications. The dependence of the thermally reversible 1,5-electrocyclization of betaines under investigation on the temperature change is the most promising phenomena in this subject. Indeed, the chemical and thermal stability of the investigated betaines in polymer (PMMA) will open a new era for application of this family of compounds.

In the second part (part B), thermally irreversible photochromic material based indolylfulgimide has been synthesized through multi-steps reactions. Some of these reactions are really bottlenecked for fulgimide synthesis. Controlling the reaction conditions to obtain the desired product has been done and the optimum conditions have been determined. Pure 1,5-sigmatropic shift product has been separated in pure form and well characterized using both analytical and spectroscopic tools. Irradiation of the mixture of *E* and *Z* form with UV- light led to the formation of the colored *C*-form which upon irradiation with visible light led to the formation of the colored *E*-form. The kinetic behavior of both forward and back reactions has been measured. The functionalized fulgimide is promising candidate for finding applications in nanotechnology area as well as in the electronic devices.