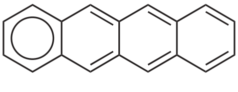
CHROMOGENIC MATERIALS, PHOTOCHROMIC

1. Introduction

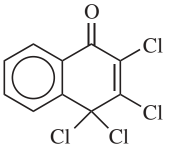
Photochromism can be simply defined as a light-induced reversible change of color. References to photochromism have found dating back to the 1800s (1,2).

Fritzche reported in 1867 (3) the bleaching of an orange-colored solution of tetracene (**1**) in daylight and regeneration in the dark.

Later, ter Meer (4) found a change of color of the potassium salt of dinitroethane in the solid state (yellow in the dark, red in the daylight). Another early example was published by Phipson and Oor (5) who noted that a post gate painted with a zinc pigment (probably some kind of lithopone) appeared black all day and white all night. In 1899 Markwald studied the reversible change of color of 2,3,4,4-tetrachloro naphthalene-1(4*H*)-one(βTCDHN) (**2**) in the solid state (6)



(**1**)



(**2**)

Interest in photochromism was continuous, but limited until the 1940–1960 period when there was an increase in mechanistic and synthetic work, particularly by the Israeli research group of Hirshberg and Fischer. In 1950 Hirshberg (7) suggested the term photochromism [(from the Greek: photos (light) and chroma (color))] to describe the phenomenon.

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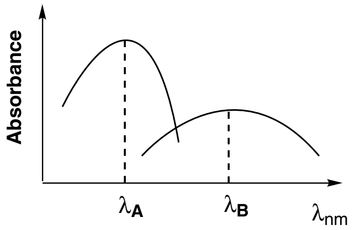


Fig. 1. Absorbance of A and B form.

However the phenomenon 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.

Photochromism concerns the reversible transformation of a chemical species (pigment) between two forms A and B having different absorption spectra and different molecular structure (see also Fig. 1).

$$A \underset{h\nu_2 \text{ and (or) } \Delta}{\overset{h\nu_1}{\rightleftarrows}} B$$

The thermodynamically stable form A generally absorbs in the uv-region (200–400 nm) and is transformed by irradiation ($h\gamma_1$) into the form B which absorbs in the visible region (400–750 nm). The reverse reaction can occur thermally (Δ) or photochemically ($h\gamma_2$). Some systems can function both thermally and photochemically.

The most general phenomenon is referred to as positive photochromism when the colored form B has $\lambda_{max}(B) > \lambda_{max}(A)$. Photochromism is called negative or inverse when $\lambda max(A) > \lambda max(B)$.

The most important application of this phenomenon is in variable optical transmission materials such as lenses that darken in the sun and return to their initial transparency in diffuse light. The first commercially glasses were made of glass lenses impregnated with inorganic (mainly silver) salts. In recent years organic photochromic lenses, which are lighter and therefore more confortable to wear despite their limited lifetime, have made an important jump in the world market.

Organic pigments are also more reactive, more photocolorable, and compatible with polymer matrices (8).

The photochromic phenomenon is generally observed in solution or in polymer matrix (viscous solution) and sometime in the solid state depending on the system.

Fatigue (or photodegradation) is defined as a loss in photochromic behavior, as a result of the existence of side reactions that decrease the concentration of the active species (as A or B forms) or lead to the formation of by-products that inhibit the photochemical formation of B.

$$A \underset{h\nu_2 \text{ and (or) } \Delta}{\overset{h\nu_1}{\rightleftarrows}} B \longrightarrow \underset{\substack{\text{degradation}\\ \text{products}}}{C}$$

Light and the oxygen are the two main causes of fatigue (9). The inhibition can result from quenching of the excited states of A (singlet or triplet) or from screening of the actinic light. Therefore, the reversibility of the phenomenon is not totally possible.

Photochromic pigments are generally used as embedded into supports such as polymer matrices, liquid crystals, or other materials and constitute photochromic systems.

These photochromic systems can be divided into two broad categories: organic and inorganic. The two types are quite different in their behavior and observable mechanisms and their characteristics are discussed giving different examples. It is noteworthy that the most important development of these organic systems has occurred during the twenty last years.

2. Inorganic Photochromic Systems

2.1. Silver Halide-Containing Glasses. The most important examples of inorganic systems are those containing silver halide crystallites dispersed throughout a glass matrix. The first description of photochromic silver halide-containing glasses appeared in 1964 (10,11). In general, these systems are characterized by broad absorption of visible light by the colored species and excellent resistance to fatigue.

The principle behind the generation of a photochromic glass with silver halide is the controlled formation of silver halide particles or crystallites suspended throughout the glass matrix (12–14). The formation of crystallites of the correct size and concentration is the key to a useful photochromic system. The general procedure involves the initial melting of a glass-forming mixture which is then cooled to a solid glass shape. Rapid cooling to room temperature results in a nonphotochromic glass. Holding the solid at a temperature in the range of 500–600°C for several minutes to hours causes the nucleation and growth of silver halide crystallites, the active photochromic species. Again, the size of the crystallites is important. With a size of less than 10 nm, significant darkening upon exposure to sunlight is not achieved. Above 20 nm, the scattering of visible light becomes a problem, leading to haziness. Also, with the larger particles the rate of thermal fading slows to an unacceptable rate.

