Photochromic Systems for Energy Transfer Switching

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Chapter 1

Introduction
1.1  General Introduction

Photochromic compounds are systems existing in two forms that can be interconverted using excitation with light of different wavelengths as an external stimulus. The two forms generally differ in their physicochemical properties such as the molecular geometry, electronic delocalization, color and reactivity. Much effort has been devoted to their investigation,\textsuperscript{1-3} since these interesting compounds may be employed as components in molecular electronics and data storage applications,\textsuperscript{4-7} as first suggested by Hirshberg in 1956.\textsuperscript{8}

Photochromic molecules can be divided into several important classes, such as azo-compounds, diarylethenes, spiropyrans and spirooxazines, fulgides and fulgimides, chromenes and sterically overcrowded alkenes.\textsuperscript{9} Diarylethenes, spiropyrans and fulgimides have been employed in the work described in this Thesis. The properties of these classes of compounds (and those of fulgides, which are very closely related to fulgimides) are therefore discussed in detail in this Chapter.

1.2  Woodward-Hoffmann Rules

Many photochromic processes involve pericyclic reactions, i.e., reactions in which a ring structure is either formed or broken. Robert Woodward and Roald Hoffmann introduced a set of rules aimed at predicting the steric course of these reactions.\textsuperscript{10} Given the importance of this theory for the discussions in this Thesis, it is briefly described here.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1}
\caption{Molecular orbital diagram for buta-1,3-diene.}
\end{figure}
The governing concept of the Woodward-Hoffmann rules is that of orbital symmetry. Using simple Hückel theory, orbitals of different energies can be constructed for conjugated polyenes from suitable linear combinations of atomic p-orbitals. The lowest energy molecular level has all p-orbitals aligned in a $\pi$-bonding combination, and the highest energy state has the atomic orbitals alternately oriented up and down in a $\pi$-antibonding combination, resulting in the maximum number of nodal planes. This concept is demonstrated for buta-1,3-diene in Figure 1.1.

In the Woodward-Hoffmann approach, only the frontier orbitals are considered. The orbital symmetry of the highest occupied molecular orbital (HOMO) dictates the fashion in which a thermal (ground-state) reaction can take place, while the lowest unoccupied molecular orbital (LUMO) is associated with photochemical (excited-state) reactions. A cyclization reaction can either take place in a conrotatory fashion, where both terminal bonds rotate in the same direction in order to create an orbital overlap, or in a disrotatory fashion, where the terminal bonds rotate in opposite directions. For the cyclization reaction to be energetically favorable, a positive overlap between the atomic orbitals on the termini of the polyene system must be achieved by the rotation.

For buta-1,3-diene, the frontier orbitals are $\Psi_2$ (HOMO) and $\Psi_3$ (LUMO) (see Figure 1.1). The orientation of the atomic orbitals on the termini dictates that the thermal reaction must take place in a conrotatory fashion, and the photochemical reaction in a disrotatory one (see Figure 1.2). It can be shown that for a $4n+2$ $\pi$-electron system, the thermal reaction takes place in a disrotatory fashion and the photochemical reaction in a conrotatory one.

![Figure 1.2](image.png)

**Figure 1.2.** Favorable cyclization paths for thermal and photochemical reactions of buta-1,3-diene.

### 1.3 Diarylenes

The first example of a reversible photochromic reaction of diarylenes was reported by Irie and Mohri in 1988.\(^{11}\) The design of their system was inspired by the photoreactivity of stilbene. Upon irradiation with UV light, stilbene not only undergoes a cis/trans-isomerization, but it can also cyclize to produce 4a,4b-dihydro-phenanthrene (see Scheme 1.1).\(^{12}\) In the presence of oxygen, the latter compound is converted to phenanthrene by rapid hydrogen elimination. In the absence of oxygen, fast thermal cycloreversion to stilbene occurs.
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Scheme 1.1. Photochemical cyclization reaction of stilbene, followed by oxygen-assisted hydrogen elimination producing phenanthrene.

