Chapter 2

Photochromic Switches

2.1 Introduction

Extensive research has been devoted to the study of molecules whose physical properties can be reversibly switched using light. Such behavior forms the basis of what is termed photochromism. Photochromic systems are used for applications in photooptical technology as well as in the design of devices which can be photomodulated.\(^1\) Two significantly different and stable molecular states (A and B) that can be interconverted by irradiation using different wavelengths, are required for these applications (Scheme 2.1). A and B differ from one another not only in their absorption spectra, but also in their refractive indices, dielectric constants, geometrical structure and oxidation/ reduction potential.

\[
\begin{array}{c}
A \xrightarrow{\lambda_1} B
\end{array}
\]

Scheme 2.1 Optical switch.

2.2 Photochemical transformations

Photochromic molecules can be divided into several classes on basis of their transformations induced by light. These structural changes can be tautomerizations, cis-trans isomerizations and electrocyclic ring closures.

2.2.1 Photochromic tautomerism\(^2\)

Tautomerism refers in general to the reversible interconversion of isomers. In the case of photochromic tautomerism this interconversion occurs after irradiation with light. A major type of photochromic tautomerism is hydrogen transfer. The most extensively studied systems that undergo light-induced hydrogen transfer are the salicylidene-anilines (Scheme 2.2). After irradiation with UV light a prototropic rearrangement from 2.1 to 2.2 occurs.\(^3\) These molecules are photochromic or thermochromic in the solid state and in rigid glasses. No salicyldene-aniline derivative exhibits both properties.\(^4\) The enol-form (2.1) is pale yellow and after irradiation the keto-form (2.2) appears, which is reddish or brown. This quinoid-keto tautomer appears to exist in two forms: an intramolecular hydrogen bonded cis-keto form (2.2) and a rotated trans-keto form (2.3). The cis-keto form is not thermally stable and has a thermal activation barrier of \(\Delta H_{\text{act}} = 83.8 \text{ kJMol}^{-1}\) in case of 2.2 when R=R’=H to go back to 2.1.\(^5\) In this case the quantum yield for the conversion of enol to keto form is about
Current research interest in these compounds is still mainly fundamental. Quantum mechanical calculations are being performed in order to obtain more insight in the proton transfer in the excited state. Ultrafast spectroscopy measurements are also necessary, because there is still no conclusion on the photochromic mechanism.

\[ \text{Scheme 2.2 Light-induced hydrogen transfer tautomerization.} \]

### 2.2.2 Cis-trans isomerizations

An alkene cis-trans isomerization, a 180° rotation around an alkene double bond, takes place in your eyes as you read this thesis. Visual pigments are composed of the protein moiety opsin and 11-cis-retinal. The latter undergoes a cis-trans isomerization upon absorption of light. This simple change in shape triggers a cascade of chemical signals, which are ultimately converted into an electrical signal (nerve impulses) that propagates to the brain and allows us to see.\(^6\)

Well-known molecules that undergo cis-trans isomerization are the stilbenes (Scheme 2.3).\(^7\) The photoisomerization of the stilbenes is recognized as one of the best understood and more thoroughly studied photochemical reactions and is generally used as the model for cis-trans isomerization. Trans- (2.4) and cis-stilbene (2.5) are reversibly interconverted by light. Following direct excitation of the stilbenes, photoisomerization is confined entirely to the singlet excited state and competes with fluorescence on the trans side and photocyclization on the cis side. The ratio of 2.5 to 2.4 in the photostationary state (PSS) is 11.5 (92% 2.5), when the sample is irradiated at \(\lambda = 313\) nm in n-pentane.\(^8\) Cis-stilbenes are not thermally stable and return to the trans-form in the dark. The thermal activation barrier lies around 154 kJmol\(^{-1}\) for most stilbene derivatives.\(^9\)

\[ \text{Scheme 2.3 Photochemical reactions involving stilbenes.} \]
In very concentrated solutions trans-stilbene can undergo a [2+2] cycloaddition to form a cyclobutane derivative (2.8), which in this case is an undesired side reaction. Cis-stilbene (2.5) can also undergo a photoinduced 6\pi-electrocyclization to give the 12\pi-system 4a,4b-dihydrophenanthrene (2.6). 2.6 can either undergo ring opening back to 2.5 or, under oxidizing conditions, it can be converted irreversibly into the more stable aromatic system, phenanthrene (2.7). This photocyclization is thought to arise from the singlet \pi,\pi^* -state of the stilbene. The light-induced ring-closure is conrotatory according to the Woodward-Hoffmann rules based on \pi-orbital symmetries for 1,3,5-hexatriene, whereas the thermal ring-opening proceeds in disrotatory motion.\textsuperscript{10} The half-life of the trans-4a,4b-dihydro species is, as may be expected, highly dependent on structural features and varies from less than 1 second to 36.8 days for the ring-closed product of 1,2-bis(2-naphthyl)ethene.\textsuperscript{11} The applications of stilbenes for reversible photoswitching has thus been limited, because of all these undesired side reactions \textit{vide supra}. Despite these drawbacks stilbenes\textsuperscript{12} are still applied in organized media, because photoreactions maybe completely different at, for instance, molecular adlayers\textsuperscript{13} or silica surfaces.\textsuperscript{14}