Copper (I) (cuprous) ion serves as a catalyst for both the photochemical darkening and thermal fading reactions (10). Therefore, a small amount of cuprous ion is normally added to the glass batch.

The darkening reaction involves the formation of silver metal within the silver halide particles containing traces of cuprous halide. With the formation of metallic silver, cuprous ions are oxidized to cupric ions (10,13). The thermal or photochemical (optical bleaching) reversion to the colorless or bleached state corresponds to the reoxidation of silver to silver ion and the reduction of cupric ion to reform cuprous ion.

One of the most important characteristics of the inorganic glass matrix for a photochromic system is the temperature dependence of the solubility of silver halides (13). It is required that the solubility of silver halides be high at the temperature used to melt the glass mixture, and relatively low at the intermediate

Table 1. **Composition of a Silver Halide Photochromic Glass**[a]

Component	Wt%
SiO_2	55.8
B_2O_3	18.0
Al_2O_3	6.48
Li_2O	1.88
Na_2O	4.04
K_2O	5.76
ZrO_2	4.89
TiO_2	2.17
CuO	0.011
Ag	0.24
Cl	0.20
Br	0.13

[a] Ref. 15.

temperature at which the silver halide crystallites are formed. The approximate composition of a typical photochromic glass system that is marketed as Photogray Extra by Corning Inc., Corning, New York, is as given in Table 1 (15).

The color of the darkened state is controlled by the size and shape of the minute silver specks formed during photochemical reduction, but the relationship is not well understood. Since the shapes of the silver particles vary considerably throughout the matrix, a broad absorption over the visible range results (13,14). The color can be modified from gray to brown by changing the heat treatment for silver halide nucleation and growth and thus changing the size/shape distribution of the crystallites (16). The color can also be shifted from gray to brown by the addition of trace amounts of palladium or gold (3–4 ppm) to the glass batch (15).

An alternative to the uniform distribution of silver halide throughout the glass is the diffusion of silver ion into the surface of the glass. This has been accomplished by immersion of the glass article into a silver-containing fused salt, for example, silver nitrate plus sodium nitrate, molar ratio = 17:83 (17). Heat treatment to allow crystallite formation is still essential and copper oxide is added to the glass batch to catalyze the photochromic reactions. In general, photochromic glasses formed in this manner are not as active (do not get as dark) as the systems containing thoroughly dispersed silver, or have a slower thermal fade rate.

Thin films of photochromic glass containing silver halide have been produced by simultaneous vacuum deposition of silicon monoxide, lead silicate, aluminum chloride, copper (I) chloride, and silver halides (18). Again, heat treatment (120°C for several hours) after vacuum deposition results in the formation of photochromic silver halide crystallites. Photochemical darkening and thermal fade rates are much slower than those of the standard dispersed systems.

2.2. Other Inorganic Metal Salt Systems. An effective silver-free photochromic system can be obtained by the dispersion of crystallites containing cadmium halide and copper halide throughout an inorganic glass matrix (19,20).

Table 2. **Composition of Copper/Cadmium Halide Photochromic Glass**[a]

Component	Wt%
SiO_2	57.2–58.6
Al_2O_3	10.0–10.1
B_2O_3	21.5–22.7
Na_2O	8.1–8.2
F	1.05–1.14
Cl	0.43–0.45
CdO	0.43–0.45
SnO	0.20
CuO	0.12–0.15

[a] Ref. 20.

Heat treatment of the solid glass is again required to allow the formation of the metal halide crystallites. The mechanism of the darkening reaction is apparently the formation of colloidal copper metal particles by disproportionation of cuprous ion (20). The color of the darkened state, ranging from yellow-brown to green, is controlled by the type of heat treatment used for crystallite formation.

A typical range of glass compositions for this type of photochromic system is given in Table 2 (20).

Another inorganic photochromic glass system was prepared by the addition of europium (II) or cerium(III) to a soda–silica glass with an approximate composition of $Na_2O{-}2.5SiO_2$ (21) . The concentration of the rare-earth ion was low (100 ppm). With europium (II)-doped glass, the photochemical darkening resulted in an amethyst color that faded rapidly thermally. These glasses were subject to fairly rapid fatigue, losing all photochromic behavior after a 20-h exposure to uv radiation centered at 332.5 nm. This was probably the result of the oxidation of Eu(II) to Eu(III). Interestingly, the photochromic behavior could be recovered by exposure of the exhausted glass to high energy uv light at 213.7 nm.

Photochromic silver–copper halide films were produced by vacuum evaporation and deposition of a mixture of the components onto a silicate glass substrate (22). The molar ratio of the components was approximately 9:1 (Ag:Cu) and film thicknesses were in the range of 0.45–2.05 μm. Coloration rate upon uv exposure was high but thermal fade rates were very slow when compared with standard silver halide glass photochromic systems.

Simultaneous deposition of cadmium chloride and copper chloride by vacuum evaporation onto fused silica or optical glass resulted in photochromic thin films (23). The thickness ranged from 0.25 to 1.3 μm.

Thin films of photochromic silver complex oxides were prepared by anodic oxidation of silver metal films (24). Complex oxides, such as Ag_2VO_4, Ag_4SiO_4, and Ag_2PO_4, darkened by exposure to visible light, but required heating to 150–250°C for thermal bleaching.