The hydrogen elimination process can be inhibited by substituting the phenyl rings of stilbene with methyl groups in the 2- and 6-positions. The resulting cyclized molecule is still thermally unstable, however.\textsuperscript{11} A study by Kellogg et al. showed that replacement of the phenyl groups with thienyl rings strongly increases the thermal stability of the closed-ring structure, achieving a lifetime $t_{1/2}$ of several hours.\textsuperscript{13} In attempts to further increase the thermal stability of the closed form, Irie et al. synthesized diarylthene $G_{1o}$ and $G_{2o}$ (see Scheme 1.2).\textsuperscript{11}

\begin{align*}
G_{1o} & \quad X = S \\
G_{2o} & \quad X = O \\
G_{1c} & \quad X = S \\
G_{2c} & \quad X = O
\end{align*}

Scheme 1.2.

When irradiated with UV light, $G_{1o}$ and $G_{2o}$ convert to the closed-form structures $G_{1c}$ and $G_{2c}$, respectively. Both $G_{1c}$ and $G_{2c}$ are completely thermally stable at room temperature and resistant towards oxidation by air. Upon exposure to visible light ($\lambda > 390$ nm) $G_{1c}$ and $G_{2c}$ convert back to $G_{1o}$ and $G_{2o}$, respectively.

A disadvantage of open structures $G_{1o}$ and $G_{2o}$ is that upon excitation the cyclization reaction competes with cis-to-trans isomerization. In an attempt to inhibit this undesirable side-reaction, $G_{3o}$ was synthesized (see Scheme 1.3).\textsuperscript{11} The corresponding cyclized form $G_{3c}$ turned out to be thermally stable at room temperature, similar to $G_{1c}$ and $G_{2c}$, while the newly introduced anhydride ring structure completely prevented the cis-to-trans isomerization of the open form.

\begin{align*}
G_{3o} & \quad \text{hv} \\
G_{3c} & \quad \text{hv'}
\end{align*}

Scheme 1.3.
Semiempirical MNDO (modified neglect of differential overlap) calculations on stilbene and other diarylethenes indicated that the thermal stability of the cyclized molecules depends on the loss of aromatic stabilization energy upon conversion.\textsuperscript{14} Cyclization of stilbene strongly reduces aromaticity of the system, resulting in a large energy difference between the open and closed forms and a relatively low energy barrier for cycloreversion. Replacing the phenyl groups by furyl or thienyl substituents impedes the large loss of aromatic stabilization energy upon cyclization. Consequently, the ground-state energy difference between the two forms becomes smaller and the ground-state energy barrier increases.

In 1992, Irie et al. discovered that the durability of diarylethenes could be dramatically increased by incorporating the central double bond in a perfluorocyclopentene ring.\textsuperscript{15} Since then, the majority of the diarylethenes studied have been of this type, with 3-thienyls as the most frequently encountered aromatic groups bound to the double bond (see Chart 1.1).

![Chart 1.1](image)

**Chart 1.1.** Example of a simple bis(3-thienyl)perfluorocyclopentene molecule.

### 1.3.1 Electronic Absorption Properties

In general, diarylethenes in the open form absorb at shorter wavelengths than the corresponding closed forms. The reason for this difference is that in the cyclized form the molecule adopts a planar geometry, resulting in conjugation over the entire molecule, while in the open form the aromatic rings twist out of plane and the conjugation is broken.\textsuperscript{16} As an example, the UV-vis absorption spectra of G3\text{o} and G3\text{c} are shown in Figure 1.3.\textsuperscript{17}

By substituting the system with groups that further extend the conjugation, the $\pi\pi^*$ absorption of the closed form can be shifted to longer wavelengths.\textsuperscript{18} Introduction of electron-donating substituents extends this trend. Maximum red shift of the closed-form absorption can be achieved by placing an electron-donating group at one side of the molecule and an electron-accepting group at the other one, hereby effectively creating a push-pull system.\textsuperscript{19} Due to the lack of conjugation over the molecule, the effect of substitution on the electronic absorption spectra of the open form of diarylethenes is much less pronounced.
1.3.2 Luminescence Properties