Sterically overcrowded alkenes\textsuperscript{15} are a special type of stilbenes (Scheme 2.4) and have been exploited in our group for a long time now. Due to sterical interactions the molecules are forced into a non-planar helical shape. After irradiation these molecules undergo \textit{cis-trans} isomerization and at the same time the helix is inverted.

\begin{center}
\textbf{Scheme 2.4 Sterically overcrowded alkene.}
\end{center}
The presence of a donor and an acceptor substituent in the lower half resulted in relatively large differences in absorption spectra between \(P\text{-}\text{cis-2.9}\) and \(M\text{-}\text{trans-2.9}\) depicted in Scheme 2.4,\(^{16}\) facilitating distinct switching between the two forms. \(P\text{-}\text{trans-2.9}\) has a rather high thermal racemization barrier (\(\Delta G_{\text{rac}} = 122.2\ \text{kJmol}^{-1}\)). Irradiation of either enantiomerically pure \(P\text{-}\text{cis-2.9}\) or \(M\text{-}\text{trans-2.9}\) at \(\lambda = 365\ \text{nm}\) resulted in a PSS composed of 70% \(M\text{-}\text{trans-2.9}\) and 30% \(P\text{-}\text{cis-2.9}\), whereas irradiation at \(\lambda = 436\ \text{nm}\) resulted in a PSS composed of 10% \(M\text{-}\text{trans-2.9}\) and 90% \(P\text{-}\text{cis-2.9}\). The CD-spectra of these molecules are nearly mirror images, illustrating the pseudoenantiomeric character of both isomers. This system also showed very high fatigue resistance. It was possible to perform 80 switching cycles between both forms without racemization or degradation. One can switch between two states, one possessing a \(P\) and one possessing a \(M\) helix, with diastereomeric excesses of 80% and 40%. This switch was successfully applied as chiral dopant in liquid crystalline (LC) phases to induce a cholesteric phase, the pitch of which could be controlled by light.\(^{17}\) In order to improve the compatibility of the switch and the LC phase, thus preventing phase separation, recently the N(Me)\(_2\) group was replaced by a N(Me)-n-C\(_6\)H\(_{13}\) group.\(^{18}\)

A closely related class of molecules with more favorable photochemical properties are the azastilbenes.\(^{19}\) The molecules go from a \(\text{trans}\) isomer to a \(\text{cis}\) isomer via a \(n\pi^*\)-transition by means of irradiation with UV light. A PSS consisting of 91% of \(\text{cis}\)-isomer can be obtained, if the system is irradiated at \(\lambda = 365\ \text{nm}\).\(^{20}\) The reversed reaction takes place by irradiation with visible light or thermally. (Scheme 2.3).\(^{21}\) The \(\text{trans}\)-isomer has absorptions at 314 nm and 440 nm, whereas the \(\text{cis}\)-isomer has absorption at 280 nm and 430 nm. If the azobenzenes have electron donating substituents, like methoxy groups, their absorptions are shifted to the visible region. These are the well-known azo dyes. The \(\text{trans}\) state is thermodynamically more stable than the \(\text{cis}\) state by 96.2 kJmol\(^{-1}\) in case of 2.10. Only the \(\text{trans}\) to \(\text{cis}\) photochemical reaction is temperature dependant. The activation energy has been determined to be 0.7 kJmol\(^{-1}\).\(^{22}\) The quantum yield is 0.20 for \(\text{trans} \rightarrow \text{cis}\) and 0.70 for \(\text{cis} \rightarrow \text{trans}\).\(^{22}\)

A major drawback of the azobenzenes is that the photogenerated \(\text{cis}\) state can also thermally return to the \(\text{trans}\) state. The activation barrier is approximately 100 kJmol\(^{-1}\) for a variety of azobenzene derivatives.\(^{9}\) The photoinduced \(E,Z\)-isomerization of azobenzene has attracted
considerable attention of chemists since the late 1970s when several groups recognized the E,Z-isomerization of azobenzene to be useful as a new tool to enforce reversible changes in a variety of molecular systems. A pioneer in this field was Shinkai, who investigated photoresponsive azobenzene-bridged crown ethers. An additional advantage when azobenzenes are incorporated in supramolecular systems is that they are often forced into a certain conformation due to the surrounding media, and this leads to an increase in thermal stability. This was shown, for instance, by Willner et al., who synthesized model systems for biological self-assembly materials like DNA or proteins, which formed a complex with cis-3,3'-diacetyl-azobenzene. The thermal cis to trans isomerization was completely inhibited. Scheme 2.6 shows a completely different example of the use of azobenzenes as photoresponsive systems. In this case the trans-azobenzene derivative (2.11-trans) effectively blocked the cavity of the β-cyclodextrin moiety, thereby preventing binding of the substrate, p-nitrophenyl acetate, to the cyclodextrin and subsequent histidine induced hydrolysis. The cis-isomer (2.11-cis) does not fit into the cavity, thus after irradiation with UV light the cavity is free for substrate binding and imidazole-catalyzed ester hydrolysis can take place again. This process is reversible.

