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Introduction: Organic Photochromic Molecules

Keitaro Nakatani, Jonathan Piard, Pei Yu, and Rémi Métivier

1.1

Photochromic Systems

1.1.1

General Introduction

Nowadays, the word “photochromism” (or “photochromic”) has been entered in several dictionaries [1]. It stems from the Greek words $\phi\omega\rho\acute{o}\varsigma$ (photos) and $\chi\rho\acute{o}\mu\alpha$ (chroma) meaning light and color, respectively. A simple definition of photochromism is the property to undergo a light-induced reversible change of color based on a chemical reaction [2].

Everyone, even without being familiar with this topic, can easily understand that materials possessing such a feature can find useful applications. Generally, using light as a stimulus is extremely attractive for at least two reasons: it can be conveyed to long distances with the “speed of light”; and it is an unlimited energy source although unevenly available in time and space. In addition, the notion of reversible change can be easily connected to objects, useful in everyday life, such as knobs, buttons, dials, handles, and levers, which are used to switch on and off domestic appliance and other devices and machines. Photochromic substances are widely present in glass lenses, initially clear, which turn dark under sunshine [3] (Figure 1.1). They are also present in trendy cosmetics and clothes.

In addition to these objects that have been around for a long time, the digital age has tremendously expanded the fields, where photochromic materials may play a role. The broad and current interest is transmitting, gating, and storing digital data [5]. CD and DVD are among the widely spread storage media, where light writes (and erases) information and optical properties are used to read, just as in photochromic systems. Due their reversible feature, photochromic species match the requirement of the rewritable recording media (CD-RW, DVD-RW), where memory bits have to commute between the two binary states (“0” and “1”) upon request. In this domain, there is a race for high-capacity data storage media, where information can be written and erased at high speed. As changes in photochromic



Figure 1.1 Photochromic lenses and clothes: contributions to comfort and to fashion [4].

systems occur in sub-nanosecond timescales, these are suitable for fast switching. Moreover, molecule is the elemental switching unit, comparable to a bit, and occupies less than a cubic nanometer. This means that the memory density can potentially reach a value of more than 10^{18} bit mm^{-3} . Proofs of concept of such media are given in the literature (Figure 1.2a, b), where two-photon phenomena are used to get a high resolution [6].

More recent contributions of photochromism can be found in the topic of fluorescence microscopy imaging, which is spreading very fast in many scientific fields of applications, such as biology, medicine, and materials science. Recent technological progresses have led to faster microscopes with better resolution, along with the development of stable and bright fluorescent probes. However, the optical resolution of conventional microscopy instruments is restricted by the fundamental diffraction limit, whereas the features to be probed are often smaller than 200 nm. To break this severe constraint and limitation, “super-resolution techniques” (or “sub-diffraction imaging methods”) were developed and have shown that resolution beyond the diffraction limit was accessible by exploiting controlled optical deactivation processes of fluorescent probes. Among them, microscopy based on photoswitchable fluorophores, such as photochromic fluorescent labels, has been successfully implemented. Figure 1.3a–e shows an example of the comparison between conventional wide-field microscopy and sub-diffractive imaging of

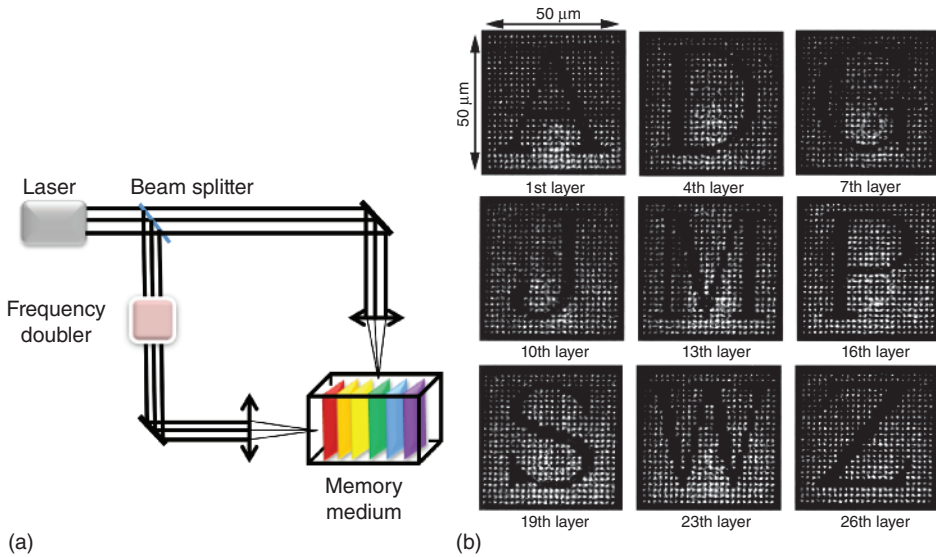


Figure 1.2 Rewritable optical memory medium based on photochromic compounds: (a) general structure of the recording medium [6d] and (b) alphabet letters recorded on the different layers [6b].

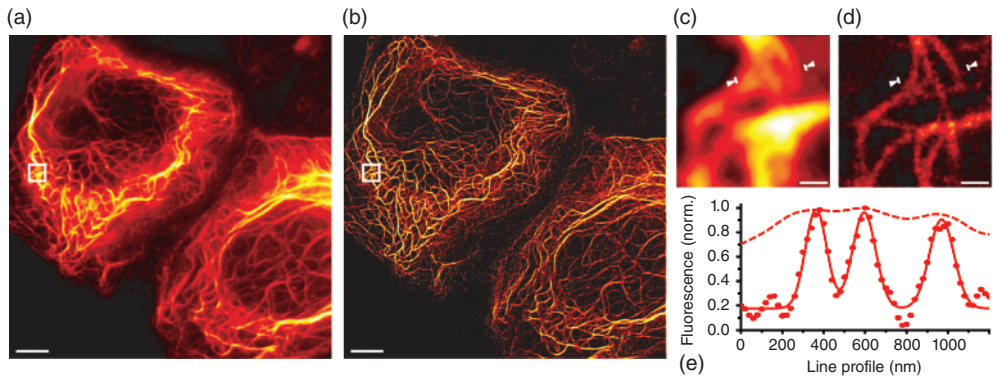


Figure 1.3 Super-resolution image of HeLa cells expressing keratin19 rsCherryRev1.4 by wide-field conventional microscopy (a) and by RESOLFT microscopy (b) (scale bar = 5 μm) and the corresponding magni-

fications of the highlighted area (c and d, scale bar = 500 nm). Line profiles (e) across the region between the arrows marked in (c) (full line) and (d) (dashed line) [7].

live HeLa cells expressing fluorescent photochromic proteins. No wonder photochromic compounds have entered the bio- and nano-worlds [8].

Light reflection or transmission change, used in the above-mentioned application, is the representative property modified in the photochromic process. As for color, in photochromic systems, traditionally, light is used as a trigger not only to

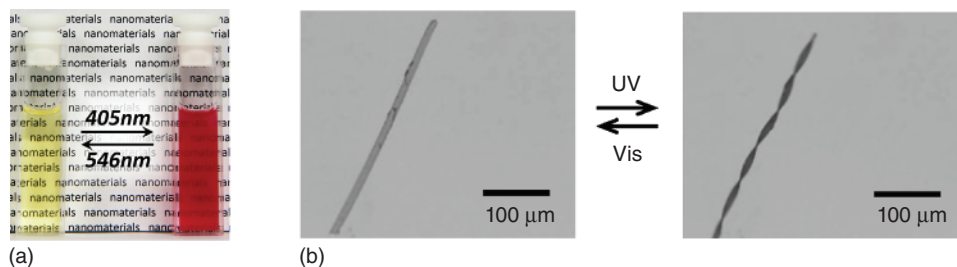


Figure 1.4 (a) Concomitant color and solubility changes of a photochromic solution [13a] and (b) color and shape changes of a photochromic crystal [14c].

induce the change but also to reveal the state of the system at a given moment. Other properties related to light, such as refractive index [9], fluorescence [8c, 10], and even nonlinear optical properties [11], are employed to read out. Indeed, concomitantly to the color, these properties are changed.

Photoswitching other physical or chemical characteristics, such as magnetic, electrical, conductive, or redox properties, is also a matter of interest [12]. Furthermore, one can take advantage of photochromism upon altering or taking the control of features, such as phase, solubility, reactivity, stereochemistry, complexation, or interaction between molecules or ions (Figure 1.4a) [13]. In materials, photochromism can induce shape changes, and opens up a wide field of interest in photo-induced mechanics (Figure 1.4) [14].

1.1.2

Basic Principles

In order to describe photochromism, the most common model introduced is a simple two-way reaction between two molecular species A and B. Although it may sometimes involve other species, the reaction is assumed to be unimolecular (Figure 1.5a).

A and B are separated by a potential barrier (ΔE). If this barrier is low, B is metastable and can revert back spontaneously to A. Previously described photochromic glass lenses operate according to this scheme. Such systems are called *T-type* referring to the thermally induced reaction from B to A. On the contrary, a high barrier features a bistable system. In this case, only photons are able to cause the reaction, and such systems are called *P-type*. In other words, nothing changes in the absence of light.

This last characteristic is important since it makes the difference between photochromic bistable systems and others, such as ferroelectric or (ferro)magnetic systems. In the latter, shuttling between the two states of the bistable system does not follow the same route, displaying the well-known hysteresis, when the polarization or the magnetization is plotted versus the electric or the magnetic field. In photochromic systems, no concept of hysteresis is involved in the rationale of bistability.

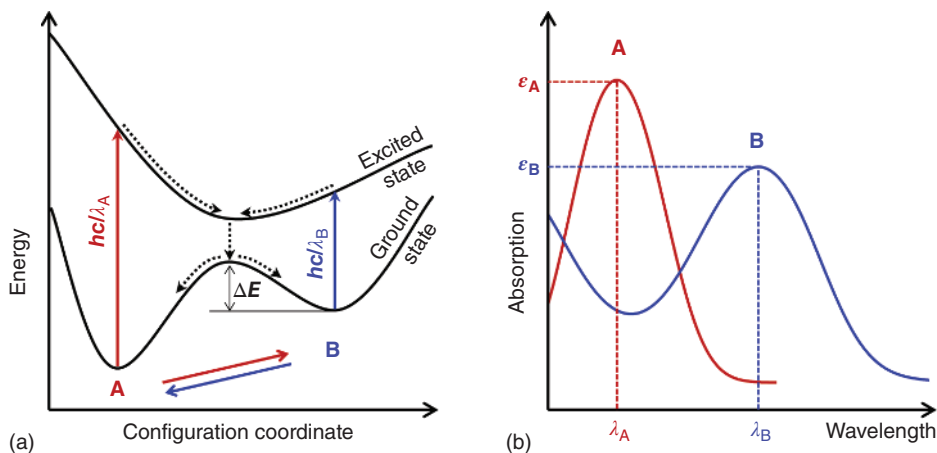


Figure 1.5 Photochromism: a two-way light-induced reaction between two molecules A and B. (a) Potential energy diagram and (b) the related schematic absorption spectra.

In usual photochromic systems, A absorbs in the UV or near-UV, with a characteristic absorption band at wavelength (λ_A). The absorption coefficient of A at this wavelength is ϵ_A . When a photon at λ_A is absorbed, A is excited from the ground to the excited state. The excited A yields B with a probability of $\phi_{A \rightarrow B}$ (see Appendix), known as the *quantum yield*. On the other hand, B reverts back to A, provided that the B is excited at λ_B , where it absorbs. The spectral position of the absorption bands gives an indication of not only the color of light needed to induce the reaction but also the color of the molecule itself (Figure 1.5b). Further quantitative development of this scheme is given in Appendix.

1.1.3

Photochromic Molecules: Some History

The historical reference of photochromism dates back to ancient times and the era of the Alexander the Great (356–323 BC). As King of Macedonia, he got into a vast world conquest. He conquered Asia Minor (now western Turkey) and extended his kingdom to the northwest of India in the east and Egypt to the south. Strategy and carefully coordinated attacks are essential conditions for victory. Thus, Macedonian head warriors were equipped with photochromic bracelets (the compound remains unknown up to now) exhibiting a color change when exposed to sunlight. Such color change was used by all warriors to indicate the right moment to begin the fight [15].