In general, excited open-form diarylethenes and their corresponding closed forms do not emit light. However, in rare cases, weak fluorescence is detected. Most notably, bis(2-thienyl)perfluorocyclopentene-type molecules have been shown to emit light in their open forms.\textsuperscript{20,21} Fluorescence has also been observed for the open form of a diarylethene incorporating one thiophene and one benzothiophene group,\textsuperscript{22} a diarylethene dimer with one photochromic unit in the open and the other in the closed form,\textsuperscript{23} and for both the open and closed forms of a diarylethene substituted with long conjugated side-chains.\textsuperscript{24}

1.3.3 Photoreactivity

Diarylethenes with five-membered heterocyclic rings exist in two conformations in the open form, one having the two rings in the mirror symmetry (the parallel conformation) and the second one in the $C_2$ symmetry (the antiparallel conformation), as depicted in Figure 1.4.\textsuperscript{11}

![Figure 1.4.](image)

A simple bis(3-thienyl)perfluorocyclopentene in the antiparallel (left) and parallel (right) conformations.
Interconversion between these two conformations is slow, and the two forms can sometimes be distinguished by $^1$H NMR at room temperature,\textsuperscript{11,18,25} although in other cases separate signals are only observable at sufficiently low temperature.\textsuperscript{26} According to the Woodward-Hoffmann rules,\textsuperscript{10} the photochemical cyclization can only occur in a conrotatory fashion. This means that only molecules in the antiparallel conformation are photoreactive. For simple diarylethenes, the ratio between the parallel and antiparallel conformations is approximately 1:1.\textsuperscript{18} As a consequence, the cyclization quantum yield for these molecules cannot exceed 0.5. For the first generation of diarylethenes (such as $G\textsubscript{1o}$, $G\textsubscript{2o}$ and $G\textsubscript{3o}$ (see Schemes 1.2 and 1.3)) photocyclization quantum yields lie in the range of 0.1-0.2.\textsuperscript{11,26} In contrast, simple dithienylperfluorocyclopentenes were found to be much more reactive, with photocyclization quantum yields close to the limiting value of 0.5 in many cases.\textsuperscript{18}

In order to achieve quantum yields higher than 0.5, the antiparallel-to-parallel conformation ratio has to be increased. Several methods have been developed to achieve this goal. A number of studies have shown that introducing bulky substituents in the 5- and 5′-positions of the thiophene rings of bis(3-thienyl)cyclopentene-type structures increases the antiparallel-to-parallel ratio and, hence, the cyclization quantum yield, often to values exceeding 0.5.\textsuperscript{27-30} Another approach is to incorporate the diarylethene in a polymer backbone, thereby forcing it to adopt the antiparallel conformation.\textsuperscript{31}

The efficiency of the cycloreversion process depends on other factors than that of the cyclization reaction. Some types of diarylethenes show intrinsically high cycloreversion quantum yields,\textsuperscript{20,25,26,32} but for simple representatives of the popular class of dithienylperfluorocyclopentenes the yields only occasionally exceed 0.1 and often are much lower.\textsuperscript{18} Cycloreversion quantum yields depend on the extent of conjugation in the closed-form molecule. Upon substitution of the diarylethene with groups extending the $\pi$-conjugation, the cycloreversion efficiency decreases.\textsuperscript{33,34} Irie et al.\textsuperscript{33} ascribed this feature entirely to a decrease in anti-bonding nature of the reactive C-C bond in the singlet excited state, while Bens et al.\textsuperscript{34} assume that a decrease of the excited state lifetime upon increase of the conjugation also plays a role. Significantly higher cycloreversion quantum yields can be achieved by substituting the methyls in the 2-positions of the thienyl rings with electron-withdrawing cyano groups.\textsuperscript{35} The inverse effect is observed when the methyls are replaced by electron-donating methoxy groups. These substitutions do not significantly affect the cyclization efficiency.