2.2.3 Photocyclizations

Another light-induced transformation that molecular switches can undergo is an electrocyclic reaction. This was already shown for the formation of dihydrophenanthrene (1.6). This may be illustrated by a 1,3,5-hexatriene derivative, which undergoes a photocyclization to 1,3-cyclohexadiene (Scheme 2.7). The ring closure is conrotatory for photochemical reactions, resulting in a trans deposition of R₁ and R₂. The thermal ring closure is disrotatory resulting in a cis arrangement of R₁ and R₂. This stereochemical outcome is predicted by the Woodward-Hoffmann rules.¹⁰

![Scheme 2.7 Photocyclization of a 1,3,5-hexatrien derivative.](image-url)
Among the photochromic compounds that undergo these ring closures are (a) the spiropyrans \(2.12\), (b) the fulgides \(2.13\) and (c) the diarylethenes \(2.14\) (Scheme 2.8).

![Scheme 2.8 Compounds that undergo photocyclizations.](image)

The photochromic behavior in spiropyran compounds\(^{26}\) arises from a photochemical \(6\pi\) electron ring-closure reaction leading to the colorless closed spirostructure \(2.15c\) and the colored open merocyanine structure \(2.15o\) (Scheme 2.9). The \(\lambda_{\text{max}}\) for several derivatives of \(2.15o\) are for \(R = \text{Me}\); 532 nm (ethanol) and 610 nm (toluene), for \(R = \text{Et}\); 590 nm (dioxane) and for \(R = \text{Ph}\); 559 nm (ethanol) and 610 nm (toluene). The quantum yields for \(2.15\) \(R = \text{Me}\) at r.t. in ethanol are as follows: \(\Phi_{c \rightarrow o}(313) = 0.15\), \(\Phi_{c \rightarrow o}(366) = 0.12\) and \(\Phi_{o \rightarrow c}(546) = 0.10.\(^{27}\)

![Scheme 2.9 Switching of a spiropyran derivative \((c = \text{closed}, o = \text{open})\).](image)

Spiropyrans have several drawbacks such as low thermal stability of the merocyanine form,\(^{28}\) photooxidation\(^{29}\) as side reaction and thermochromic behavior.\(^{30}\) The thermal activation barrier is 8.8 kJ\(\text{Mol}^{-1}\) for \(2.15o\) \(R = \text{Me}\) at 25\(^\circ\)C.\(^{31}\) Nevertheless spiropyrans are widely employed in photochromic polypeptides,\(^{32}\) holographic recording\(^{33}\) and optobioelectronic devices.\(^{34}\) An intriguing application of spiropyrans was published recently by Raymo et al.\(^{35}\) This deals with the problem of making devices in which organic molecules are integrated. The difficulty is the establishment of electrical communication between the molecules. Raymo and coworkers used a three-state spiropyran switch\(^{36}\) to communicate intermolecular signals to pyrene, a fluorescent probe (Scheme 2.10). The fluorescence intensity of pyrene \(2.17\) decreases in presence of the switch due to coabsorption of the exciting light by the switch and secondly by reabsorption of the emitted light by the switch. However only the contribution of one of these two factors varies upon switching. The absorption at \(\lambda_{\text{exc}}\) of
pyrene increases 17% in presence of spiropyran 2.16c. After switching to 2.16o with UV light and further treatment with acid to 2.16oH this absorption stays at the same level. Thus the coabsorption effect remains the same. The absorption properties of 2.16c, 2.16o and 2.16oH are different in the emission area of pyrene, e.g. the readsoption efficiency of 2.16c is smaller than that of 2.16o and 2.16oH, which display the same efficiency. The emission of pyrene is not influenced by UV, Vis or H⁺ in the absence of the switch. In presence of equimolar amounts of spiropyran (2.16c) and pyrene (2.17) in acetonitrile, after excitation at \( \lambda = 336 \) nm the emission of pyrene decreased to 60% of the original value. When this solution was irradiated at \( \lambda = 254 \) nm, 2.16c opens to 2.16o, which has a larger reabsorption efficiency, and now the emission of 2.17 dropped to 50% after excitation. When acid is added to switch 2.16o to form 2.16oH, the emission level stays the same. Sequences of alternating UV and visible light regulate the fluorescence intensity of pyrene, thus demonstrating that intermolecular communication is possible.