2.3. Polyoxometalates. Photochromism of materials in which electron transfer and energy transfer within polyoxometalate and related metal oxide solids have been described (25). Structural characterization of both oxidized and reduced polyoxometalates is discussed in connection with the coloration mechanism.

2.4. Sols–Gels. Research on doping a photoactive organic phase into a transparent inorganic host matrix at molecular level to obtain optical composite has intensified in recent years.

The success of low temperature synthesizing sol-gel derived gel glasses doped with photoactive organics led to some new application opportunities in non-linear optics, the solid state tuneable laser, the visible display, and photochemical hole burning for example.... The recent development of preparation techniques and characterization methods to determine the structures and properties of the organic-inorganic hybrid optical functional materials, as well as the applications in luminescence, lasers, wave guide, wavelength division multiplexing, photochromism are reviewed in Ref. 26.

The new sol-gel derived materials for optics, organically modified metal oxide matrices have widely demonstrated their great potential (27). Most of the work performed in this area was concentrated on embedding organic or organo-metallic chromophores in an oxide network to make optical devices. The main advantages of the use of hybrid organic–inorganic nanocomposites result from their high versatility in offering a wide range of possibilities to fabricate tailor-made materials in terms of their chemical and physical properties, and macroscopic shape molding. Such materials emerging in this field are known as sol-gel photonics. There were some striking examples of the use of room-temperature processed hybrids to design materials with emission, absorption, second order nonlinear optical, and photochromic properties.

Ref. 28 contains a review on the design, synthesis, and some optical properties of hybrid organic–inorganic nano composites materials. Their properties depend on the chemical nature of the components, but also on their synergy.

The interface in these nanocomposites is important and one key point of their synthesis is the control of this interface. These nanocomposites can be obtained by hydrolysis and condensation reactions of organically functionalized alkoxide precursors. Striking examples of hybrids made from modified silicon, tin and transition metal alkoxides are presented. Some optical properties (photochromic, luminescence, NLO) of siloxane based hybrids are also discussed in this review (28).

3. Organic Photochromic Systems

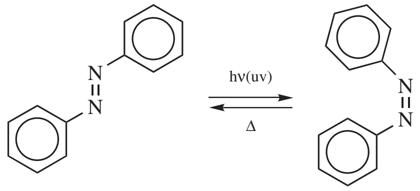
The organic photochromic molecular systems are numerous and it is necessary to classify them in different families based upon the mechanism of the photochromic reaction. Their photochemical or thermal reverse reaction lalso links them to different types of applications.

The most prevalent organic photochromic systems involve unimolecular reactions: the most common photochromic molecules have a coloress or pale yellow form A and a colored form B (orange, red, blue, purple or green).

Other systems are bimolecular such as those involving photocycloaddition reactions.

3.1. Photochromism Based on Geometric Isomerism.

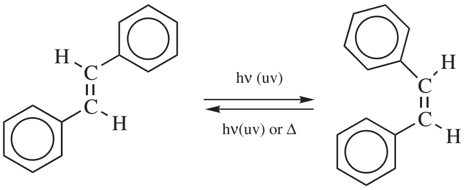
The simplest example of a photochromic reaction involving a reversible cis-trans isomerization is azobenzene [103-33-3] (29).



trans (anti) *cis* (syn)

This easy reaction produces a modest change in the absorption of visible light, largely because the visible absorption band of *cis*-azobenzene [1080-16-6] has a larger extinction coefficient than that of *trans*-azobenzene [17082-12-1]. Several studies have examined the physical property changes that occur upon photolysis of polymer systems in which the azobenzene structure is part of the polymer backbone (30).

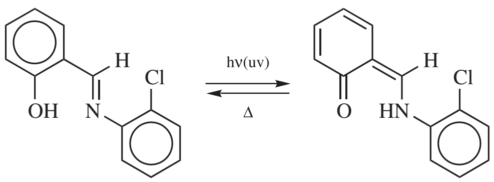
The cis-trans isomerization of stilbenes is another photochromic reaction of the same type (31). Although the absorption bands of the stilbene isomers occur at nearly identical wavelengths, the extinction coefficient of the lowest energy band of *cis*-stilbene [645-49-8] is generally less important than that of *trans*-stilbene [103-30-0].



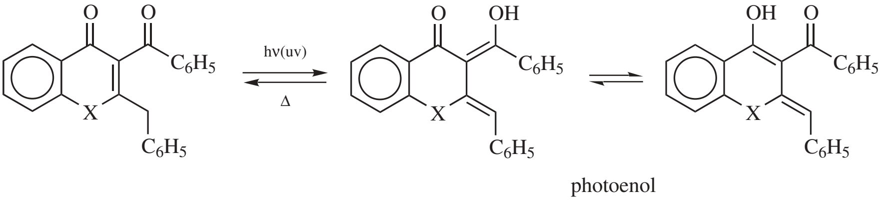
trans *cis*

3.2. Photochromism Based on Tautomerism or Hydrogen Transfer.

Several substituted anils (or imines or Schiff bases) of salicylaldehydes are photochromic, but only in the crystalline state. The photochromic mechanism involves an hydrogen transfer and a geometric isomerization (32). An example is the *N*-salicylidene-2-chloroaniline [3172-42-7].