Over 2000 years later in 1867, Fritzsche reported for the first time the following peculiar behavior of tetracene solution: the initial orange color of the solution fades when the sample is irradiated by sunlight but can be recovered as initially when placed in a dark room (Figure 1.6) [16].

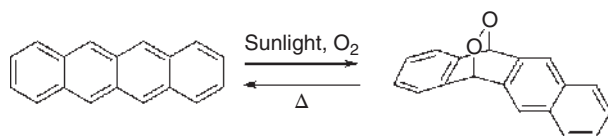


Figure 1.6 Photochromic reaction of tetracene.

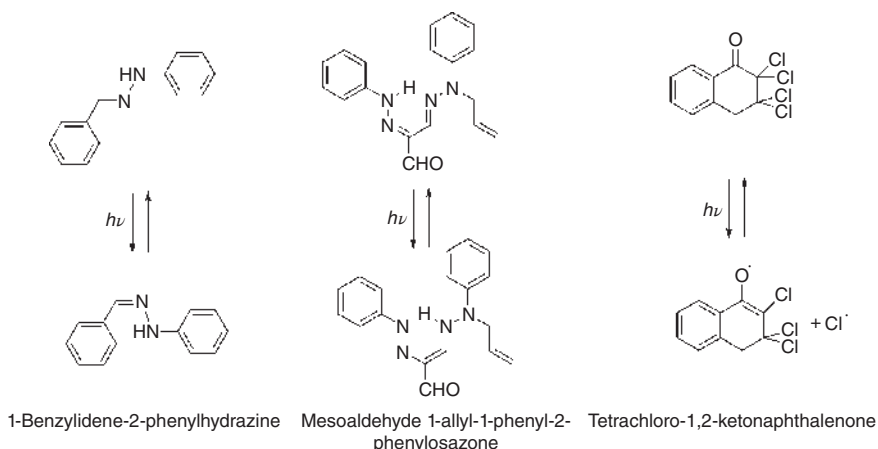


Figure 1.7 Examples of photochromic compounds deriving from phenylhydrazine, phenylosazone, and naphthalenone.

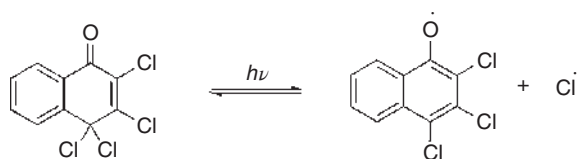


Figure 1.8 Solid-state photochromic reaction of 2,3,4,4-tetrachloronaphthalen-1-(4H)-one.

This first observation was followed by some studies [17] on solutions and materials with a similar behavior. Wislicenus noticed the color change of benzalphenylhydrazines (Figure 1.7) [17d]. Later, Biltz confirmed these observations and demonstrated the same behavior for some osazones (Figure 1.7) [18]. Finally, in 1899 Markwald, apart from his work on 1-benzylidene-2-phenylhydrazine (Figure 1.7) and tetrachloro-1,2-ketonaphthalenone (Figure 1.7), discovered the first solid-state photochromic organic compound [19]: the 2,3,4,4-tetrachloronaphthalen-1-(4H)-one (Figure 1.8). By that time, he was the first person to recognize this phenomenon as a new reversible photoreaction and gave the name (in German) of “Phototropie.”

Other main families of photochromic molecules dating back to this period are fulgides [20], salicylideneanilines (also called *anils*) [21], stilbenes [22], and nitrobenzylpyridines [23].

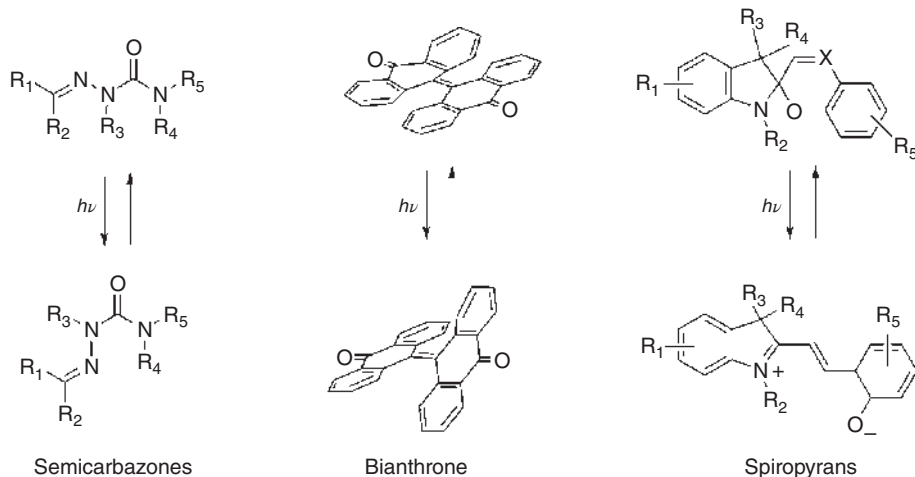


Figure 1.9 Photochromic reactions of semicarbazones, bianthrone, and spiropyrans.

Until the 1920s, much of the work was dedicated to the study of the phenomenon under a practical and descriptive approach than under a deeper scientific approach, that is, on the understanding of mechanisms. Therefore, all the efforts were focused on the synthesis of new molecules and on the optimization of irradiation conditions and fatigue resistant properties [24]. In the 1930s, although attraction for photochromism was low, nevertheless some major advances took place during this period. Indeed, Harris and Gheorghiu were pioneers in mechanistic studies of this phenomenon, respectively, on malachite green [25] and semicarbazones (Figure 1.9) [26].

The 1950s and 1960s probably represent a significant period for photochromic compounds, with the advent of technologies and methods enabling their investigations, especially spectroscopy, contrasting with the period described previously. Many new molecules, both organic and inorganic, were then synthesized and further studies on the mechanism were conducted during this period [15b, 24, 24g, 27]. Among all studies, the work of Hirschberg with the synthesis of the first bianthrone [28] and spiropyrans [29] (Figure 1.9) enabled major advances in the field of photochromism. Also, it was the period when it became usual to call this phenomenon “photochromism.”

Although there is a considerable amount of research going on azobenzene derivatives and other photochromic systems such as azine [30] and thioindigoides [31] (Figure 1.10), bottlenecks such as the lack of photoresistance of organic photochromic molecules, leading to degradation, prevented a fast development of applications in the 1960s and the early 1970s. However, during the 1980s, spirooxazines [32], particularly spironaphthoxazines, were developed for their high fatigue resistance, along with chromenes. This marked a significant turning point for photochromism in their use in variable transmission glasses. In such applications, T-type systems are required. In the meantime, compounds such as

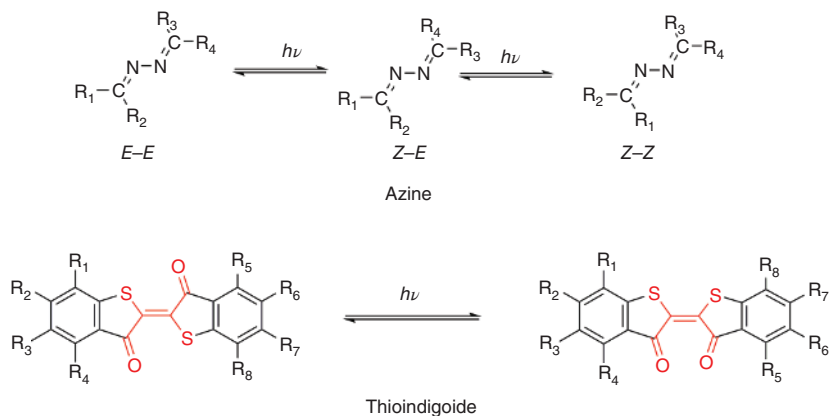


Figure 1.10 General formula and reaction schemes for azines and thioindigoide.

azobenzene derivatives, known for long as dyes and reported to be photochromic half a century earlier [33], were being intensively investigated for their photo-switching properties [34]. Other families of photochromic compounds, such as dihydropyrenes [35], anthraquinones bearing aryloxy groups [36], viologens, based on a photoinduced electron transfer [37], or flavylum [38] and oxazolidines [39], exhibiting both photochromism and acidochromism can be mentioned.

Regarding families of P-type molecules, applications for data storage [6c, 40] and molecular switches emerged in the 1990s. Although molecules such as fulgides have a century-long history as already mentioned, this period corresponds to the discovery of the diarylethene family. This domain certainly contributes to a tremendous increase in the number of publications since the 1990s. More details are given in the following section, which focuses on the most widely investigated photochromic systems.

Photochromism can be considered as being a fast growing domain of research, as it can be substantiated by a simple survey on the evolution of the number of publications in this subject (Figure 1.11). Since the 1990s, a fivefold increase in this number was observed. It is noteworthy to mention that a large number of special issues and review articles appeared during recent years [41] in addition to the references already cited.

1.2

Organic Photochromic Molecules: Main Families

The molecules presented in the previous section made the history of organic photochromism of the twentieth century. Some families of compounds spread, and others almost disappeared from the scientific scene. From the year 2000 to the present, most studies on organic photochromism deal with a group of less than 10 families of compounds. More than 2000 publications concern the diarylethene family. An approaching number of publications is reached when spiropyran,

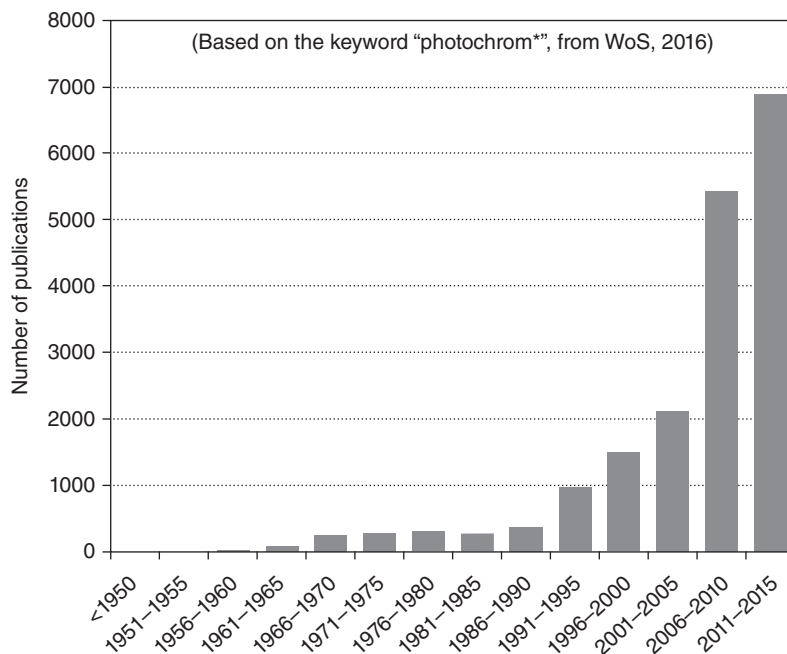


Figure 1.11 Number of publications on photochromism. (Source: ISI Web of Science.)

spiroxazine and chromene are added up. Azobenzene derivatives are also widely studied, and these totalize more than 1000 publications during the same period. A few other families of organic photochromic molecules exceed 100 publications, such as salicylideneanilines (anils), fulgides, and hexaarylbiimidazoles (HABIs).

This section mainly focuses on the families that are categorized by the type of chemical reaction involved during the photochromic process.

1.2.1

Proton Transfer

Derivatives of salicylideneaniline are probably the most studied photochromic molecules involving a proton transfer [42]. Also called *anils*, they are mainly substituted salicylideneanilines and variants, where aniline is replaced by groups, such as aminopyridine or aminothiophene. In fact, anils are Schiff bases. Reports on the photochromism of anils date back to the beginning of the twentieth century [21]. However, thorough studies leading to significant characterization started only during the 1960s [43]. Proton transfer reactions are present in different mechanisms involving natural systems [44]. Photochromism of anils can be performed in several media, from solution to inclusions or encapsulated media [6, 41, 45], and even in some cases in the solid state, with medium-dependent behavior.