![Scheme 2.10 Signal communication at the molecular level.](image)

Fulgides\(^{37}\) are another class of photochromic molecules that undergo photocyclization. Fulgides possessing at least one aryl group on the methylene carbon atoms were first studied by Stobbe\(^{38}\) and these derivatives are still in use today. Upon irradiation with UV light the colorless (or faintly colored) isomer of the fulgide (E-form) changes into a deeply colored isomer (C-form). During UV irradiation the E-form can also undergo \textit{cis-trans} isomerization to the Z-form (scheme 2.11). The C-form of the fulgide (C-2.18) depicted in Scheme 2.11 is thermally not stable, but when the phenyl group was replaced by a furyl group, and a methyl group was introduced at the ring-forming carbon atom (R₂ or R₃) of the aromatic ring, together with an isopropylidene as the other methylene unit, the system became a thermally irreversible (2.19, Scheme 2.12).\(^{39}\)
After this development the fulgides were suddenly very promising optical materials, even more since, other side reactions like oxidative aromatization and sigmatropic proton shifts appeared also to be suppressed effectively by these structural changes. If R is a methyl group the quantum efficiency is 20%, but when R is isopropyl the quantum efficiency is as high as 62%. In both cases the absorption maximum of the E-form is about 360 nm and of the C-form about 500 nm. The quantum yields measured for R = isopropyl in toluene are 0.58 for \( \Phi_{E \rightarrow C} \) (366 nm) and 0.043 for \( \Phi_{C \rightarrow E} \) (492 nm). The \( E \) to \( Z \)-isomerization did not occur. Fluorescence can be used as a non-destructive read-out method in case of fulgides, because E-form fulgides rarely emit fluorescence unless they bear fluorescent substituents, whereas C-forms often fluoresce at low temperatures. Fulgides have also been used extensively to switch biological activities and to switch the anisotropy of liquid crystalline phases.

Yokoyama et al. showed that binaphthol derivatives 2.20 and 2.21 induced a cholesteric phase in nematic LC 2.23 (Scheme 2.12). Upon irradiation the pitch changed dramatically. Addition of 1.1 mol% of 2.21 resulted in changes of pitch length of 15.8 \( \mu \)m and 2.6 \( \mu \)m respectively for the E-form and the p.s.s. (C/E mixture) after UV irradiation. For 2.22 a less pronounced change in the pitch occurred on UV irradiation and the sense of the induced
helices was also different form 2.20 and 2.21 although the helicity of the fulgide core part remained the same.\textsuperscript{45}

### 2.3 Diarylethene

Last but certainly not least of the photochromic molecules that will be discussed are the diarylethenes (Scheme 2.13).\textsuperscript{46}

![Scheme 2.13 Switching cycle of diarylethene.](image)

Upon irradiation with UV-light the diarylethenes (2.24\textsubscript{o}) undergo a ring closure to the colored closed form (2.24\textsubscript{c}). This closed form is thermally stable (\textit{vide infra}) and upon irradiation with visible light the system returns to the ring opened form. The most important properties of these compounds are the thermal stability of the closed form and the high fatigue resistance.

For our purposes, namely incorporation of a switch in a supramolecular system, we need an optical switch that is thermally stable after irradiation, and that can be colored and bleached repeatedly. Furthermore all properties should be retained after incorporation in a supramolecular system. Of all the photochromic switches that were described in this chapter only the fulgides and the diarylethenes show thermal stability. Moreover the diarylethenes have a much higher durability than the fulgides. Coloration and bleaching cycles can be repeated more than $10^4$ times while maintaining satisfactory photochromic performance, whereas in most cases the furylfulgides are seldom stable for more than 100 cycles.\textsuperscript{47} Another advantage is the more easier accessibility of the diarylethenes compared to the fulgides. Therefore we have chosen to use the diarylethenes as the photochromic system. In order to provide a literature background to the research described in this thesis, the remaining part of this chapter is dedicated to the diarylethenes. An overview of the fundamental properties of these compounds and their recent developments is given.

Irradiation of \textit{cis}-stilbene (2.5) can lead to the formation of dihydrophenanthrene (2.6), actually a closed diarylethene (Scheme 2.3). As was already pointed out (\textit{vide supra}), this compound is thermally not stable. In order to develop thermally stable compounds it is necessary to establish which properties are responsible for this thermal instability. It appeared that the thermal stability of the ring-closed form is controlled by the energy barrier, which
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correlates with the ground-state energy difference between the open and photochemically closed form.\textsuperscript{48} When the energy difference in the ground state is large as in the case of stilbene 2.5 (114.2 kJ\text{Mol}\textsuperscript{-1}) (depicted in Scheme 2.14 left), the energy barrier for ring opening becomes smaller and the cycloreversion reaction readily takes place. On the other hand the barrier becomes large when the energy difference is small, as is the case for 1,2-bis(thien-3-yl)ethene 2.25 (-13.8 kJ\text{Mol}\textsuperscript{-1}). The aromatic stabilization energy of the aryl groups in the open form correlates well with the ground-state energy difference. The highest energy difference was calculated for the phenyl group (115.9 kJ\text{Mol}\textsuperscript{-1}) and the lowest for the thiethyl group (19.7 kJ\text{Mol}\textsuperscript{-1}).

\begin{scheme}
\begin{center}
\includegraphics[width=\textwidth]{Scheme_2.14.png}
\end{center}
\end{scheme}

\textit{Scheme 2.14 Relative ground state energy differences between the open and photochemically closed isomers.}

Aromaticity is the key property that controls the energy barrier required for thermal stability of the closed form. To meet these requirements for a thermally stable system, thienyl, benzothienyl or thiazole groups have to be introduced as the aryl groups in order to introduce a large energy barrier for the cycloreversion reaction. The closed forms of diarylethenes (2.24c) having phenyl, pyrrolyl or indolyl groups are thermally unstable, because the energy barrier of these compounds is small.