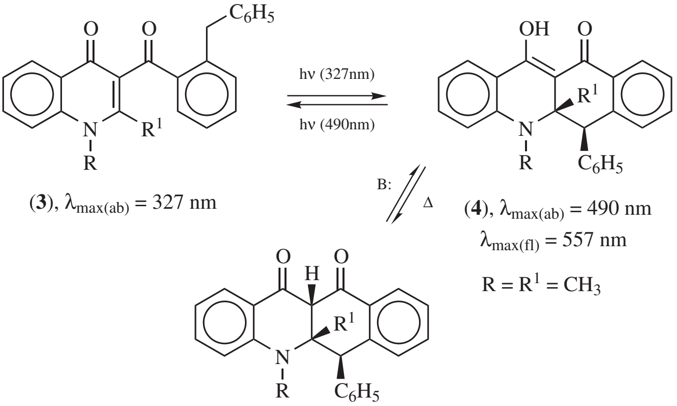


Phototropic photochromism of 3-benzoyl-2-benzyl chromones (33–35) (X = O), thiochromones (X = S) (35), or quinolones (X = N-R) (36) is another example:



The main limitation in this category is the weaker photosensibility (10 to 10^2 times) toward conventional photochromic pigments involving electrocyclization such as spiropyrans, spirooxazines, or naphthopyranes.

Some selectively substituted quinolones, such as 3-(2-benzylbenzoyl)-1,2-dimethyl-4(1*H*) quinolones (**3**) after irradiation in degassed toluene, lead to the formation of (5a*S*, 6*R*)-12-hydroxy-5,5a-dimethyl-6-phenyl-5a,6-dihydrobenzo[b]-acridin-11(5*H*)-one (**4**) (37).



(**3**), $\lambda_{max(ab)} = 327$ nm

(**4**), $\lambda_{max(ab)} = 490$ nm
$\lambda_{max(fl)} = 557$ nm

$R = R^1 = CH_3$

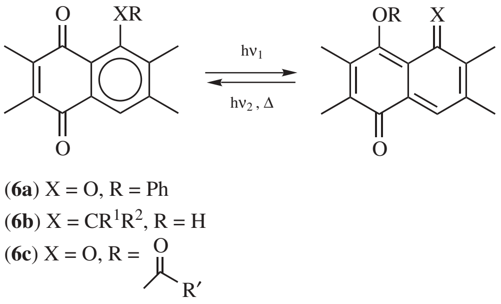
(**5**), $\lambda_{max(ab)} = 383$ nm
$\lambda_{max(fl)} = 443$ nm

Upon irradiation, derivative (**4**) ($\lambda_{max} = 490$ nm) can be converted back to (**3**). In the dark, derivative (**4**) is slowly converted to (5a*S*, 6*R*, 11a*S*)-5, 5a-dimethyl-6-phenyl-5a, 11a-dihydrobenzo[b]acridine-11,12(5*H*,6*H*)-dione (**5**) ($\lambda_{max} = 386$ nm). In the presence of catalytic amounts of a base, the equilibrium, (**4–5**), is established rapidly and irradiation of such solutions at 490 nm leads to the recovery of (**3**). Both (**4**) and (**5**) are fluorescent (λmax = 557 and 443 nm in toluene, respectively). No transients are detected and two isosbetic points are observed before the photostationary state is reached. Similar behavior is observed in acetonitrile, however, formation of the colored product (**4**) and its dark conversion into (**5**) proceeded more rapidly.

In a proposed mechanism, the initial photoenol or a biradical (formed upon irradiation, which is in fact a triplet state of the photoenol) can undergo further reversible cyclization owing to delocalization of the spin over the heterocyclic moiety.

This is a novel photoreversible photochromic system involving hydrogen transfer and photocyclization sequences.

Photochromic quinones exhibit photochemical migration of different hydrogen (6**b**), aryl (6**a**), or acyl groups (6**c**) (38).



(**6a**) X = O, R = Ph
(**6b**) X = CR^1R^2, R = H
(**6c**) X = O, R =

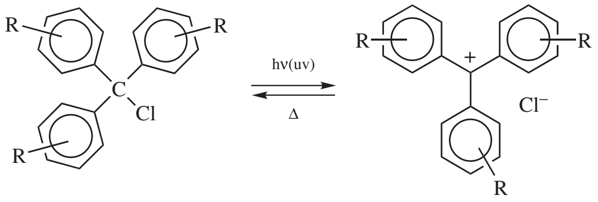
Quinones are a class of organic photochromic compounds that have been known as photochromic substances quite recently as compared to other compounds (39). They were discovered during the synthesis and studies of the properties of anthraquinones derivatives (40–42). It was determined that anthraquinone derivatives with an aryloxy group at the *peri*-position relative to the carbonyl group change color reversibly in the presence of uv light. Their photochromism is explained by the reversible photoinduced para-ana-quinoïd transformation due to photochemical migration of different hydrogen, aryl and acyl groups (43).

An example of ring-chain tautomerism and hydrogen transfer is perimidinespirocyclohexadienones (44), a novel type of heterocyclic photochrome.

When uv irradiated, an octane solution of 2,3-dihydro-2-spiro-4′-(2′,6′-di-*tert*-butylcyclohexadien-2′,5′-one) perimidine (7**a**) (R = H, Allyl) changes its color from yellowish to deep blue. The initial spectrum is slowly restored at room temperature (the effective life time of the colored form at room temperature is about 10^4s). No concentration dependence of the rate of the dark reaction was observed, which is in agreement with the intramolecular nature of the reactions (see Fig. 2).