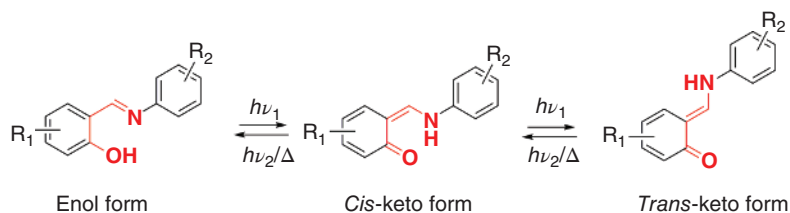


Figure 1.12 Photoreaction (phototautomerism) of anils: the enol to keto reaction.

Under UV irradiation, an intramolecular proton transfer is induced and allows the passage from the enol (in fact a phenol) to the *cis*-keto (ketone) form in the excited state called excited-state intramolecular proton transfer (ESIPT). This transfer is quickly followed by a *cis*–*trans* isomerization at an excited state to reach a *trans*-keto form (Figure 1.12). Considering the result of this reaction, it may also be called *phototautomerism*. All the process occurs within a few picoseconds in solution, and a few hundred picoseconds even in solid state [46].

Enol form absorbs only in the UV (or near-UV) and is pale yellow in most cases, whereas the keto isomer is usually red. Conjugation is less extended in the latter, so such feature may sound unexpected; however, the bathochromic shift is due to an $n-\pi^*$ transition evolving in the keto form [47]. Upon UV excitation, a luminescence can be observed (Figure 1.13). Investigations during the last few decades show that this is concomitant to the ESIPT: the deexcitation of the keto state is then responsible for it, leading to a Stokes shift of more than 150 nm [46d, 48].

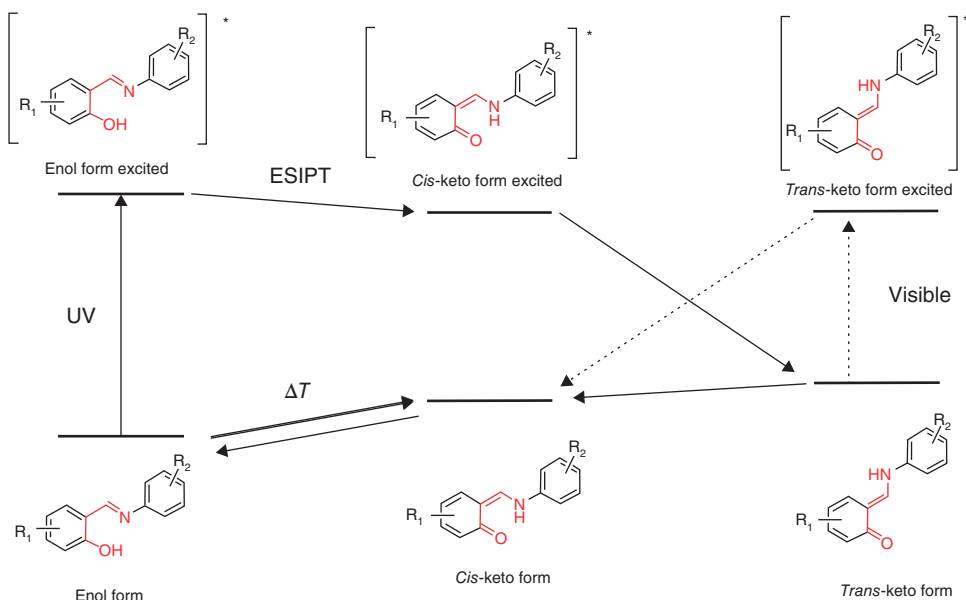


Figure 1.13 Photochromism of anils: schematic diagram illustrating the UV and visible light-induced reactions, and the excited-state intramolecular proton transfer (ESIPT).

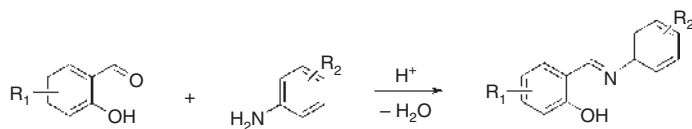


Figure 1.14 Synthesis of anils: basic method by condensation of salicylaldehyde and aniline derivatives.

Anils are of T-type. In a solution, the keto photoproduct reverts back to the enol very quickly, typically within a few milliseconds [47d, 49], whereas in the solid state, it may vary from a few seconds to several months [42b, 50]. A consequence of this is that the photochromism of anils can barely be observed in solution (see Section 1.3.4 for detailed explanations), but only in the solid state.

The synthesis of anils is rather straightforward (Figure 1.14). Based on the condensation of salicylaldehyde and aniline derivatives in an acidic medium, hundreds of molecules with various substituents providing steric and/or electronic features were synthesized.

The second most studied family of compounds with a proton transfer is the dinitrobenzylpyridine (DNBP). Although its color change upon UV irradiation was evidenced in the 1920s [23], unraveling the nature of the species and the reactions involved was possible only several decades later [51]. The colorless CH form (Figure 1.15) is the most stable, and UV excitation yields the OH and NH forms.

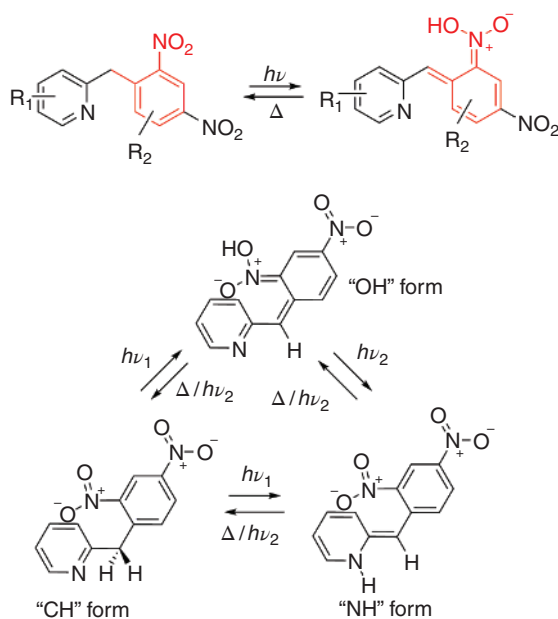


Figure 1.15 Photochromism of dinitrobenzylpyridine (DNBP) between the CH and NH forms, involving the OH species.

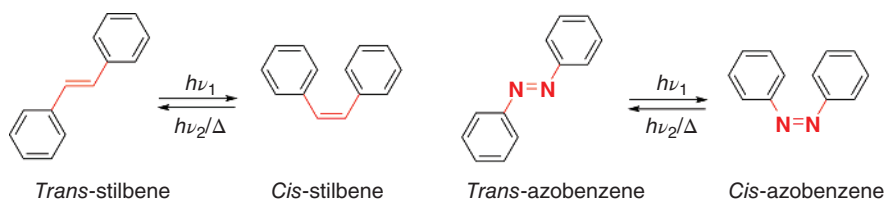


Figure 1.16 *Trans*–*cis* isomerization of stilbene and azobenzene.

The OH form is the least stable and spontaneously converts to its isomers. DNBP can be obtained by nitration in $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture from benzylpyridine.

1.2.2

Trans–Cis Photoisomerization

Most chemists have heard about the isomerization around carbon–carbon double bonds at the early stage of their studies when they learn about *trans*–*cis* (or *E*–*Z*) isomerism. Textbook cases are stilbene, as well as azobenzene (Figure 1.16) and their derivatives. These reactions can be induced by light, which circumvents the relatively high-energy barrier in the ground state. Moreover, in many photochromic systems, *trans*–*cis* reaction is one step of the process, as it is the case for anils and spiropyrans (see Sections 1.2.1 and 1.2.4), and appears as an alternate photoinduced process in fulgides or diarylethenes (see Section 1.2.4).

The knowledge of the development of azobenzene derivatives that has been used as dyes for more than a century is essential; nowadays, they represent the main family of photochromic molecules based on *trans*–*cis* reaction. It would not be possible to cite the over thousand publications, but there are some reference book chapters and book reviews [34, 52].

For the sake of simplicity, in the following, the derivatives of the azobenzene called *azobenzene(s)* are discussed. The color of azobenzene is generally yellow and its substitution yields a bathochromic shift, providing an orange or red color. Both isomers have two characteristic bands, π – π^* and n – π^* , the latter one lying in a lower energy region and being less intense, as it is symmetry forbidden.

Changes in the absorption spectra between the two forms are generally not very pronounced due to a small difference in electron delocalization between the two isomers, and the color change is invisible by the naked eye. In contrast, the photochromic reaction induces very significant change of the free volume of the molecule [53]. Therefore, these molecules are extensively used to induce mass rotation or migration in materials, leading to dichroic and birefringent media, surface relief patterning (Figure 1.17a–c) [11, 54], or mechanical effects [14b,d]. In addition, azobenzenes are introduced for their switching ability when properties not related to color, for example, magnetic, are sought [55].

There are several different methods to synthesize azobenzenes and are thoroughly described in a recent review article [52b]. The most widely used methods

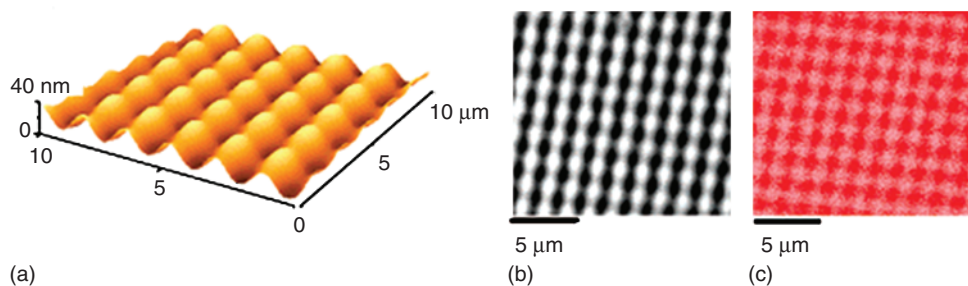


Figure 1.17 Crossed surface relief grating obtained by 2D photopatterning on a thin film of azobenzene derivative: (a) atomic force microscope (AFM) topographic image, (b, c) one- and two-photon transmission images with dark areas corresponding to hills [54b].

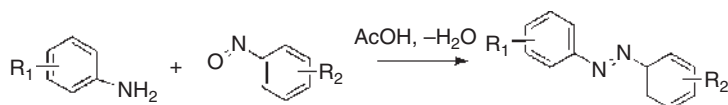


Figure 1.18 Synthesis scheme of the Mills reaction used to obtain azobenzenes.

are the diazo coupling and the Mills reaction between aromatic nitroso and aromatic amine compounds (Figure 1.18).

1.2.3

Homolytic Cleavage

In this class of compounds, HABI discovered by Hayashi and Maeda in the 1960s and its derivatives play an essential role [56]. The homolytic cleavage of the C–N bond between the two imidazole rings involved in this type of compound can be induced by heating, light irradiation, or pressure. It leads to the formation of two radicals (TPIR triphenylimidazolyl radical) as depicted in Figure 1.19. Recombination to revert back to the starting imidazole dimer (also called TPID triphenylimidazolyl dimer) can be carried out thermally and driven by radical diffusion.

TPIR has a large absorption band in the visible light, whereas TPID absorbs only in the UV light and is thus colorless. Compounds of this family exhibit

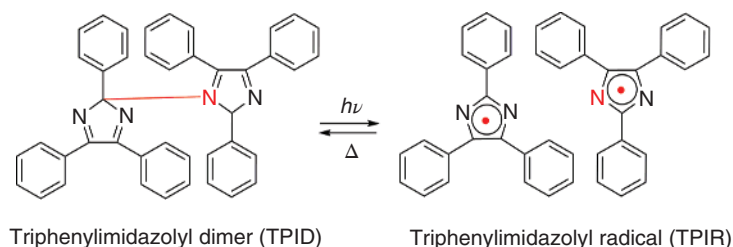


Figure 1.19 Photochromism of hexaarylbiimidazole (HABI) between the triphenylimidazolyl dimer (TPID) and the triphenylimidazolyl radical (TPIR) pair.