In order to prevent \textit{cis-trans} isomerization during the photochemically induced ring-closing reaction, in most compounds the alkene connecting the thiophenes is part of a cyclic structure. Rings of different sizes have been employed. For example, 1,2-bis(benzothien-3-yl)perfluorocycloalkenes have been synthesized with 4, 5 and, 6 membered rings.\textsuperscript{49} The absorption maxima of the ring-closed isomers shifted to longer wavelengths with decreasing ring size. The ring size controls the planarity and thus the extent of \pi–conjugation in the ring-closed isomers. Furthermore the quantum yield also depends on the ring size and the highest value was measured for the six-membered ring.\textsuperscript{50} The five-membered ring is the most
appropriate choice if these two factors are taken into account. Several different bridging units have been used, the perfluorocyclopentene (2.27),\textsuperscript{49} cyclopentene (2.28),\textsuperscript{51} dihydrothiophene (2.29),\textsuperscript{52} maleic anhydride (2.30)\textsuperscript{53} and the maleimide-bridge (2.31),\textsuperscript{54} depicted in that order in scheme 2.15, of which the perfluorocyclopentene (2.27) is the most frequently used.

![Scheme 2.15 Different bridging alkene ringstructures used in diarylethenes.](image)

The non-trivial to resort the understatement synthesis of these perfluorocyclopentene based diarylethenes prompted us to develop a new synthetic route to this system.\textsuperscript{55} This will be discussed in further detail in chapter 3, as well as the synthesis of the dithienylcyclopentene analogs.\textsuperscript{51a}

In order to prevent oxidation of the ring-closed product to a molecule with a central aromatic ring, exemplified by the formation of 2.4 by photooxidation of 2.3, hydrogens at R\textsubscript{1} and R\textsubscript{4} must be avoided and these are usually replaced by methyl groups.

During the photochemical reactions of ring opening and ring closing undesirable side reactions can take place. Eventually if one wants to use an optical switch for practical purposes the performance has to be 100\%, e.g. the switching cycle should be repeatable millions of times without degradation. This can be illustrated with the following example: if there is an undesirable reaction with a quantum yield of 0.001, then after 1000 switching cycles 63\% of the initial switch is decomposed. The dithienylethenes show very good fatigue resistance properties, especially in degassed solutions,\textsuperscript{1b} if the proper substituents at R\textsubscript{3} and R\textsubscript{6} are present.

![Scheme 2.16 Deposition product after prolonged irradiation with UV-light.](image)

Recently a degradation product (2.33) was isolated by Irie \textit{et al.}\textsuperscript{56} (Scheme 2.16) and later on it was shown that a similar degradation product also appeared after long irradiation of the
cyclopentene analog (Scheme 2.22). Radical migration in the \( \pi \)-conjugated system is believed to be the cause of the formation of the by-product.

Figure 2.1 shows a typical example of an absorption spectrum of a diarylethene (3.31, bisaldehyde, see chapter 3). The open form absorbs only in the UV region, whereas the closed form owing to destabilization of the ground state and lowering of the HOMO/LUMO barrier exhibits a distinct absorption in the visible region. UV-light, which is absorbed by the open form, is used to induce the ring closing reaction. During this reaction a photostationary state (PSS) will always be reached. Due to non-zero absorption of the closed form in the entire UV spectral region, both ring-closure and ring-opening take place on irradiation, leading to an equilibrium situation determined by the quantum yields of ring-closing and ring-opening. It is thus not possible to obtain 100% of the closed form in this way. Visible light is used in order to switch the closed form back to the open form, a conversion, which does proceed in a 100% yield. The red shift of the closed form depends on the bridge connecting the aryl rings and the substituents that are attached to the arylgroups.

**Figure 2.1** Absorbance of 3.31 in benzene (—) before and (---) after irradiation at 313 nm.

**Scheme 2.17** Diarylethene with longest absorption band thus far observed.
The longest wavelength absorption band thus far reported for a closed form (2.34c) is 828 nm in benzene. Here a strongly electron-donating CH=benzodithiole and a strong electron-withdrawing dicyanoethylene were introduced to 1,2-bis(2-methyl-thien-3-yl)perfluorocyclopentene (Scheme 2.17). However, the closed form of this switch is thermally unstable and \( t_{1/2} = 186 \text{ min at } 60^\circ \text{C} \) was found.