### 1.3.4 Electrochemistry

In their closed form, diarylethenes are oxidized\textsuperscript{36-38} and reduced\textsuperscript{39} more easily than in their open forms. In 1995, Koshido et al. described a diarylethene that underwent cycloreversion upon oxidation of the closed-form molecule.\textsuperscript{36} Since then, it has been shown that both the cyclization\textsuperscript{38,39} and the ring-opening\textsuperscript{36,37,40,41} reactions can be triggered by oxidation in certain cases.
In 2005 three research groups independently published studies on the mechanism behind the oxidative cyclization/cycloreversion process. Their results are largely in agreement. It has been found that most diarylethenes can either undergo the oxidative cyclization or the oxidative cycloreversion reaction. The direction of the reaction depends on the relative stability of the cationic species. If the open-form cation is lower in energy than the cation of the cyclized molecule, electrochemical ring-opening will occur. If the cation of the cyclized species is lower in energy, however, oxidative cyclization will be observed. By introducing proper substituents, the stability of the cations can be influenced and the direction of the reaction can be reversed.

1.3.5 Energetics

Early studies on diarylethenes employing transient absorption techniques with picosecond time resolution showed that both the cyclization and cycloreversion processes are very fast, with time constants $\tau < 10$ ps. Ern et al. conducted a thorough study of the excited-state properties of dithienylcyclopentene G4o (see Chart 1.2), combining femtosecond transient absorption techniques and excited-state potential energy surface calculations.

They found that upon excitation of the open-ring species, structural relaxation occurs along a barrierless pathway on the $S_1$ potential energy surface, followed by a decay to the ground state via a conical intersection (see Figure 1.5). From this point, either the closed form is formed, or the molecule returns to the open form. The high quantum yield for the cyclization of this molecule shows that the former process is preferred. The entire cyclization process occurs with a time constant $\tau = 2.0$ ps.

Upon excitation of the closed form, an excited state species is formed with a lifetime $\tau = 13$ ps. The relatively long lifetime reveals that for the closed form, barrierless relaxation along the excited state surface toward the conical intersection is not possible. Instead, the species relaxes to a local minimum on the excited state energy surface, and from there the decay to the ground state is dominated by internal conversion (see Figure 1.5). Only a small fraction of the excited-state species crosses the barrier to the conical intersection and proceeds in the direction of the open-ring structure.
Figure 1.5. Schematic illustration of the $S_0$ and $S_1$ potential energy surfaces of G4o/G4c as sections along the reaction coordinate. Adapted from ref. 49.

Further studies by the same research group on several other diarylethenes showed that this excited-state model is generally applicable to diarylethene-type molecules.\textsuperscript{28,29} Quantum chemical calculations carried out by another group support the findings of Ern et al.\textsuperscript{50} Uchida et al. reported that, in rare cases, relaxation to an unreactive local minimum on the excited-state energy surface can occur upon excitation of an open-form diarylethene,\textsuperscript{51} but for most systems this pathway is unimportant.

### 1.4 Spiropyrans

Spiropyrans are molecules consisting of two orthogonal heterocyclic parts linked through a common spiro-carbon atom, of which at least one part is a pyran-type structure, typically a benzopyran (see Chart 1.3). A special category is formed by spiropyrans with a nitro substituent in the 6'-position (see Chart 1.3, $X = \text{NO}_2$), often simply referred to as nitrospiropyrans. This substitution strongly affects some of the properties of spiropyrans and their open merocyanine forms. Where relevant, nitrospiropyrans will therefore be discussed separately in this section.

\begin{center}
\textbf{Chart 1.3.} A general representation of a spiropyran. When $X = \text{NO}_2$, the structure is referred to as a nitrospiropyran.
\end{center}
The photochromism of spiropyrans was first described by Fischer and Hirshberg in 1952. At that time, spiropyrans in solution were known to exist in a thermal equilibrium with a colored modification. Fischer and Hirshberg showed that the same colored species formed upon UV excitation. The colored form reverts thermally to the parent spiropyran at room temperature. This process can be accelerated by excitation with visible light.

Researchers postulated that in the colored species the bond between the oxygen atom and the spiro-carbon was broken, but initially there was no general agreement on the exact structure of this molecule. In the 1960s, the colored modification was proven to be a merocyanine-type molecule, with a delocalized structure in between the quinoid and zwitterionic forms (see Scheme 1.4).