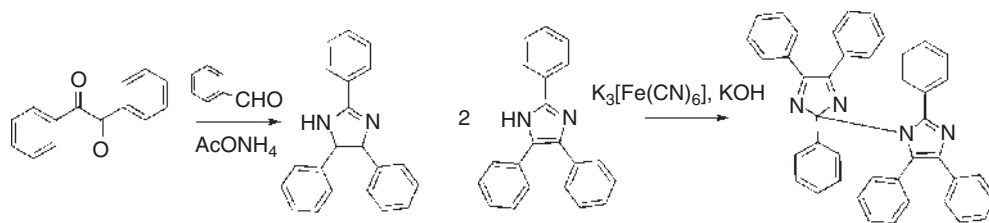


Figure 1.20 Basic synthesis scheme of HABI.

a T-type photochromism. Although the cleavage upon UV irradiation takes place within less than 100 fs, recombination can take up to few minutes at room temperature [57].

The preparation of HABI is rather straightforward (Figure 1.20), at least for the simplest and basic methods. The precursor, triarylimidazole (lophine), known since the end of the nineteenth century, can be obtained by the reaction between benzoin and an aldehyde in the presence of ammonium acetate.

Along with photochromism, HABI also exhibits piezo- or thermochromism. This has to be related to the controversy about the way the two imidazole moieties are connected: in fact, upon the synthesis of the TPID form, several isomers are formed. Studies carried out during several decades lead to the conclusion that C–N bonded ones lead to photochromism, whereas C–C bonded ones lead to piezo- or thermochromism [58]. During the 1970s, HABI was used as industrial photoinitiator for imaging and photoresists. In the process, the TPIR abstracts hydrogen atoms from crystal violet precursor enabling imaging [59].

1.2.4

Cyclization Reaction

In the mostly encountered photochromic systems, the reaction is a cyclization. In most examples, the reaction involves six π electrons delocalized over six different atoms. This is the case for spiropyran, fulgides, and diarylethenes and some related families such as spirooxazine, chromene, and fulgimides. Overall, they represent a largely predominant part of the research carried out on organic photochromism during the last decades.

1.2.4.1 Spiropyrans, Spirooxazines, and Chromenes

As illustrated in Figure 1.21, the most common type of spiropyran is based on indoline and benzopyran. This basic structure can bear substituents (alkyl, alkoxy, nitro, halogeno, etc.), and it can also be extended to larger structures (e.g., naphthopyran instead of benzopyran) or to modified structures (e.g., thioindoline in place of indoline) [29, 60].

Spiropyrans have been extensively studied along the past half-century. For such compounds, UV light irradiation of the colorless closed form (also called the *spiro* or the *N form*, for normal) leads to the carbon–oxygen bond cleavage (open ring

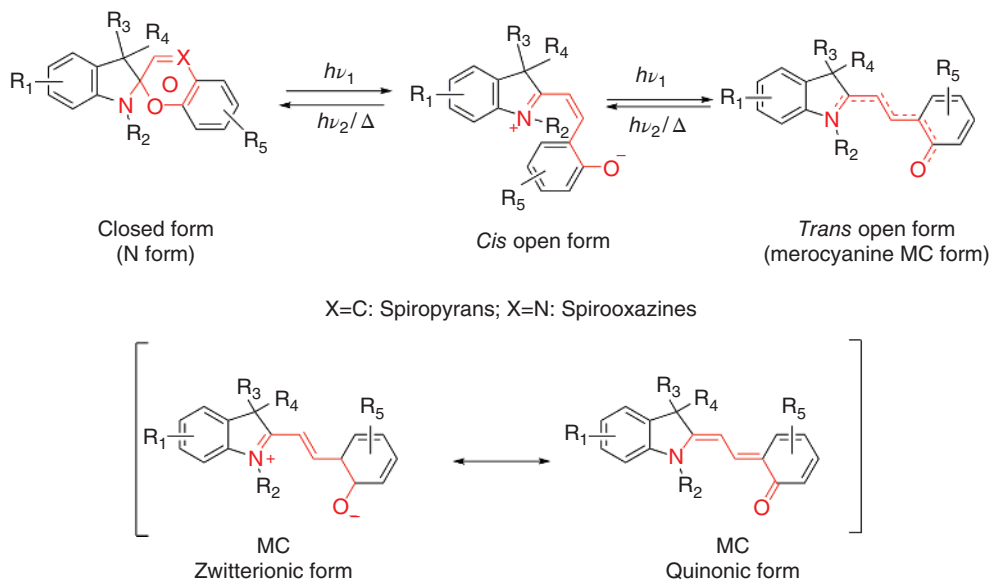


Figure 1.21 Photoisomerization of spiropyrans between the closed and open merocyanine (MC) forms. Resonant zwitterionic and quinonic forms of MC.

reaction) of the pyran ring, followed by a *cis*–*trans* isomerization to finally reach the colored merocyanine (MC) form. The latter is highly conjugated and has two mesomeric (resonant) forms, zwitterionic and quinonic. This feature can be connected to the presence of an intense absorption band in the visible, and the color of the MC form. On the contrary, in the closed form, conjugation is broken at the spiro carbon atom and the molecule is colorless and absorbs only in the UV region.

Spiropyran is a typical example of T-type compounds family as no P-type molecule has been reported yet. In a majority of cases, the closed form is the more stable one, the MC form being metastable, although a noticeable amount of the MC may exist at equilibrium for some compounds [61] and also in polar media [62]. Due to its electronic structure, the MC form is highly solvatochromic and its stability is strongly solvent dependent: for example, in one representative compound, the so-called 6-nitro-BIPS (1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2'-2*H*-indole)), the rate of the thermal reaction is 300 times slower in ethanol than in benzene and is related to a higher activation barrier of the ground state of the former than that of the latter [63].

In spiropyrans, nonbonding orbitals bearing lone pairs of the nitrogen and oxygen atoms connected to the spiro carbon, respectively, interact with the antibonding orbitals of the C–O ($\sigma^*(\text{C}-\text{O})$) and the C–N ($\sigma^*(\text{C}-\text{N})$) bonds. As illustrated in Figure 1.22, the former is stronger than the latter and leads to a weakening of the C–O bond even in the ground state. This C–O bond is then cleaved upon UV irradiation.

Two electron-stabilizing interaction

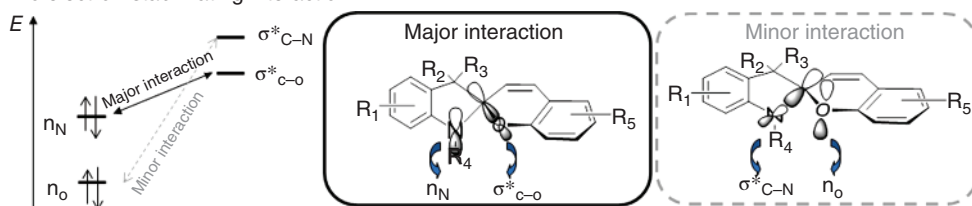


Figure 1.22 Orbital interactions depicting the interactions between the nonbonding and the antibonding orbitals in spiropyrans around the spiro carbon, leading to the weakening of the C–O bond.

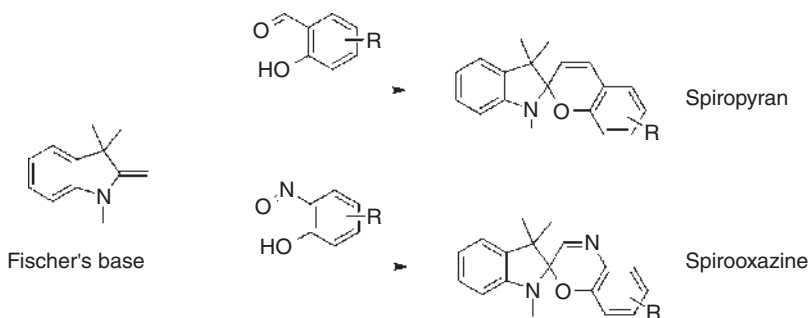


Figure 1.23 Common synthesis scheme for indoline-based spiropyrans and spirooxazines, involving the Fischer's base.

Spirooxazines and chromenes are other families of molecules featuring photochromism under a similar reaction pattern, and also they are of T-type. In spirooxazines, a CH group has been replaced by a nitrogen atom (Figure 1.23) [32b,c, 64]. As shown in this synthesis scheme, the simplest method to obtain the most common indoline-based spiropyran or spirooxazine is a reaction between the Fischer's base (1,3,3-trimethyl-2-methylene-indoline) and the corresponding salicylaldehyde or the nitrosophenol derivative.

When applications are targeted, molecules are introduced in a polymer matrix as dopants, or covalently attached to a polymer chain, the more so because spiropyrans are photochromic in the pure solid state only in a few cases [65]. Due to their high fatigue resistance, spirooxazine with an extended group (naphthopyrans rather than benzopyrans) finds applications in the field of eyewears, in fact more than spiropyrans. Another family of compounds named chromene [64, 66] is also used industrially for the same purpose, and its photochromism is based on a similar reaction (Figure 1.24).

However less common, it is worth mentioning that there are other examples where color is evolved upon light-induced ring opening, with other types of bond cleavage: spirodihydroindolizines where a C–C bond is broken [67] and spiroperimidines [68] based on a C–N bond cleavage.

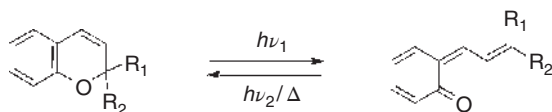


Figure 1.24 Photochromism of chromenes.

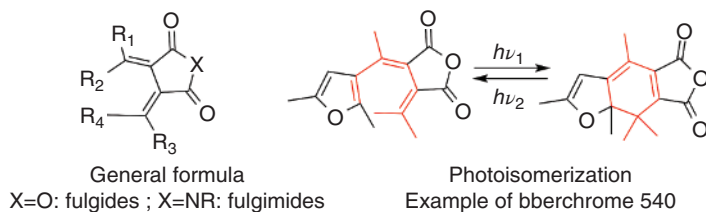


Figure 1.25 General structure of fulgides and fulgimides. The photochromic reaction is written for an example of furylfulgide, Aberchrome 540.

1.2.4.2 Fulgides and Fulgimides

Similar to spiropyrans and the related compounds described previously, photochromism in fulgides and fulgimides (Figure 1.25) is based on a cyclization reaction. More specifically, a conversion between π and σ bonds leads to an electrocyclization, and the main difference with the case of spiropyrans is that the open form is colorless and the cyclized form is the colored species.

Fulgides have been known since the early twentieth century and their name comes from the Latin “fulgere” meaning “shine” [69] because the first compounds synthesized by Stobbe in 1905 exhibited a bright character when crystallized [20, 70]. Nevertheless, to have interesting photochromic features, fulgides must have at least one exo-methylene carbon substituted with an aryl group. By this method, a 1,3,5-hexatriene-type structure is constructed and may lead to an electrocyclic reaction [71]. The first fulgides had a significant thermal back-reaction and were T-type photochromic compounds. But during the 1980s, the introduction of heterocycles as aryl groups (e.g., furylfulgides or indolinofulgides) enabled the thermal stabilization of the closed form and the P-type photochromic compound could be obtained [71, 72]. The open form may undergo *trans*–*cis* reactions, especially the one swapping R_1 and R_2 . Although studies on fulgides report on such observations [73], this reaction is less appealing because it induces only a minor change of color and other properties compared to the ring-closure reaction.

In addition to their use in rewritable optical storage devices of information [74], furylfulgides are also well known as *chemical actinometers* [2, 75], particularly the Aberchrome 450 [76] (Figure 1.25). Fulgimides [69c–e, 77] have also been widely studied because of the possibility to attach a broad variety of substituents, without deeply affecting the photochromic properties [77]. Thus, fulgimides have been substituted with not only polymer chains [78] but also fluorophores [79] or proteins [80].