A diarylethene with five membered heterocyclic rings is found in two conformations: (1) the parallel conformation (Scheme 2.18 left), with the two rings in mirror symmetry (plane of symmetry) and (2) the anti-parallel conformation (Scheme 2.18 right), with the rings in a \( C_2 \) orientation (\( C_2 \) symmetry axis). In general the ratio of the two conformational isomers is 1:1. This ratio may sometimes be determined by \(^1\text{H} \) NMR, because in some cases the methyl signals of both conformers are visible. This is the case with benzothiophene diarylethene analogs. The interconversion rate between the two conformations is estimated to be much slower than the lifetime of the photoexcited states. Therefore, both conformers are excited independently, and only the photoexcited anti-parallel conformer can be converted to the closed form. The ground state disrotatory ring closure from the parallel form, predicted by the Woodward-Hoffmann rules is prohibited because of both steric hinderance caused by the central methyl groups and the higher ground state energy of the closed form than that of the corresponding open form. In practice this means that the maximum quantum yield of the ring closing reaction is 0.5. In order to increase the quantum yield the ratio of the anti-parallel conformation has to be increased. This has been accomplished in three different ways:

1. By introducing bulky substituents at the 2- and 2'-positions of the arylgroups (2.35).
2. By incorporating the switch in a polymer backbone (2.36).
3. By including the switch in a confined space, e.g. a \( \beta \)-cyclodextrin.

2-Isopropyl groups (2.35) instead of methyl groups at the 2- and 2'-positions increased the cyclization quantum yield from 0.35 to 0.52, but unfortunately the closed form of this compound is not thermally stable. When the switch is incorporated in a polymer backbone (2.36), the anti-parallel conformation is the only conformation that can exist.
This system gives the largest quantum yield for the ring closing reaction so far reported ($\Phi = 0.86$). The molecule in the anti-parallel conformation has an extended rodlike structure, whereas the molecule in parallel conformation has a cubic structure. In case of $\beta$-cyclodextrin the anti-parallel conformer fits better into the cavity than the parallel conformer, thus enhancing the quantum yield. This effect was not only found with $\beta$-cyclodextrin, but also with $\gamma$-cyclodextrin, in the latter case the change is less pronounced. The cavity of $\alpha$-cyclodextrin appeared to be too small.

Both the energies of the states and the probabilities of transitions are influenced by the physical properties of the medium. As “medium” a very wide range of states should be considered including, like liquids, solids, micelles, organized thin films and even vacuum. As an example, a change in the dielectric constant of a solvent affects the values of the maxima of both absorption and emission spectra. Technical applications of photochromic systems to optoelectronic devices require dispersion of compounds into solid matrices. The photochromic reactivity is supressed in most cases in polymer media. Moreover the quantities of compounds which can be dispersed in polymer matrices are limited. Therefore it is desired to develop bulk photochromic systems. Crystalline and amorphous diarylethenes are thus of great promise in potential applications.

Compounds that show photochromic reactivity in crystalline phases are very rare. In most cases the photogenerated closed forms are thermally unstable. Some of the diarylperfluorocyclopentenes undergo photochromism in the crystalline phase and are thermally stable (Scheme 2.20). The molecules in the crystal lattice should, of course, have an anti-parallel conformation in order to be able to undergo ring closure.
Provided there is no steric hindrance that will force the molecule to adopt the parallel conformation, the switch will show this behaviour. All the molecules described in this thesis show solid-state photochromism. An exception is found for some switches described in chapter 5, but they do not show photochromic reactivity in solution either. We did not determine the thermally stability of the solid states. Other examples of crystalline photochromism are found among coordination complexes. A copper complex of 1,2-dicyano-1,2-bis(2,4,5-trimethylthien-3-yl)ethene\(^7\) and a linear coordination polymer composed of 1,2-bis[2’-methyl-5’-(4’’-pyridyl)-thien-3’-yl]perfluorocyclopentene and bis(hexafluoroacetyl-acetonato)zinc(II) (Scheme 2.21) have been reported.\(^7\)

![Scheme 2.21](image)

**Scheme 2.21** Photochromism of a linear chain polymer in the crystalline phase.

In solution there was no difference in absorption maxima of the closed form of the compound shown in Scheme 2.21 between the free ligand and the complex, whereas in the solid state the absorption maxima of the polymer complex showed a redshift of 10 nm. This shift is due to the increased strain in the crystal due to complexation.

### 2.4 Applications of diarylethene photochromic switches

In this section some recent examples from the diarylethene-research areas will be discussed. Beginning with the first system that was synthesized starting from the dithienylcyclopentene-switch developed by us.\(^5\) Branda *et al.* reported the photochromic behaviour of covalently linked double 1,2-dithienylethenes.\(^5\) When 2.37 is irradiated with light of 365 nm, only one diarylethene moiety is closed, this was determined by \(^1\)H NMR in
cyclohexane-$d_{12}$. Prolonged irradiation did not result in the ring closure of the diarylethene unit, but resulted in the formation of the decomposition product (2.39), similar to the one reported previously by Irie et al.\textsuperscript{56} When the same system was prepared starting from 1,2-bis-(2’-methyl-thien-3’-yl)perfluorocyclopentene, similar observations were made. Only one diarylethene moiety was closed and after prolonged irradiation the same decomposition product appeared, but in this case much longer irradiation times were needed to obtain this decomposition product compared to 2.37.