Fischer et al. found that, depending on the temperature, different species were formed upon excitation of a spiropyran. They attributed this phenomenon to the formation of different geometric isomers. In the merocyanine, all three bonds between the two ring structures have a bond order >1 and are therefore rigid. This situation yields a total of eight possible isomers (see Chart 1.4). All the experimentally observed isomers were assumed to have a trans-arrangement at the central bond. The corresponding cis-isomers were ruled out for steric reasons. Theoretical calculations predict the TTC isomer to be the most stable one. Time-resolved absorption techniques have shown that the different isomers can be interconverted by irradiation.

Although in most cases the closed-ring spiropyran is the more stable structure at room temperature, several systems have been identified in which the open merocyanine form is the thermally stable one.
**Chart 1.4.** The four merocyanine isomers with a central trans bond (top and middle) and one example of the isomers with a central cis bond (bottom) (T = trans, C = cis).

**Figure 1.6.** UV-vis absorption spectra in THF at 223 K of G5c (---) and G5o (—).
1.4.1 Electronic Absorption Properties

Spiropyrans typically absorb in the UV region. Tyer and Becker compared the UV-vis absorption spectra of several spiropyrans with those of two molecules representing the separate halves. They found that the sum of the individual absorptions was virtually identical to that of the entire spiropyran. This is convincing evidence that the communication between the two orthogonal halves of a spiropyran is limited, which also explains the absence of absorption in the visible region. Their conclusions were later confirmed by calculations. It should be noted that the electronic absorption spectra of some spiropyrans deviate from the sum of the spectra of the separate halves, pointing to some degree of electronic interaction between them. This interaction is weak, however, and does not result in the appearance of low-energy absorption bands.

Upon ring-opening, the molecule adopts a planar geometry. The conjugation becomes extended over the entire structure, which results in strong visible absorption of the corresponding merocyanine form. As an example, the UV-vis absorption spectra of nitrospiropyran $G5c$ and its corresponding open merocyanine form $G5o$ (see Scheme 1.5) are shown in Figure 1.6. Unlike their spiropyran counterparts, the polar merocyanine structures are solvatochromic, exhibiting a blue shift of the visible absorption with increasing solvent polarity.

![Scheme 1.5.](image)

1.4.2 Luminescence Properties

Excited closed-form spiropyrans do not emit light at room temperature. Very weak fluorescence for spiropyrans and rather strong phosphorescence for nitrospiropyrans were observed at 77 K. The excited states involved in the emission are localized on the pyran half of the molecule. For the open merocyanine species, which are highly conjugated species, emission is regularly observed both at low and ambient temperatures. As an example, the emission spectrum of $G5o$ (see Scheme 1.5) is shown in Figure 1.7.

Fischer et al. studied the luminescence properties of merocyanines and have found that only some of the various isomers formed upon spiropyran ring-opening emit. They were unable to assign the luminescence to specific isomers.
Figure 1.7. Emission spectrum in THF at 223 K of G5o. Excitation wavelength $\lambda_{\text{exc}} = 334$ nm.

1.4.3 Thermal and Photochemical Reactivity

Despite the complex nature of the photochromism of spiropyrans (see below), some general observations can be made about this process, as well as about the thermal decoloration reaction. It has been shown that the ring-opening quantum yield of a spiropyran decreases with increasing solvent polarity.\textsuperscript{76,81} The polarity of the solvent also has an effect on the thermal fading rate. Decoloration is slower in more polar solvents which stabilize the charge-separated merocyanine structure.\textsuperscript{82} The thermal cyclization reaction can also be strongly inhibited by confining the space around the spiropyran,\textsuperscript{83} or by attachment of a positively charged group.\textsuperscript{84} An anionic substituent has the opposite effect. These substituents do not significantly affect the ring-opening process.

1.4.4 Electrochemistry

Only a few electrochemical studies have been performed on spiropyrans. One study showed that, within the normal potential scan ranges of electrochemical experiments, unsubstituted spiropyrans are essentially inert.\textsuperscript{85} The electrochemical behavior of substituted spiropyrans is more interesting, especially that of nitrospiropyrans.