One classical synthesis method of fulgides is mainly based on a double Stobbe condensation, which involves a dialkylsuccinate reacting sequentially in aldol-like

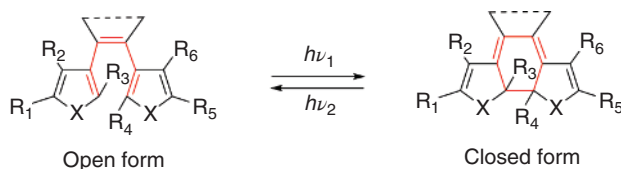


Figure 1.26 Typical reaction scheme of the photochromism of diarylethene when the aryl group is a heterocycle (e.g., X = O, N, S).

reactions with a ketone bearing the R_3 and R_4 moieties, and another one bearing the R_1 and R_2 moieties followed by ester hydrolysis and a dehydration, which enables the formation of the anhydride ring.

1.2.4.3 Diarylethenes

The first report on the photochromism of diarylethenes dates back to 1988 by Irie [81]. They represent the most studied family of photochromic compounds due to their very good fatigue resistance and their highly bistable character [82], and hence they were considered as very serious candidates for optoelectronic applications (memories, switches, etc.). Molecular engineering, based on theoretical and experimental basis, to improve the performances of diarylethenes has occupied (and still occupies) an important place in the scientific topics since that time and will be described later.

As for fulgides, diarylethenes undergo a ring-closure reaction between a colorless open form and a colored closed form (Figure 1.26). Although “aryl” may include other aromatic structures, most of the diarylethenes are based on heterocycles. For reasons developed in 1.3.3, the dithienylethene subgroup is nowadays the most widespread group.

All diarylethenes display a 1,3,5-hexatriene structure in the colorless open form. According to Woodward–Hoffman rules [82] based on the symmetry of π orbitals, electrocyclization reactions on such structures follow a conrotatory mechanism under photochemical control. Under UV irradiation, a 1,3-cyclohexadiene (colored closed form) is evolved. The reverse reaction (cycloreversion) is induced by irradiation in the visible range. Extension of the delocalization of the π system explains the color of the closed form.

A previously introduced compound in the part dealing with *trans*–*cis* photoisomerization, stilbene, is in fact a type of diarylethene, as the two phenyl groups are linked by an ethene bridge. In addition to the *trans*–*cis* isomerization, its *cis* isomer is known to undergo a light-induced cyclization reaction, leading to the formation of dihydrophenanthrene [83] (Figure 1.27). However, it oxidizes irreversibly to yield phenanthrene by the elimination of hydrogen. Introducing substituents on the reacting carbon atoms can avoid this undesirable reaction, thus hydrogen atoms are replaced in diarylethenes (R_3 and R_4 positions, Figure 1.26) by a large variety of groups, the most common ones being alkyl and alkoxy.

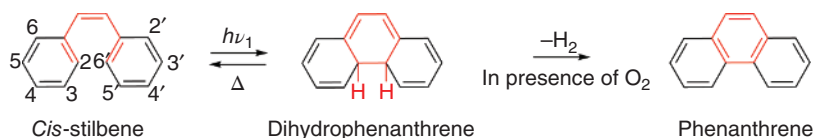


Figure 1.27 Photocyclization reaction of *cis*-stilbene and the subsequent oxidation to phenanthrene.

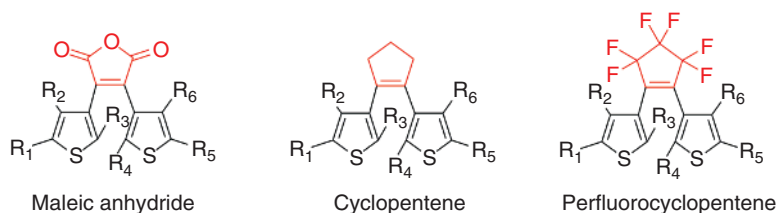


Figure 1.28 Typical examples of rings including the ethene bridge in diarylethenes (more specifically, dithienylethenes).

The analogy with *cis*-stilbene leads us to care about the *trans*–*cis* reaction, which competes with the cyclization reaction. Since the former induces less change than the latter for most properties, it is usually considered to be less interesting and is even avoided. In order to do so, in many molecules, the ethene bridge is included in a cyclic group (Figure 1.28).

At the time diarylethenes emerged in the world of photochromism, spiropyran and the related compounds, as previously described, were occupying the front scene for T-type compounds. Diarylethenes quickly showed some potential as P-type systems, and much effort was invested in the molecular engineering to increase the stability of both forms of the molecule (see Section 1.3.3).

Various synthetic methods have been developed for the preparation of diarylethenes [64]. Diarylethenes with hexafluorocyclopentene as ethene bridge can be, in general, synthesized by the reaction of appropriate heteroaryl organolithium reagent with octafluorocyclopentene (Figure 1.29a). However, Pd-catalyzed cross-coupling, Suzuki cross-coupling, for example, is another quite general synthetic approach to diarylethenes (Figure 1.29b) [84].

It would be unrealistic to list all the diarylethene derivatives that have been developed based on dithienylethenes, even if one focuses only on compounds with dithienylperfluorocyclopentene bridges. A lot of modifications in diarylethene structure were done in order to modify their photochromic properties. Beyond dithienylethenes, variants of diarylethenes with thiazolyl cycles (see Section 1.3.5), terarylenes [85], or arylbutadienes [86] can be mentioned as other photochromic systems.

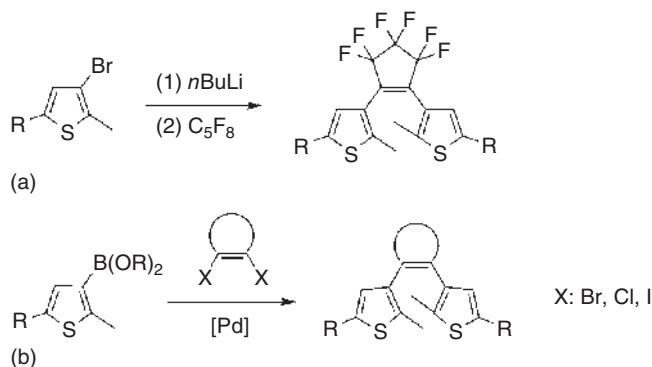


Figure 1.29 Synthesis of diarylethenes: typical reaction binding the ethane bridge with the aryl cycles (here thienyl).

1.3

Molecular Design to Improve the Performance

1.3.1

Figures of Merit

In order to fulfill the requirements as photoswitches, several characteristics are necessary and a lot of research has been carried out to improve them.

Some of them are rather obvious and “universal”:

- 1) The number of cycles that a photochromic system is capable to complete should be as high as possible. In other words, fatigue resistance is an important feature.
- 2) The switching should not be greedy in energy, in order to have an efficient conversion in terms of extent and speed. To be under such conditions, the quantum yield of the photoreaction should be high (see Appendix).

There are also other important characteristics; however, the expectations may vary according to the targeted application. For instance:

- 3) The absence of a thermal reaction leading to a complete bistability (the composition remains the same as in the absence of light) is essential in P-type systems, whereas for a T-type system, the reversion from B to A state is desired to occur in a glance.
- 4) Usually, a large absorption spectrum shift between A and B states is sought: not only this means a large color change but it is also linked to a large change of other properties. However, in some applications, performing as much A–B cycles as possible is necessary, and a large overlap of their spectra can be advantageous.

Finally, in terms of most applications, photochromic systems should be capable to operate in the solid state, and structural properties of the molecules have an important influence on their ability to undergo reactions in the solid state.

In the following, for a selection of figures of merits, such as fatigue resistance, bistability for P-type systems, or speediness of the back-reaction for T-type systems, molecular design related to their improvement is presented.

1.3.2

Fatigue Resistance: Increasing the Number of Operating Cycles

To work as a switch, photochromic systems should be able to undergo a large number of cycles. For example, it would be inconceivable to change a glass panel on a building or a car windshield every year. In applications where a 10-year product lifetime would be reasonable, one should consider not only that the material should withstand the 3650 day/night cycles but also that the A–B photoreaction is permanently occurring during daytime, even at photostationary state (PSS) where the global composition of the medium remains constant (see Appendix).

Unfortunately, as in all reactive media, fatigue is also present in photochromic systems. A few decades ago, investigation on side products and degradation mechanism was intensively conducted on spiropyrans [87]. Electronic effects of the substituents showed that the introduction of electron-donating groups (EDGs) at almost all positions improved the fatigue resistance, whereas the introduction of electron-withdrawing groups (EWGs) had the opposite effect [88]. In addition, comparative studies between spiropyrans and analogous spirooxazines were carried out and showed that the latter had a better fatigue resistance [89]. A difference of deactivation processes with molecular oxygen between the two compound families was reported: in spirooxazines, the mechanism is more photophysical than photochemical.

Diarylethenes are reputed for their good fatigue resistance, owing to many molecular engineering works, although not totally exempt from irreversible side reactions under some conditions [84c, 90]. In Section 1.2.4, issues related to *trans*–*cis* photoisomerization and oxidation of a tricyclic compound were discussed in the case of stilbene. Substituting hydrogen wherever this atom can be involved in a side reaction, is an answer to avoid it. The same design is applied in fulgides [91].

Back to diarylethenes, the extent of side reactions depends on both the molecular structure of the switch and experimental conditions, leading to diarylethenes with cycling ability ranging from a few tens to hundreds of thousands cycles [90a]. Despite the abundance of literature data on diarylethenes, it is still impossible to predict the photoresistance of a diarylethene, as there are several different methods of degradation [92]. Nevertheless, some empirical correlations are observed between the fatigue behavior of a diarylethene and its molecular structure. When the reacting carbon atoms are not substituted, a possible side reaction is an oxidation reaction concomitant to the cyclization, analogously to the one described for stilbene (see Section 1.2.4, Figure 1.27).

First, all else being equal, hexafluorocyclopentene as ethenic bridge confers, in general, higher fatigue resistance to diarylethenes than cyclopentene does [93].

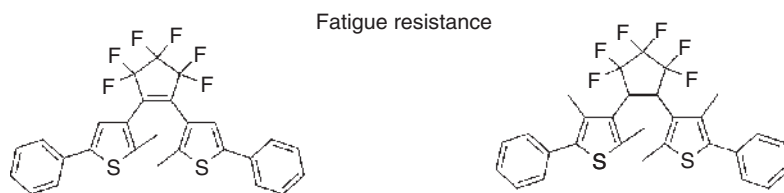


Figure 1.30 Effect of the substitution by methyl groups on thiophene rings on fatigue resistance.

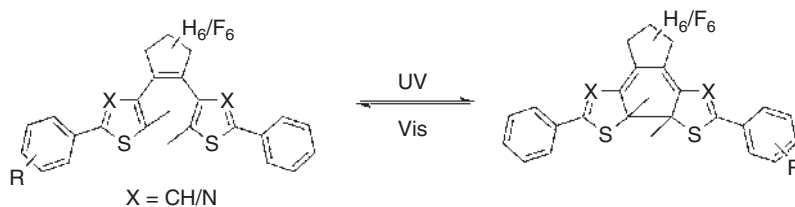


Figure 1.31 Substituted dithienylethenes ($X = \text{CH}$) and dithiazolyethenes ($X = \text{N}$).

Note that maleic anhydride or maleimide as ethenic bridge offers comparable photoresistance to hexafluorocyclopentene but has lower chemical stability [90a].

Second, diarylethenes with benzo[*b*]thiophenes as heteroaryl are, in general, more fatigue resistant than those with thiophenes. Within the thiophene-based diarylethenes, the fatigue resistance is very sensitive to small structure changes. For instance, a simple methyl substitution of thiophene ring was found to bring about a spectacular improvement in its photoresistance (Figure 1.30) [90a]. Note also that diarylethenes with thiazole or oxazole, which are more electron deficient than thiophene and benzothiophene, are also known for their high fatigue resistance [90a, 94].

Finally, the fatigue resistance of a diarylethene is sensitive not only to the nature of the two heteroaryl groups directly involved in the photochromic reactions but also to peripheral structure changes. Indeed, a clear correlation has been established between the fatigue resistance and the peripheral substitution of phenyl groups in two families of diarylethenes, dithienylethenes and dithiazolyethenes (Figure 1.31) [84c].