The mechanism of the photochromic reaction involves cleavage of a C-N bond in the first singlet excited state of (7**a**) followed by the conformational rearrangement of the thus formed zwitterionic (biradical) intermediate (8) that precedes the final step of the intramolecular hydrogen transfer.

3.3. Photochromism Based on Dissociation Processes. Both heterolytic and homolytic dissociation processes can result in the generation of photochromic systems. An example of an heterolytic process is the reversible formation of triaryl methyl cations by photolysis of triarylmethylchloride in acetonitrile (45).



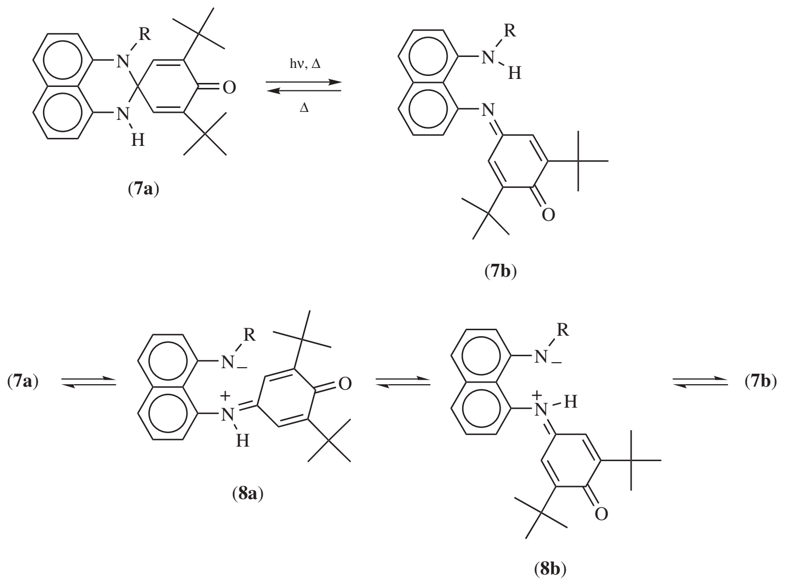
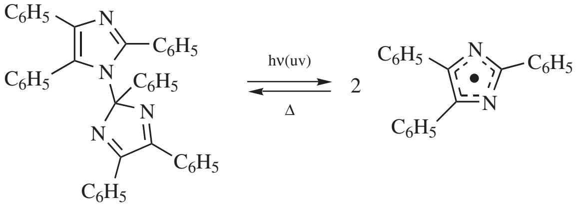


Fig. 2. Mechanism of a photochromic reaction involving perimidinespirocyclohexadienones.

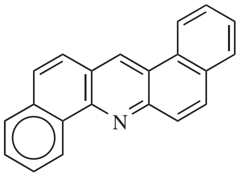
The classical example of a photochromic process involving an homolytic dissociation is the formation of a red-purple free radical by photolysis of bis (2,4,5-triphenylimidazole) (46).



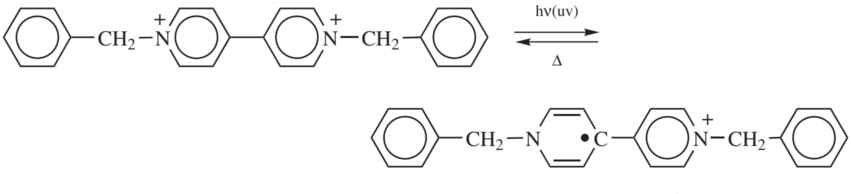
3.4. Photochromism Based on Triplet Formation.

Upon absorption of light, many polycyclic aromatic hydrocarbons and their heterocyclic analogues undergo transitions to their triplet state which has an absorption spectrum different from that of the ground state (47). In rigid glasses and some plastics, the triplet state which may absorb in the visible has a lifetime of up to 20 seconds (stabilization by the medium).

An example of such a polycyclic system is 1,2,5,6-dibenzacridine [226-36-8] which in a rigid matrix, absorbs uv irradiation to form a triplet state absorbing strongly in the visible with a λ_{max} at approximately 550 nm.

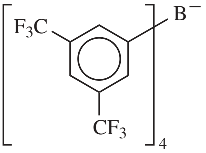


3.5. Photochromism Based on Redox Reaction. Although the exact mechanism of the reversible electron transfer is often not defined, several viologen salts (pyridinium ions) exhibit a photochromic response to uv irradiation in the crystalline state or in a polar polymer matrix (48). An example is poly (*N*-vinyl-2-pyrrolidone) [9003-39-8] (49).



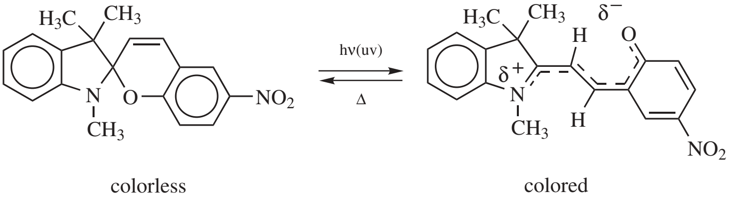
blue color (reduced form)

The reduced form (cation radical) is blue with a visible absorption maximum at 610 nm. The rate of the reoxidation of the reduced form is usually, but not always, strongly dependent on the presence of oxygen. The use of an electron-withdrawing counter ion leads to a photochromic system that is highly reversible in an inert atmosphere. An anion that has been used successfully is tetra-bis[3,5-di(trifluoromethyl)phenyl]borate [79230-20-9] (50).