Campredon et al. were the first to perform an electrochemical study on a series on nitrospiropyrans.\textsuperscript{86} The authors concluded that the reduction of these molecules was electrochemically reversible, in contrast to the irreversible oxidation. With the aid of EPR, they determined that the species formed upon reduction structurally resembled the closed spiropyran and not the open merocyanine.
Electrochemical studies of a related nitrospiropyran showed that the first reduction is localized on the nitro-group, and that the cathodic step is in fact electrochemically irreversible. Combined electrochemical and spectroelectrochemical investigations of this compound showed that its reduction followed by reoxidation leads to ring-opening of the spiropyran. The ring-opening upon oxidation of this anionic species was claimed to occur in a single step. In Chapter 5 of this Thesis, evidence will be presented that the actual mechanism is more complex.

The electrochemical behavior of hydroxy-substituted spiropyrans is also worth mentioning. For a spiropyran from this class, ring-opening was found to occur upon oxidation. This is the only type of spiropyran for which this kind of anodic response has been reported so far.

1.4.5 Other Properties

Spiropyrans have several other fascinating properties. In acidic solutions they are converted to protonated merocyanines. These cationic species absorb in the visible region at higher energy than the corresponding non-protonated merocyanines. Also, certain merocyanines can chelate metal ions. The chelate bond stabilizes the merocyanine form, and causes a blue shift of the visible absorption. Furthermore, when present in sufficient concentrations, merocyanines can form aggregates in solution. As these properties fall outside the scope of this Thesis, they will not be discussed in detail here.

1.4.6 Energetics

Based upon the electronic absorption spectra of spiropyrans, Heiligman-Rim et al. concluded that the transition involved in the ring-opening process is localized on the pyran half of the molecule. Tyer & Becker assigned a \( \pi \rightarrow \pi^* \) character to this transition. This assignment, and the singlet nature of the corresponding excited state, were later confirmed by theoretical calculations. The triplet levels of spiropyrans are normally not populated upon UV excitation. Triplet sensitization experiments have shown, however, that their population results in highly efficient ring-opening.

For nitrospiropyrans, the lowest excited singlet state was found to have an \( n \rightarrow \pi^* \) character. Calculations later supported this assignment. The \( n\pi^* \) excited states are believed to be non-reactive, and the ring-opening reaction of nitrospiropyrans should therefore take place from the lowest-lying triplet level, which has a \( \pi\pi^* \) character.

Although the singlet reactivity of spiropyrans and the triplet reactivity of nitrospiropyrans are often taken as a fact, several authors have expressed their doubts about how strictly this rule applies, especially when nitrospiropyrans are concerned.
Heiligman-Rim et al. first suggested the existence of an intermediate ("X") in the course of the photochemical formation of an open merocyanine from a spiropyran.\textsuperscript{60,94} Their conclusion was based on the temperature and solvent dependence of the distribution among the possible photoproducts. They postulated that this intermediate X is in fact a ground-state merocyanine structure with a cis-arrangement of the central bond, which is still very close to the original spiropyran structure.

The existence of a semistable cisoid ground-state merocyanine structure has both been proven experimentally and predicted by calculations.\textsuperscript{102,106-109} It was found to have an absorption maximum around 450 nm. However, the fact that this species exists does not necessarily mean it is involved in the ring-opening mechanism of spiropyrans.

In the 1980s, several transient absorption studies were performed on nitrospiropyrans. Although results were often very similar, they were interpreted in different ways. Krysanov and Alfimov assigned a feature in the transient absorption spectrum at 440 nm to intermediate species X.\textsuperscript{110} They believed X to be a ground-state species, which lived for approximately 100 ns, and was formed from the higher excited triplet levels of the nitrospiropyran within the picosecond time domain, in competition with a decay to the lowest excited triplet state. Kalisky et al. assumed that both the triplet state of the spiropyran and X, which they also identified as a ground-state species, absorb around 440 nm, and that both are formed from a common precursor.\textsuperscript{111} They assigned a ns lifetime to the triplet excited state, while X was believed to live for merely several hundreds of picoseconds. The interpretation by Lenoble and Becker is again slightly different.\textsuperscript{112} They attributed the absorption at 440 nm solely to the triplet state of the nitrospiropyran, and an absorption at 530 nm to ground state species X. Formation of X is assumed to occur from the singlet excited state of the nitrospiropyran, in competition with intersystem crossing, with a time constant of several hundreds of ps. X then has a lifetime of approximately 20 ns. Interestingly, all these suggested mechanisms contradict the earlier theory that the ring-opening reaction of nitrospiropyrans occurs from the lowest $\pi\pi^*$ excited state.