Contrary to spiropyrans, substitution of phenyl rings by EWG was clearly found to have beneficial effect on their photoresistance, while that of EDG produced the opposite effect. The most spectacular improvement of the fatigue resistance was observed when the phenyl rings are substituted at 3- and 5-positions by chemically inert and strongly electron-withdrawing trifluoromethyl group (CF_3) or pentafluorosulfanyl group (SF_5). More importantly, this enhancement of fatigue resistance was achieved without altering their photoreactivity [84c].

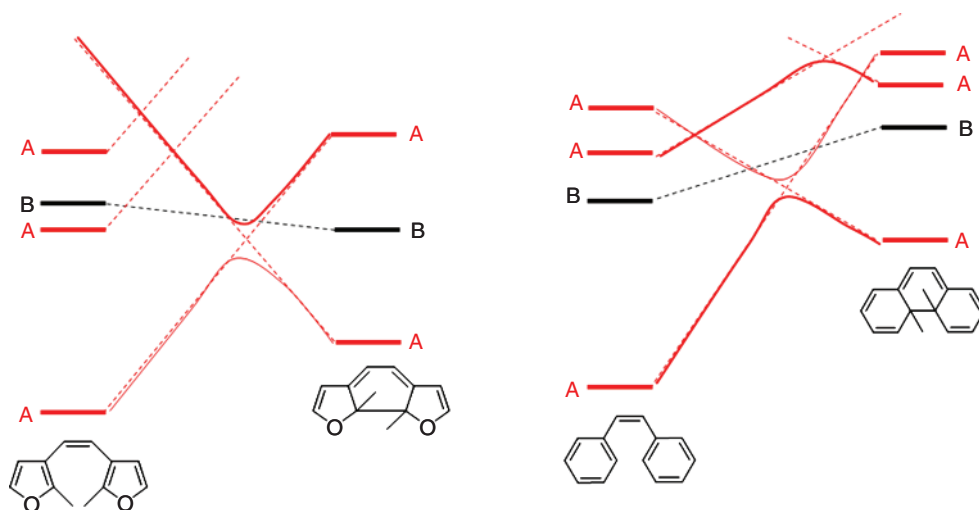


Figure 1.32 Correlation diagram showing the influence of the ground-state energy difference between B and A forms on the potential barrier for the B form.

1.3.3

Bistability: Avoiding Unwanted Thermal Back-Reaction in the Dark

In some applications, the required system should undergo switching only during the application of the light stimulus. For example, in memories, recorded information should not be altered in the dark. To reach this goal, P-type systems are sought where the ground-state potential barrier is particularly high for the B form (ΔE in Figure 1.5).

In the case of diarylethenes, a comparative study between different types of aromatic groups leads to the result: the lower the aromaticity of the aryl group, the smaller the ground-state energy difference between B and A forms, and thus, the higher the ΔE value [82, 90a]. Figure 1.32 shows the comparison between diphenylene and difurylene where the ground-state energy differences are, respectively, 27.3 and 9.2 kcal mol⁻¹. For dithienylene, this energy difference is -3.3 kcal. Consequently, for aryl moieties with a low aromatic stabilization energy, such as furans, thiophenes, and thiazoles, the B form is thermally stable compared to phenyl, pyrrole, or indole [90a]. This is the reason why a large majority of diarylethenes bears thiophene (or benzothiophene) moieties, although molecules based on other groups, such as thiazole and oxazole, are now growing in importance.

It is also important to note that one can also play with the substitution of these heteroaryl groups as well as the nature of the ethenic bridge to tune the thermal stability of the colored B form of such a diarylene, as exemplified below.

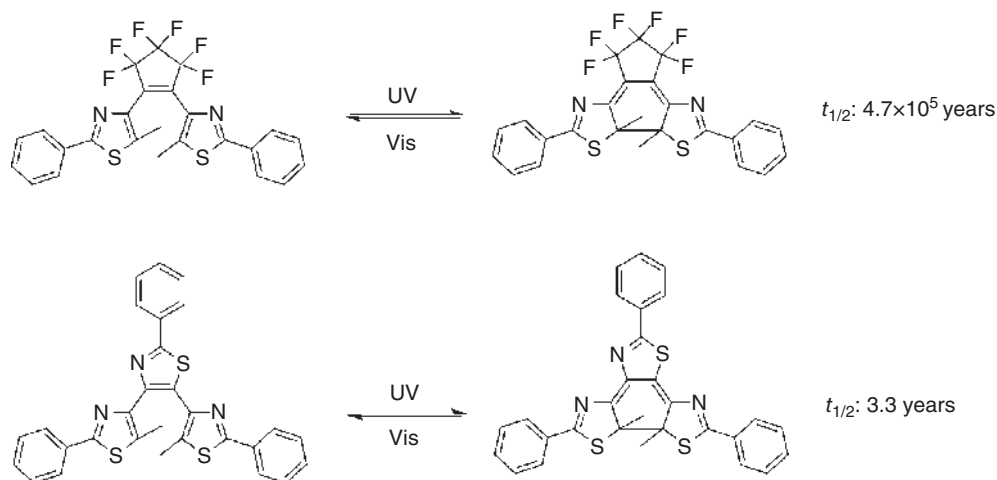


Figure 1.33 Comparison between hexafluorocyclopentene- and phenylthiazole-bridged diarylethenes: effect of the bridge on the thermal stability of the B form.

1.3.3.1 Influence of Ethenic Bridge on the Thermal Stability of the B Form

With hexafluorocyclopentene as the ethene bridge, the B form is extremely thermally stable, with a half-lifetime estimated to be 4.7×10^5 years at 30°C [95], while that of the analog with a phenylthiazole bridge is only about 3.3 years at 20°C [96] (Figure 1.33). The main reason for such a huge difference is that the cyclization results in a larger energy loss in the case of a phenylthiazole bridge than with hexafluorocyclopentene due to an extra loss of aromatic stabilization energy associated with the central thiazole. In other words, the ground-state energy difference between A and B forms is larger with phenylthiazole than that with hexafluorocyclopentene, leading to a smaller energy barrier for the thermal back-reaction, therefore a lower thermal stability of the B form with a phenylthiazole bridge.

Introducing six-member rings to bridge the aryl groups can be advantageous to develop new molecular structures and functionalities and also to increase the quantum yield of $\phi_{A \rightarrow B}$ to some extent [97]. However, concomitantly, it induces a high aromaticity, thus leading to T-type systems, unless EWG such as benzo-bisthiadiazoles are introduced [98].

1.3.3.2 Impact of the Heteroaryl Substituents on the Thermal Stability of the B Form

Figure 1.34 describes two situations, where the stability of the colored form B is influenced by the strength of the C–C single bond created upon the A to B reaction. Indeed, the B form is destabilized by a weakening of this bond, which can stem from either a larger steric hindrance (Figure 1.34a) when passing from methyl to isopropyl substituent on the reactive carbon atoms [99], or a stronger electron-withdrawing effect of the substituent at 5-position of thiophene moiety (Figure 1.34b) when going from aldehyde to dicyanoethene group [12]. In both

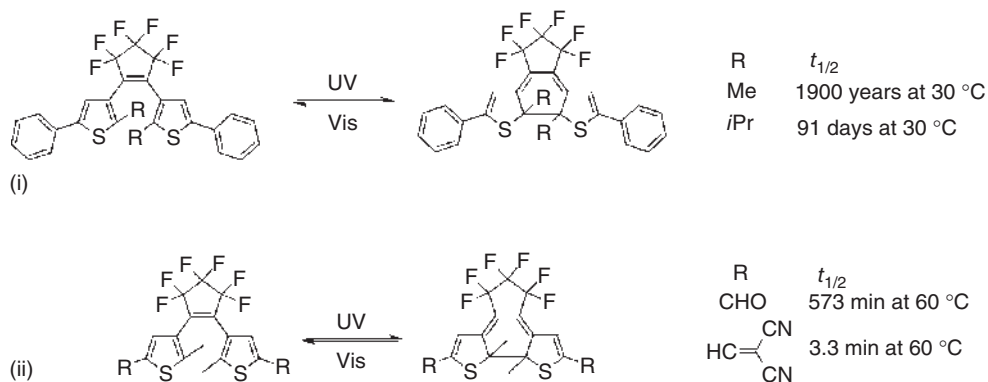


Figure 1.34 Substituent effect on the thermal stability of the B form in diarylethenes.

cases, a weaker C–C bond means a higher energy difference between B and A, thus leading to a lower energy barrier to the thermal back-reaction.

1.3.4

Fast Photochromic Systems: Reverting Back Spontaneously to the Colorless State in a Glance

In 1.3.3, the design to reach molecules with a perfect stability of both A and B forms was described, thus leading to systems that are not affected in the absence of light. These are based on P-type photochromic molecules for applications such as memories. In the contrary, another interesting development of photochromic compounds is to target systems, which revert back to the initial state when light is switched off. For example, ophthalmic applications require such a behavior. T-type molecules have appropriate characteristics, provided that the reaction occurs in a glance from A to B when light is switched on, and the other way around when it is switched off.

Evidently, a high thermal B to A reaction rate (k) is required for a rapid color fading when light is switched off. However, as described in Appendix, a high k value would inconveniently lower the conversion extent, $\alpha_B(\lambda_{irr})$, under UV irradiation. The consequence would be that only a low absorbance in the visible spectrum is reached under UV irradiation. Hence, a compromise for the value of k is necessary. Since the eye's reflex rate is at the order of some 10 ms, the trade-off value is some 10 s^{-1} , considering applications where the human's vision is involved. In addition, high UV light intensity and/or strong absorption coefficient of the B form in the visible spectrum help the performance of the photochromic system.

Many efforts are carried out to control k by a careful design of molecules for several families of molecules. Within the literature on T-type molecule families, such as spiropyrans and azobenzene, thermal back-reaction rate is probably among the most discussed properties in feature chapters and reviews [29, 34, 52, 60]. For the

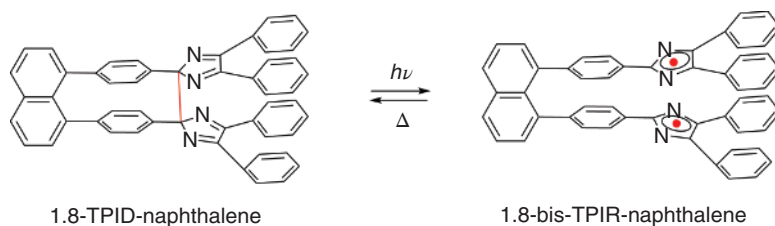


Figure 1.35 Example of fast HABI: naphthalene moiety avoids the separation in two molecules upon bond cleavage, leading to a fast thermal back-reaction [57].

latter, substituents such as amino groups or further conjugated push–pull structures speed up the thermal back-reaction, and recent work reports on the capability of fluorine substituents in slowing down the back-reaction rate drastically [100].

As mentioned previously, HABI undergoes a photochromic reaction between a TPID dimeric form and a pair of radicals TPIR (see Section 1.2.3, Figure 1.19). Once colored, the fading of the color of TPIR lasts for several minutes in solution [56]. In the last decade, an important work was carried out, leading to a series of fast HABI molecules. To speed up the thermal back-reaction, Abe has developed a new type of HABI structure where a naphthalene or cyclophane moiety bridges the two parts of the molecule and prevents the two radicals from leaving apart [101] (Figure 1.35). Diffusion of TPIR is thus annihilated [102]. The back-reaction is considerably accelerated and takes place in 180 ms. Other compounds, structured identically, have been the subject of several studies to modulate photochromic properties [103] or to understand the photodissociation mechanism [104].

In addition to the molecular structure, the environment can drastically influence k for a given molecule. The case of spiropyrans has been presented previously (see Section 1.2.4), where the stability of the colored MC is strongly solvent dependent. In addition, the case of anils can be pointed out: the thermal back-reaction ranges from a few milliseconds in solution, where the photochromism is merely visible due to an excessive value of k (see Appendix), to several days, in some cases even years, in the bulk [411, 50b, 105].