3.6. Photochromism Based on Electrocyclic Reactions. The most common general class of photochromic systems involves electrocyclic reversible reactions. Within this general class the most well-studied compounds are the indolinospiropyrans, the indolinospirooxazines, the naphthopyranes (or chromenes), the diaryl or heteroarylethenes, and fulgides.The most important applications are in the area of variable optical transmission materials (51,52), optical memories and switches (53,54).

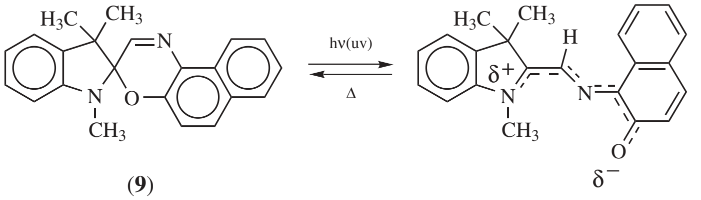
Spiropyrans. Nitro-substituted indolinospirobenzopyrans or indolinospironaphthopyrans are photochromic when dissolved in organic solvents or polymer matrices (55,56). Absorption of uv radiation results in the colorless spiro compound being transformed into the colored, ring-opened species. This colored species is often called a photomerocyanine because of its structural similarity to the merocyanine dyes. Removal of the ultraviolet light source results in thermal reversion to the spiro compound.



colorless colored

The nitro-spiropyrans present a good “colorability” (good quantum yield, high extinction coefficient absorption), but they are susceptible to fatigue which has limited their application.

Indolinospirooxazines. Indolinospirooxazines exhibit photochromism by way of a mechanism that is very similar to that of the spiropyrans (57,58).

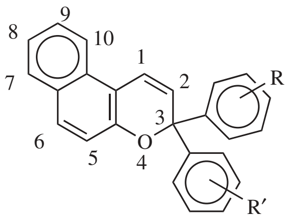


(**9**)

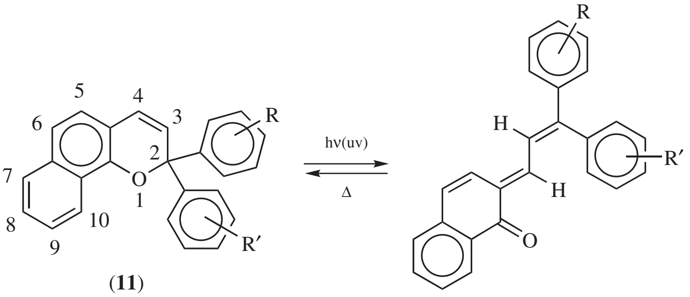
The spirooxazines however are much more resistant to fatigue and so could be used in making sunglasses.

As measured by the lifetime for photodegradation, indolinospironaphthoxazines such as (**9**) are 10 to 10^2 more stable than indolinospirobenzopyrans (59,60).

Benzo-and Naphthopyranes (or Chromenes). Intense research efforts by several groups interested in the commercialization of photochromic plastic ophthalmic lenses have, through structural modifications, dramatically enhanced the photochromic properties of benzo- and naphtho-pyrans [3,3-diaryl-3*H*-naphtho[2,1-b]pyrans (**10**) and 2,2-diaryl-2*H*-naphtho[1,2-b]pyrans (**11**)] (61).



(**10**)

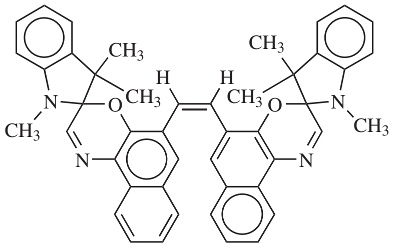


(**11**)

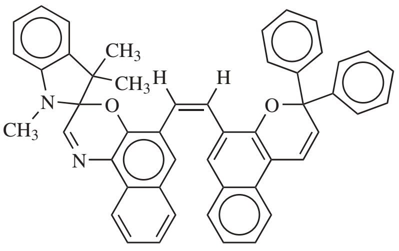
closed form

trans-quinoidal open form

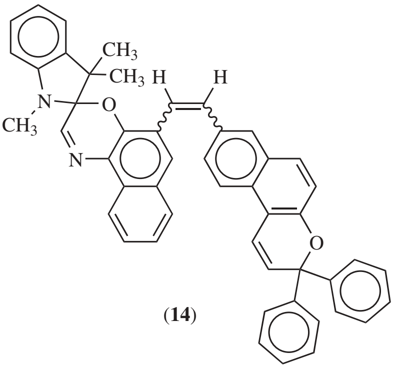
Many patents and publications cover this field of investigation and the photochromic properties depend greatly on the type of annellation, (and the possibility of hetero annellation), and the nature and the position of organic or organometallic substituents (62). In the present examples the di-aryl substitution on tetrahedral Csp3 constitutes a main structural advantage for the application of such molecules. Indeed with this kind of substitution, the main photochromic parameters (kinetics, absorption wavelength, colorability, fatigue) are greatly improved. Recently (63) new biphotochromic systems linked by a vinyl bridge have been synthesized from functionalized spirooxazine and chromene fragments using the Wittig reaction. The photochromic behavior of the above-mentioned compounds, which were thoroughly studied later (64–68), proved to be very complex. For example, not only successive opening of both oxazine or chromene rings, but also the $Z \rightarrow E$ isomerization and electrocyclization to form compound (**15**) were observed for compound (**12**) obtained in the Z configuration.