\subsection*{2.4.1 Photocontrolled magnetism}

\begin{center}
\includegraphics[width=\textwidth]{Scheme223.png}
\end{center}

\textit{Scheme 2.23 Photochromism of a diarylethene containing nitronyl nitroxides.}

It is known that molecular magnetism can be controlled by light by incorporating a photochromic moiety into the system.\textsuperscript{73} Intermolecular magnetic interaction has been controlled photochemically, but photocontrol of intramolecular magnetic interaction was still a challenge. Irie et al. succeeded in this by attaching two nitronyl nitroxides to the diarylethene switch system.\textsuperscript{74} The nitronyl nitroxide radical was chosen because of its $\pi$-conjugation and it was found to be rather persistent under UV-Vis light. The system showed excellent photochromic properties both in solution and in the crystalline phase. The closed form has a resonant quinoid structure,\textsuperscript{75} which stabilizes it. It therefore suppresses the cycloreversion reaction and that is why high conversions (>99\%) are reached for the ring closure reaction. Earlier Lehn et al. reported the same findings with the ring closed forms of bisphenolic diarylethenes, which are electrochemically oxidized to the quinoid form.\textsuperscript{76} The magnetic susceptibility was measured with crystals of both the open and the closed form. Although the two spins of open form 2.40o have a small interaction ($2J/K_B = -2.2$ K) due to the disconnection of the $\pi$-conjugation system, which was confirmed by X-ray, spins of closed form 2.40c have remarkable antiferromagnetic interaction ($2J/K_B = -11.6$ K). The change of the magnetization is thus attributed to the change in planarity and aromaticity of the molecular structure, resulting in enhanced (or diminished) spin interactions.

\subsection*{2.4.2 Switching of liquid crystalline phases}

Reversible photocontrol of the anisotropic properties of LC materials is a major challenge in the development of new molecular devices and optical data storage systems. A variety of photochromic polymer liquid crystals for the construction of these devices and storage systems have been described.\textsuperscript{77} The photochromic molecules are covalently attached
to a polymer LC or polymer LC’s are doped with photochromic molecules. Also a non-polymer based LC can be doped by photochromic molecules. The addition of small amounts of optically active guest molecules to a nematic LC host can induce a cholesteric phase.\textsuperscript{78} The resulting cholesteric phase depends on the helical twisting power (HTP), the type of LC material and the structural compatibility of the chiral dopant. Photochemically induced changes in the structure or stereochemistry of the dopant can therefore induce a significant change in the anisotropy of the LC. Azobenzenes have been used to reversible switch between nematic and isotropic LC phases.\textsuperscript{79}

\begin{center}
\includegraphics[width=\textwidth]{Scheme224.png}
\end{center}

**Scheme 2.24** Photoisomerization of bisimine diarylethene doped in LC material. (a) cholesteric fingerprint texture. (b) nematic texture (1.4 wt% of 2.41o in ZLI-389 at 52°C).

Recently in our laboratories chiral diarylenes have been used to switch reversibly between a cholesteric and nematic LC phase.\textsuperscript{80} In the open form diarylethene (2.41o) induced a stable cholesteric phase (Scheme 2.24a) in nematic LC materials K15 and ZLI-389. The HTP values were 11 µm\(^{-1}\) for K15 and 13 µm\(^{-1}\) for ZLI-389 at doping with 2.1 wt% of 2.41o. After irradiation at λ = 300 nm the closed form was generated (2.41c) and the cholesteric phase disappeared (Scheme 2.24b). The cholesteric phase was restored after irradiation with visible light. The HTP of the closed form is thus smaller than for the open form. Six switching cycles could be performed without deterioration of the LC phase. Another diarylenene derivative (2.42, Scheme 2.25) with two diarylethene units in a chiral cyclohexane\textsuperscript{81} was doped in commercially liquid crystal K15 and showed the same effect, but now the other way around. Doping of K15 with the open form resulted in a nematic LC phase.\textsuperscript{82} After irradiation at λ = 313 nm the PSS (ratio closed/open = 3/2) induced a cholesteric phase.
In this case the HTP of the open form is the smallest. Both phases, the nematic and the cholesteric phase, remained stable even after long-term storage. The switching cycle was performed 50 times without deterioration of the LC phase.

2.4.3 Gated reactivity

For a practical optical memory the wavelength needed for read-out should not interfere with the switching process, because otherwise the stored information will be erased. Nondestructive read-out is required. One possible way to accomplish this is by gated reactivity. As was pointed out only the anti-parallel conformer of the switch can undergo the ring-closing reaction. So if the switch can be ‘trapped’ in the parallel conformer it will not go to the closed form. Irie et al. used this concept by designing a diarylethene acetic acid derivative, which is fixed in the parallel conformer by intramolecular hydrogen bonds in a cyclohexane solution (Scheme 2.26). The addition of a small amount of ethanol breaks the hydrogen bonds and the system regains its photochromic activity.\textsuperscript{83} In decaline the system also regained its activity when it was heated above 100°C.