1.3.5

Gaining Efficiency of the Photoreaction: the Example of Diarylethenes

Traditionally, clear and strong color change in photochromic systems used to be the target in many cases. In such context, colorability, which is the product of ϵ_B in the visible light spectrum and the quantum yield $\phi_{A \rightarrow B}$ [106], is one indicator to measure the efficiency of a photochromic system. The advantage of colorability is that it can be determined directly from the experiment, knowing the experimental conditions, even if the value of ϵ_B is unknown. This is useful in the case for T-type systems, where the B form is metastable and difficult to characterize. However, when properties other than color change are the main interests, the relevant figure

Table 1.1 Quantum yield ($\phi_{B \rightarrow A}$): effect of substituents on 1- and 5-positions of 1,2-bis(2,6-dimethyl-3-thienyl)perfluorocyclopentene (Figure 1.26, $-R_2 = -R_6 = -CH_3$).

Substituent at R_1 and R_5 positions	$\phi_{A \rightarrow B}$	$\phi_{B \rightarrow A}$
-H	0.21	0.13
-CN	0.44	7.5×10^{-2}
-Ph	0.46	1.5×10^{-2}
-Ph-NEt ₂	0.37	2.5×10^{-3}
-Th-CN	0.12	1.3×10^{-3}
-Th-Th-CN	0.12	1.3×10^{-4}

Ph and Th stand for phenyl and thienyl, respectively.

would rather be the quantum yield(s). As it appears clearly in the expression of the conversion extent (see Appendix), the values of the quantum yields $\phi_{A \rightarrow B}$ and $\phi_{B \rightarrow A}$ count.

Coming back to diarylethenes, the bridging ethylene is included in a five-membered ring. This is the result of a compromise between the color change and the quantum yield, $\phi_{A \rightarrow B}$ [82, 90a]. Molecules of interest have a $\phi_{A \rightarrow B}$ value of a few 10^{-1} , whereas $\phi_{B \rightarrow A}$ can vary in a wide range of several decades. Regarding $\phi_{B \rightarrow A}$, it is lowered by the extension of the conjugation. For example, on 1,2-bis(2,6-dimethyl-3-thienyl)perfluorocyclopentene (Figure 1.26, $-R_2 = -R_6 = -CH_3$), $\phi_{B \rightarrow A}$ lowers from 0.13 to 7.5×10^{-2} , 1.5×10^{-2} , and 2.5×10^{-3} when, respectively, cyano, phenyl, and aminophenyl substituents are introduced at 1- and 5-positions (Table 1.1) [107]. Even the B to A photoreaction is annihilated when substituents belong to carotenoids family [108].

In addition, substituents linked to reactive carbon atoms ($-R_3$ and $-R_4$) affect $\phi_{B \rightarrow A}$ [109]: bulky groups and EDG lower its value, whereas EWG increase it, as illustrated in Table 1.2 [13e, 109b, 110].

From the data in the tables, it is difficult to draw any clear tendency about the influence of the substituent's properties on the quantum yield of the forward reaction, $\phi_{A \rightarrow B}$.

Furthermore, conformational analysis of diarylethenes shows that two conformations of the A form exist: antiparallel (ap) and parallel (p). The former

Table 1.2 Quantum yield ($\phi_{B \rightarrow A}$): effect of substituents on 3- and 4-positions of 1,2-bis(1,5-diphenyl-3-thienyl)perfluorocyclopentene (Figure 1.26, $-R_1 = -R_5 = -Ph$).

Substituent at R_3 and R_4 positions	$\phi_{A \rightarrow B}$	$\phi_{B \rightarrow A}$
-CH ₃	0.59	1.3×10^{-2}
-C ₂ H ₅	0.52	8.1×10^{-3}
-CN	0.42	0.41
-OCH ₃	0.44	$<2 \times 10^{-5}$

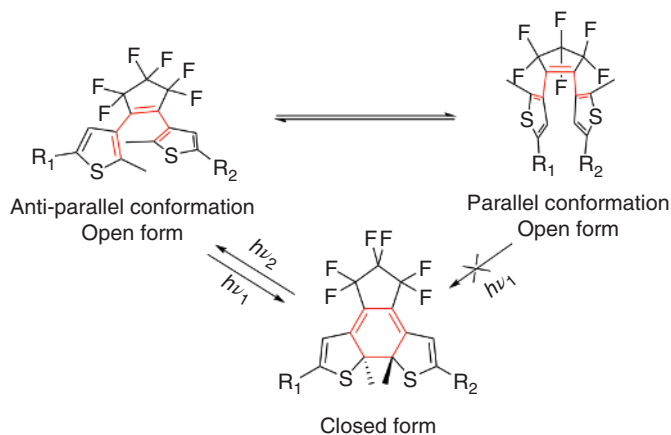


Figure 1.36 Antiparallel (ap) and parallel (p) conformations of the open form of diarylethenes. Only the ap conformer is reactive.

is symmetric with respect to 180° rotation about a C_2 axis, and the latter is symmetric with respect to reflection in a mirror plane. As it is rationalized by Woodward–Hoffmann’s rule, only the ap conformer can undergo a photochemical ring-closure reaction (Figure 1.36) [82, 90a]. Usually for conformers, both spectra overlap and it is practically impossible to irradiate selectively one of them. In this context, obtaining a diarylethene with 100% ap conformation is sought after because a 50 : 50 ratio between the conformations would fix an upper limit of $\phi_{A \rightarrow B}$ to 50%.

Assuming these considerations, the proportion of ap form, and therefore the efficiency, can be increased by placing the dithienylethenes in a confined space, such as in crystalline phase [111], in doped polymer [112] or in inclusion material like cyclodextrin [113]. In contrast, parallel conformation can be largely favored, for example, by the formation of a rigid bridge between the two aromatics arms through hydrogen bonds. Such structure freezing leads to the unresponsiveness of the compound under light irradiation [114]. Freezing/defreezing can be achieved in specific cases by acid–base reaction [115].

In addition, several strategies in the molecular design have been endeavored to increase the proportion of the ap form.

One possibility is the introduction of bulky groups. Literature reports on an example where substitution of methyl by bulkier isopropyl groups on the reacting carbon atoms increases significantly the ap:p ratio (94 : 6 instead of 65 : 35), leading to more favorable $\phi_{A \rightarrow B}$ value (0.52 compared to 0.35) [99a]. Bulkiness can also be introduced elsewhere: a high $\phi_{A \rightarrow B}$ value of 0.83 was reached by introducing four methyl groups on the five-membered bridging ring [116] (Figure 1.37a).

Also, linking the two aryl groups with an additional bridge at *ortho*-positions of the reacting carbon atoms can favor the ap conformation [117] (Figure 1.37b).

During the past 5 years, several research groups have been working on the intramolecular interactions between the aryl groups and the bridging ring,

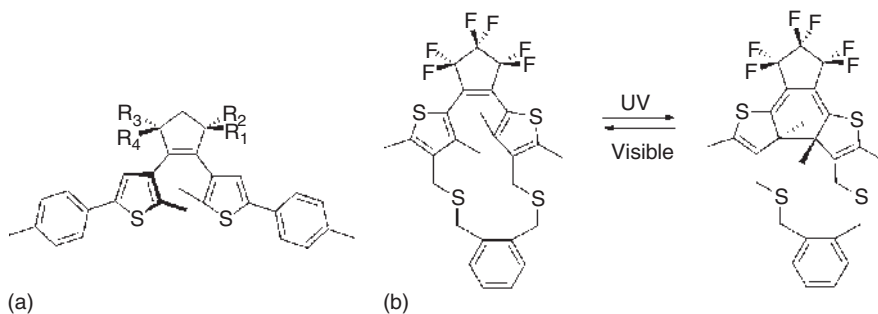


Figure 1.37 Antiparallel conformation (ap) favored by introducing bulkiness in the bridging ring (a) [116] or constraint with an additional bridge (b) [117b].

	Hexane	Methanol
	0.90	0.90
	0.98	0.54

Figure 1.38 Intramolecular interactions favoring the ap conformation and solvent effect on the $\phi_{A \rightarrow B}$ value [118b].

in order to introduce some rigidity and block the structure within the ap conformation. Representative results were obtained on a series of teraryl-type diarylethenes, where intramolecular interactions play a crucial role [118]. As a result, $\phi_{A \rightarrow B}$ reaches high values of 0.90 and 0.98 (Figure 1.38) in hexane. In methanol, the S–N bond, present in one of the molecules, apparently weakens and $\phi_{A \rightarrow B}$ is lowered, thus showing the importance of these intramolecular interactions. This is also illustrated in another example where the methanol solvent plays a crucial role in the intramolecular interactions, fixing the conformation to ap and increasing $\phi_{A \rightarrow B}$ compared with what is observed in hexane (Figure 1.39) [119].

Blocking the conformation, in order to prevent the interconversion between ap and p conformers, has also been achieved in a diarylethene with thiazole groups and in a bridging six-membered benzo(thiadiazole) ring. A quantum yield as high as 0.91 was obtained for the cyclization of the ap form [120]. The energy barrier between the ap and p conformers was calculated to be more than 140 kJ mol^{-1} .

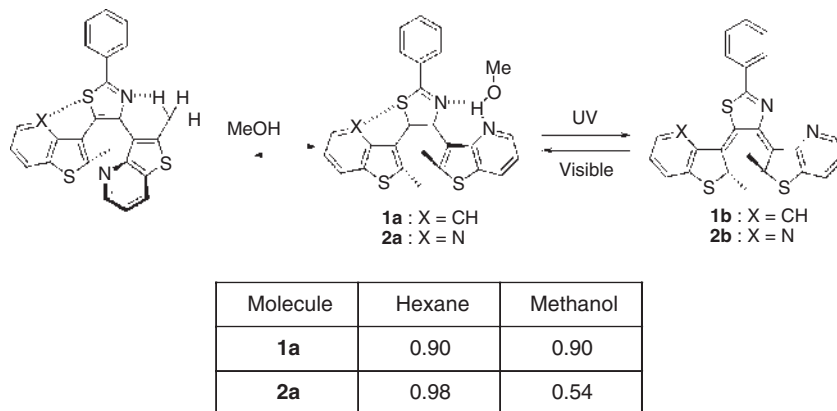


Figure 1.39 Solvent–solute hydrogen bond favoring the ap conformation and increasing the $\phi_{A \rightarrow B}$ value [119].

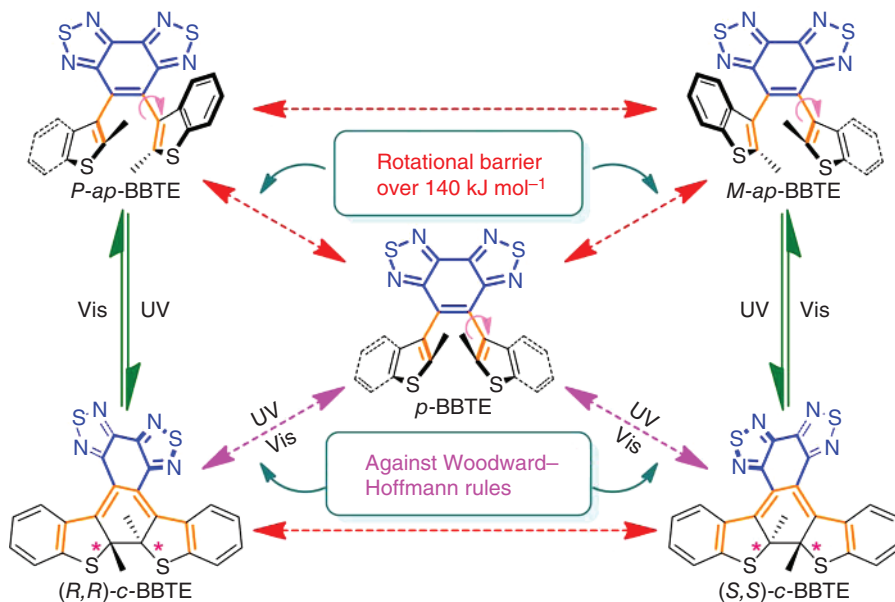


Figure 1.40 Enantiospecific photochromism resulting from a high-energy barrier between the open form conformations [121].