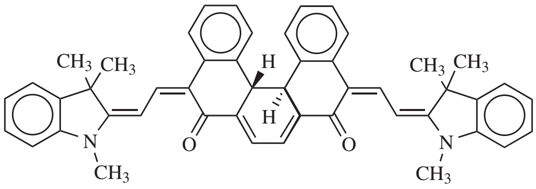
(**12**)



(**13**)



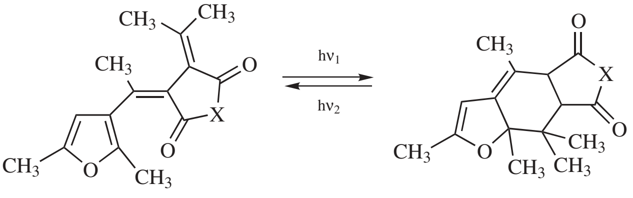
(**14**)



(**15**)

Heterocyclic, Fulgides, and Fulgimides. Another class of photochromic compounds, which operate through an electrocyclic mechanism, is the fulgides and fulgimides (69), although, with this class, the colored species is formed through a ring formation rather ring-opening (70,71). The reversion to the coloress species does not occur thermally at ambient temperature but can efficiently be driven photochemically with visible light.

The name "fulgides" (from the Latin fulgere, to glisten) was given by their first investigator, Stobbe (72) because they were isolated as fine glittering crystals. Their photochromic properties have been studied extensively by H. G. Heller and co-workers (73).



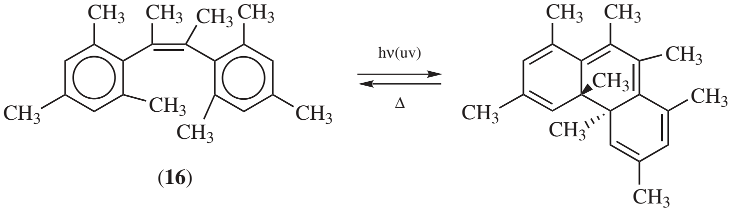
open form

closed form

X = O (fulgides)
X = NR (fulgimides)

Judiciously substituted (for example they do not have a labile hydrogen on the site of cyclization), fulgides have both high quantum yields for ring closure and opening and good fatigue resistance.

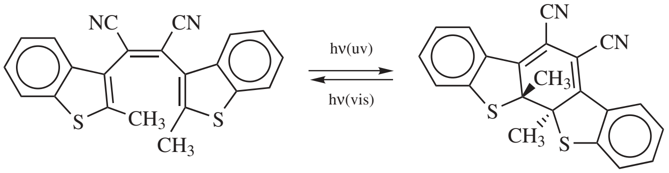
Stilbenes, Heteroarylethenes and Related Compounds. The photochemical ring closure of certain stilbenes, [eg, the highly methyl substituted compound (**16**)] and their heterocyclic analogues is the basis for another class of more sophisticated photochromic compounds (74–76).



(**16**)

By changing the substituents on the ethylenic linkage and replacing phenyl rings for heteroaromatic rings, photochromic systems (that are thermally reversible) are transformed into systems that are thermally irreversible, but photochemically reversible.

The transition between the benzothiophene-derivative isomers (**17**) and (**18**) is an example.



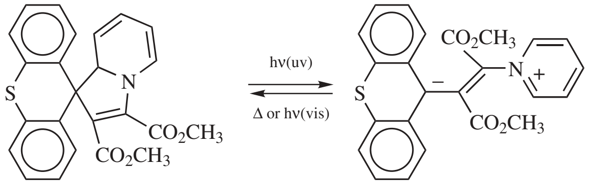
(**17**) (**18**)

M. Irie and co-workers (77), in Japan, have intensively studied such photochromic systems. They have developed synthesis, investigated physico-chemical properties and applications in the area of optical memories and switches. These systems have a good resistance to fatigue and the colored forms absorb from 425 to 825 nm. The photochromism of diarylethenes molecules as single crystal was also studied (78).

Dihydroindolizines. The dihydroindolizines are photochromic compounds that undergo a photochemical ring opening reaction to form a colored zwitterionic species (79–81).

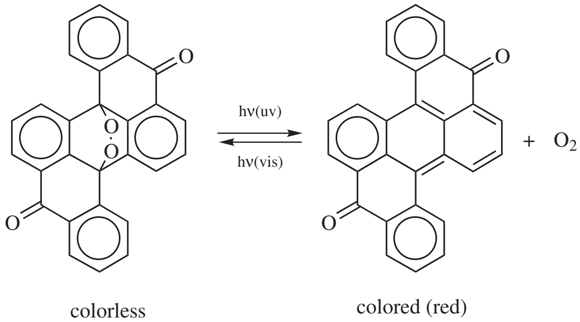
In general, this class of compounds involves complex methods of synthesis, and as in other photochromic systems, the colored species present a variety of colors depending on the substitution pattern.