Dual-mode type switching systems can be considered to undergo gated photochromic reactions. These systems combine two reversible processes that can be addressed by two independent stimuli. Lehn et al. synthesized a molecule having both photochromic and electrochromic active units (Scheme 2.27).\textsuperscript{84}
The electrical behavior is controlled in an on-off fashion by light and the photochromism is likewise regulated electrochemically. After irradiation with UV light (\(\lambda = 312\) nm) the closed form was generated, which was converted chemically to the quinonoid compound by addition of excess K\(_3\)Fe(CN)\(_6\) and aqueous KOH. This compound could also be obtained by irradiating \(2.43o\) at \(\lambda = 254\) nm, which leads to the formation of \(2.43c\), which is then irreversibly oxidized to \(2.43q\). The open form is electrochemically inert within the \(-1\) to \(+1\) V range, whereas the closed form has a reversible oxidation wave corresponding to the formation of quinonoid form \(2.43q\). The quinonoid form is photochemically stable (< 2% change after 8 h of irradiation at \(\lambda > 600\) nm). Thus \(2.43c\) is photochromic, whereas oxidation to \(2.43q\) can be used to block effectively the ring-opening reaction. Recently the same group also developed a similar gated system based on photocontrolled PK\(_a\)-modulation.\(^8\)}
The quantum yield of the photochemical ring opening reaction of 2.44 is 0.00013 at ambient temperature (Scheme 2.28). This increased up to 34 times when the temperature was increased from 25 to 150°C. This system can also thus be considered to employ thermal-gated reactivity.

### 2.4.4 Fluorescence

The fact that the optical properties of the diarylethene molecule change after irradiation can be used to circumvent destructive read-out. Changes in these optical properties, such as transmittance, reflectance, refractive index, optical rotation, IR or fluorescence are used for this application. Fluorescence is highly sensitive and is therefore a very suitable read-out method. Fluorescence can be used as a nondestructive readout method if (a) there is a difference in fluorescence emission between the open and closed form of the diarylethene, (b) the fluorescence excitation wavelength does not interfere with the switching process of the diarylethene.

Lehn and coworkers synthesized a series of dithienylethenes functionalized with oligothiophenes. They found that the open form of the switches depicted in Scheme 2.29 were very strongly fluorescent both in the methylated form and in the non-methylated form, whereas the closed form of these compounds emitted very weakly. The absorption bands that are used for the fluorescence excitation are inactive with respect to the opening-closing photoreactions.

![Fluorescent dithienylethenes](image)

**Scheme 2.29** Fluorescent dithienylethenes.
2.4.5 Reversible Surface Morphology

![Scheme 2.30](image)

**Scheme 2.30** Single crystal that shows reversible surface morphology.

The surface morphology of a single crystal of 2.49 (Scheme 2.30) was observed with AFM under irradiation with 366 nm light to form the closed form. The initially flat (100) surface (A) of the crystal turned blue and steps of about 1 nm height appeared, corresponding to one molecular layer. The (010) surface (B) showed valleys with a depth of about 10 to 50 nm after irradiation with 366 nm. Both the steps and the valleys disappeared after irradiation of the crystal with \( \lambda > 500 \) nm. These reversible morphological changes can be attributed to the molecular changes of the diarylethenes regularly packed in the single crystal. Morphological changes of photo-reactive single-crystal surfaces were reported earlier by Kaupp\(^93\) but these changes were irreversible. When the irradiation times of surface A were prolonged, the number of steps increased and steps with heights of 2 and 3 nm appeared. The height was always a multiple of the minimum step height of 1 nm. X-ray studies of both surfaces revealed a decrease in the thickness of the molecular layers. This shrinking produces vacancies in the crystal bulk. Accumulation of vacancies deep within the crystal allow the surface molecular layer B to descend as much as one layer. Upon prolonged irradiation the vacancies increase and two or more layers descend, which explains the observed step formation at surface A. These crystals could potentially be used as photodriven nanometer scale actuators.

2.5 Conclusions

Various types of photochromic switches are known. Most of them have the disadvantage of the thermal reversibility of the photogenerated form. Major drawbacks are the side reactions that can occur like photooxidation or undesired *cis-trans* isomerizations. For the application of these switches in devices diarylethenes are the best choice. They are thermally stable, fatigue resistant and synthetically rather easily accessible. Therefore we have chosen to use the diarylethenes as the photochromic system. The fundamental properties of diarylethenes have been elaborately discussed in the latter part of this chapter. The (recent) applications showed that they could be successfully applied to construct switching systems, such as, for instance, photoactive liquid crystals, and molecular magnets.
2.6 References and notes


61 Drawings made by Rosanna Telesca using WebLab.


67 Kahn, O.; Molecular Magnetism, VCH, New York, **1993**.


71 Kahn, O.; *Molecular Magnetism*, VCH, New York, **1993**.