Such a design gives the possibility to isolate not only the ap and p conformers but also the pair of enantiomers of the p conformation. This feature was exploited further to undergo stereospecific reactions, where each enantiomer of the open form leads to a specific closed-form enantiomer [121] (Figure 1.40). Another example with a chiral center leads to a 100% diastereoselective process with a $\phi_{A \rightarrow B}$ value of 85% (Figure 1.41) [122].

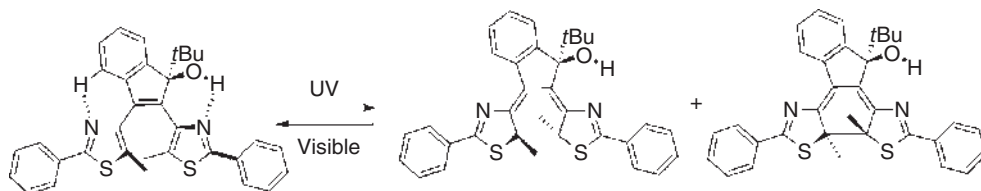


Figure 1.41 Stereospecific photochromism resulting from the control of the conformation of the open form by intramolecular hydrogen bonds [122].

1.4

Conclusion

The world of organic photochromism is full of variety and versatility because of the infinite possibilities of molecular engineering. Different geometrical and electronic considerations lead to different properties, and much effort has been done to tune these. In addition to what has been described in this chapter, obtaining molecules active in the solid state is another issue, where the design of the molecule has some influence, although this property involves the material. Criteria on intramolecular distances [101] or angles [42b] were established, and strategies such as introducing bulky groups [9b] were followed in order to ensure reactivity in the bulk state.

Appendix

General Kinetics of a Photochromic Reaction and Determination of the Conversion

Extent $\alpha_B(\lambda_{\text{irr}})$

When a homogeneous sample (under constant stirring), containing a given photochromic species that exists in its two isomeric states A and B, is exposed to light irradiation (at a wavelength λ_{irr} , see Figure 1.A.1), the composition of the mixture evolves with the following general differential equation:

$$\frac{dC_A(t)}{dt} = -\frac{dC_B(t)}{dt} = \varphi_{B \rightarrow A} I_B^{\text{abs}}(\lambda_{\text{irr}}, t) - \varphi_{A \rightarrow B} I_A^{\text{abs}}(\lambda_{\text{irr}}, t) + k_{B \rightarrow A} C_B(t) \quad (\text{A1})$$

with t the time; $C_A(t)$ and $C_B(t)$, respectively, the concentrations of A and B; $\varphi_{A \rightarrow B}$ and $\varphi_{B \rightarrow A}$ the photochromic quantum yields of the $A \rightarrow B$ and $B \rightarrow A$ reactions; $k_{B \rightarrow A}$ the thermal back-reaction rate from B to A (kinetics is assumed to be of first order); and $I_A^{\text{abs}}(\lambda_{\text{irr}}, t)$ and $I_B^{\text{abs}}(\lambda_{\text{irr}}, t)$ the intensities of the irradiation light absorbed by A and B, expressed as follows:

$$I_A^{\text{abs}}(\lambda_{\text{irr}}, t) = \frac{[1 - 10^{-\text{Abs}(\lambda_{\text{irr}}, t)}]}{\text{Abs}(\lambda_{\text{irr}}, t)} I_0(\lambda_{\text{irr}}) \varepsilon_A(\lambda_{\text{irr}}) \ell C_A(t) \quad (\text{A2})$$

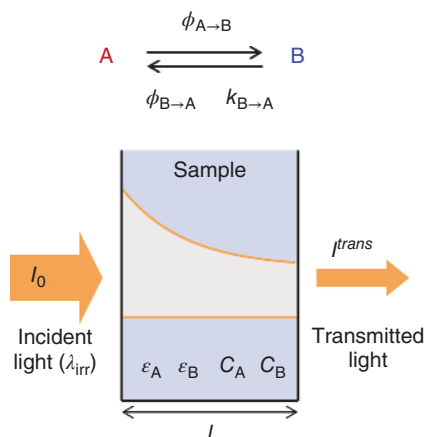


Figure 1.A.1 Definition of the system under irradiation and its variables.

$$I_B^{\text{abs}}(\lambda_{\text{irr}}, t) = \frac{[1 - 10^{-\text{Abs}(\lambda_{\text{irr}}, t)}]}{\text{Abs}(\lambda_{\text{irr}}, t)} I_0(\lambda_{\text{irr}}) \varepsilon_B(\lambda_{\text{irr}}) \ell C_B(t) \quad (\text{A3})$$

where $\varepsilon_A(\lambda_{\text{irr}})$ and $\varepsilon_B(\lambda_{\text{irr}})$ designate the molar absorption coefficients of the A and B species at the wavelength λ_{irr} , ℓ the optical path of the sample, $I_0(\lambda_{\text{irr}})$ the irradiation light intensity per volume unit of the sample, and $\text{Abs}(\lambda_{\text{irr}}, t)$ the absorbance of the sample, which follows the Beer–Lambert law:

$$\text{Abs}(\lambda_{\text{irr}}, t) = \varepsilon_A(\lambda_{\text{irr}}) \ell C_A(t) + \varepsilon_B(\lambda_{\text{irr}}) \ell C_B(t) \quad (\text{A4})$$

Often, the term *photokinetic factor* is employed to designate the nonlinear quantity $[1 - 10^{-\text{Abs}(\lambda_{\text{irr}}, t)}] / \text{Abs}(\lambda_{\text{irr}}, t)$.

In the general situation, in the absence of any approximation, the differential equation (A1) shows no analytic solution. Indeed, the “photokinetic factor,” and thus $I_A^{\text{abs}}(\lambda_{\text{irr}}, t)$ and $I_B^{\text{abs}}(\lambda_{\text{irr}}, t)$, vary upon time, as it can be seen from Eqs. (A2) and (A3).

Irradiation at a Specific Wavelength: Isosbestic Point

When irradiation is performed at the isosbestic point, the molar absorption coefficients of both A and B species are equal to the same value ε , and the absorption of the sample $\text{Abs}(\lambda_{\text{irr}}, t)$ holds a constant value during the irradiation process ($\text{Abs}(\lambda_{\text{irr}})$), as well as the “photokinetic factor.” Then, we can define the constant K :

$$K = \frac{I_0(\lambda_{\text{irr}})}{C_{\text{tot}}} [1 - 10^{-\text{Abs}(\lambda_{\text{irr}})}] \quad (\text{A5})$$

where $C_{\text{tot}} = C_A(t) + C_B(t)$. As a consequence, the general differential kinetic equation simplifies on

$$\frac{dC_A(t)}{dt} = (K\varphi_{B \rightarrow A} + k_{B \rightarrow A})C_{\text{tot}} - (K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A})C_A(t) \quad (\text{A6})$$

Then, the time evolution of the molar fractions $x_A(t)$ and $x_B(t)$ of, respectively, A and B takes the expression of an exponential function:

$$\begin{aligned} x_A(t) = & \left(x_A^0 - \frac{K\varphi_{B \rightarrow A} + k_{B \rightarrow A}}{K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A}} \right) \\ & \times \exp[-(K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A})t] \\ & + \frac{K\varphi_{B \rightarrow A} + k_{B \rightarrow A}}{K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A}} \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} x_B(t) = & - \left(\frac{K\varphi_{A \rightarrow B}}{K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A}} - x_B^0 \right) \\ & \times \exp[-(K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A})t] \\ & + \frac{K\varphi_{A \rightarrow B}}{K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A}} \end{aligned} \quad (\text{A8})$$

where x_A^0 and x_B^0 represent the initial molar fraction of, respectively, A and B.

Then, the conversion extent $\alpha_B(\lambda_{\text{irr}})$ at the PSS, corresponding to the molar fraction of B isomer in the sample after an infinite time of irradiation, can be easily expressed:

$$\alpha_B(\lambda_{\text{irr}}) = \frac{K\varphi_{A \rightarrow B}}{K(\varphi_{A \rightarrow B} + \varphi_{B \rightarrow A}) + k_{B \rightarrow A}} \quad (\text{A9})$$

Coming back to the general case (irradiation at any wavelength), the photochromic kinetics does not follow an exponential behavior. In the following, we focus on the conversion extent of the B isomer at the PSS ($\alpha_B(\lambda_{\text{irr}})$) and consider the case of P-type and T-type photochromic systems.

This situation is obtained either by extrapolating the expression of $x_B(t)$ to infinite time (as it was done with Eq. (A8) to obtain Eq. (A9) in the case of the irradiation at the isosbestic point) or by writing that $\frac{dC_A(t)}{dt} = 0$ in Eq. (A1).

Case A: When the Thermal Back-Reaction is Negligible Compared to the Photochemical Reaction (Typically P-type)

In this situation, $k_{B \rightarrow A}C_B \ll \varphi_{B \rightarrow A}I_B^{\text{abs}}$ and the last term of the general kinetic equation is suppressed. In the following, the PSS is simply characterized by

$$\alpha_B(\lambda_{\text{irr}}) = \frac{\varepsilon_A(\lambda_{\text{irr}})\varphi_{A \rightarrow B}}{\varepsilon_A(\lambda_{\text{irr}})\varphi_{A \rightarrow B} + \varepsilon_B(\lambda_{\text{irr}})\varphi_{B \rightarrow A}} \quad (\text{A10})$$

It is worth noticing that the composition at PSS does not depend on the irradiation conditions. Only the kinetics to reach PSS does.

Table 1.A.1 Values of $\alpha_B(\lambda_{\text{irr}})$ as a function of the thermal back-reaction rate $k_{B \rightarrow A}$.

$k_{B \rightarrow A}$ (s^{-1})	10	1	0.1
$\alpha_B(\lambda_{\text{irr}})$	0.01	0.10	0.54

Case B: When the Thermal Back-Reaction is More Efficient than the Photochemical $B \rightarrow A$ Reaction (Typically T type)

In this situation, $k_{B \rightarrow A} C_B \gg \varphi_{B \rightarrow A} I_B^{\text{abs}}$ and the first term of Eq. (A1) is suppressed. In order to have a simple analytic resolution of the equation, we need to consider the case where the absorption of the sample at the irradiation wavelength is low enough ($\text{Abs}(\lambda_{\text{irr}}) \ll 1$) to allow the linearization of the differential equation with $([1 - 10^{-\text{Abs}(\lambda_{\text{irr}})}] = \ln 10 \times \text{Abs}(\lambda_{\text{irr}}))$. In this case, Eq. (A1) becomes

$$\frac{dC_A(t)}{dt} = -\ln 10 \times I_0(\lambda_{\text{irr}}) \ell \varepsilon_A(\lambda_{\text{irr}}) \varphi_{A \rightarrow B} C_A(t) + k_{B \rightarrow A} C_B(t) \quad (\text{A11})$$

and the conversion extent at the PSS $\alpha_B(\lambda_{\text{irr}})$ is dependent on the irradiation intensity $I_0(\lambda_{\text{irr}})$:

$$\alpha_B(\lambda_{\text{irr}}) = \frac{1}{1 + \frac{k_{B \rightarrow A}}{\ln 10 \times I_0(\lambda_{\text{irr}}) \ell \varepsilon_A(\lambda_{\text{irr}}) \varphi_{A \rightarrow B}}} \quad (\text{A12})$$

From Eq. (A12), we can deduce that the limit of $\alpha_B(\lambda_{\text{irr}})$ approaches 0 when $k_{B \rightarrow A}$ is very high.

Let us assume

- a sample of 1 ml, $\ell = 1$ cm,
- containing the isomer A, which has the following characteristics: $\varepsilon_A(\lambda_{\text{irr}}) = 10000 \text{ mol}^{-1} \text{ l cm}^{-1}$ and $\varphi_{A \rightarrow B} = 0.5$,
- under an irradiation of 3 mW at $\lambda_{\text{irr}} = 400$ nm, which corresponds to an intensity per unit volume of $I_0(\lambda_{\text{irr}}) = 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$.

Table 1.A.1 shows that, under the above-mentioned conditions, if the thermal reaction rate is close to 1 s^{-1} , the conversion extent is 10%, whereas if it is 10 times faster, only 1% of A is transformed to B. This explains why a fast thermal back-reaction can be an obstacle to visualize photochromism.

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