The colored zwitterion reverts to the uncolored or slightly colored starting material either thermally or photochemically in the example below.



Some molecules have been linked to polymers or to inorganic salts giving supramolecular systems (80).

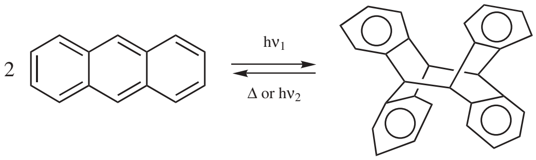
3.7. Photochromism Based on Cycloaddition Reactions Involving a Bimolecular Mechanism. The photochemically reversible formation of endoperoxides is an example of this type of system (82,83) involving $(4n+2)$ electrons. The reaction with singlet oxygen with some polycyclic aromatic compounds to form the endoperoxide and the photochemical elimination of singlet oxygen can be realized quantitatively.



The reaction is also accompanied by a rather drastic color change because of the disruption of the polycyclic chromophore during endoperoxide formation. A good example is the reversible formation of the endoperoxide of dibenzo(a, j) perylene-8, 16-dione (83).

In this case, the endoperoxide is colorless and the parent compound is red.

Another system concerns the dimerization of anthracenyl hydrocarbons involving $4n$ electrons [(4 + 4) cycloaddition] (84).



4. Uses

Although the proposed applications for photochromic systems are numerous few have received broad as commercial use.

4.1. Variable Optical Transmission Materials. The convenience of having lenses that darken automatically upon exposure of sunlight has proven appealing to spectacle wearers (85). By far, the most successful commercial applications is the use of photochromic silver halide-containing glasses in prescription eyewear.

The desire for plastic lenses in the ophthalmic market has also accelerated the research on organic photochromic pigments that are more compatible with polymer matrices and more photoresponsive (51,52).

In order to achieve an organic photochromic system for the eyewear market, two primary problems had to be solved. The first problem of fatigue resistance was alleviated with the discovery of indolinospirooxazines and naphthopyranes which are inherently more fatigue-resistant than other systems such as spiropyrans. The photostability of the spirooxazines can be improved even further by protecting them from oxygen (86,87) or by the addition of chemical stabilizers, specifically nickel complexes (88) or hindered amine light stabilizers (89). The second problem is caused by the relatively narrow absorption bands of activated organic photochromic molecules in the visible range of light. This problem can be handled by mixing compatible compounds such as indolinospirobenzoxazines or indolinospironaphthoxazines (57) and naphthopyranes (61) giving a much broadened visible light absorption (90).

Photochromic lenses for eyewear serve as variable density optical filters. Other applications for photochromic light filters have been proposed including glazing applications for solar attenuation, variable transmission camera lenses, and shields for protection against the light flash from a nuclear explosion.

Besides the use of photochromic systems in light filters, their color development has also received considerable attention. For example, the introduction of photochromic components into product labels, tickets, credit cards, etc, aids in the verification of authenticity (91,92). The active components are invisible until activated with an uv light source and then they are detected easily.

The color development of photochromic compounds can also be used as a diagnostic tool. The temperature dependence of the fading of 6-nitroindolinospiropyran served as the basis for a nondestructive inspection technique for honeycomb aerospace structures (93). One surface of the structure to be examined was covered with a paint containing the photochromic compound and activated to a violet color with uv-light. The other side of the structure was then heated, the transfer of heat through the honeycomb structure caused bleaching of the temperature-dependent photochromic compound. Defects in the honeycomb where heat transfer was inhibited, could be detected as darker areas.

Photochromic compounds that can be thermally faded have also been used in engineering studies to visualize flows in dynamic fluid systems (94–96).

Most photochromic compounds undergo large structural changes while being transformed from the uncolored to the colored form. This property has been used to examine the pore size of polymers by using the relationship of pore size and the kinetics of the photochromic response (97).

4.2. Optical Memories and Switches. The molecular property changes of photochromic molecules and especially the photoreversible ones can be applied to various photonic devices such as erasable optical memory media and photo-optical switch components.

The erasable memory media developed so far have been inorganic materials which use the magneto-optic effect or phase change as the basis for optical recording. But during the last years, the worldwide acceptance of CD-R (Compact Disk-Recordable) which uses organic dyes as the memory medium, has changed the situation and has given an impetus to find photochromic materials that change their refractive index by photoinduction.

Fulgides (98) and diarylethenes (99) are the main families involved in these applications. Nevertheless spiropyrans and spirooxazines could be used in association with polymers (PMMA or PVK) or liquid crystals (100).

The chirality is also used for chiroptical molecular switches in overcrowded alkenes, diarylethenes, binphthyl derivatives, fulgides, spiropyrans, photochromic polymers, polymer liquid crystals. (101)

4.3. Miscellaneous Applications. Azobenzenes, spiropyrans, fulgides, diarylethenes, anils coupled to polymers are used in the determination of linear and nonlinear optical properties of photochromic molecules and materials (102).

Photochromic materials can be used also for holographic recording (100).

The photoalignment control of liquid crystals could be realized through reversible photochromic molecules in three-dimensional networks (103).

Bacteriorhodopsin, a photochromic retinal protein having a biological function for the conversion of light energy into chemical energy, is used in data storage applications (104).

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