For unsubstituted spiropyrans, a transient feature with a maximum at 440 nm was also observed.\textsuperscript{113} This extremely short-lived species ($\tau \approx 1$ ps) was assigned to an open-ring cisoid structure on the S$_1$ surface, decaying concomitantly to a high-energy ground-state molecule that can either reform the closed spiropyran or transform into the merocyanine photoproduct. Another transient absorption study on a similar structure again contradicted this conclusion, though, proposing that spiropyran excitation produces a cisoid ground-state molecule within picoseconds.\textsuperscript{114} From this "state X", isomerization to the transoid merocyanines takes place on a 100 ps timescale. Further time-resolved studies again described X as an excited-state species on the S$_1$ surface, with a lifetime of at most several tens of picoseconds.\textsuperscript{115,116}

Görner et al. were the first to suggest for nitrospiropyrans that the precursor X might in fact be an excited-state species.\textsuperscript{104,105,117} They found that the transient absorption spectra obtained upon excitation of a nitrospiropyran strongly resembled that observed after laser excitation of the
corresponding merocyanine species. Based upon this and several other observations, they postulated that excitation of either species results in the population of a triplet excited state that is in a transient position between the cis and trans conformations. The authors referred to this state as $^3\text{perp}$ (from perpendicular). When this species decays to the ground state, either a cis- or trans-merocyanine can be formed. A recent gas-phase study supports the existence of an excited-state intermediate structure in the ring-opening process.\textsuperscript{118} The reformation of the spiropyran is assumed to occur in the ground state only, from the cis-merocyanine isomer. For a similar compound, however, Hobley et al. found that cyclization can occur directly from the $^1\text{perp}$ state.\textsuperscript{119}

Computational studies on a model system indicate that upon irradiation of spiropyran or merocyanine molecules, the excited-state structure relaxes to a conical intersection between the $S_1$ and $S_0$ surfaces.\textsuperscript{120,121} From that point either the closed spiropyran or the open cisoid merocyanine structure can be formed. No stable excited-state species exist in this mechanism, and the intermediate structure X is therefore once again identified as a ground-state cisoid structure. It should be noted that the $S_1$ state of this model system is ascribed an $n\pi^*$ character, whereas the $S_1$ state of an unsubstituted spiropyran is generally considered to have a $\pi\pi^*$ character.

There is no complete agreement that an intermediate species X is necessarily involved in the ring-opening of nitrospiropyrans. Holm et al. have suggested that a direct reaction path exists from the singlet excited state of a nitrospiropyran to the triplet state of a transoid merocyanine species, without the involvement of any intermediates.\textsuperscript{122}

In essence, it can be concluded that despite several decades of research on the subject, a consensus on the exact mechanism of the photochromic reaction of spiropyrans and nitrospiropyrans has not yet been achieved.

### 1.5 Fulgides

Fulgides are derivatives of dimethylene succinic anhydrides (see Chart 1.5). They were first described by Stobbe in 1904,\textsuperscript{123} who named them fulgides after the Latin verb *fulgere* ("to glisten" or "to shine"), as they were often obtained as shiny colored crystals.\textsuperscript{124} Fulgides can contain up to four different substituents ($R_1$ to $R_4$ in Chart 1.5), giving rise to a maximum of four different geometrical isomers, viz. ($E,E$), ($E,Z$), ($Z,E$) and ($Z,Z$).

![Chart 1.5](image)

*Chart 1.5.*
Stobbe observed that these crystals commonly changed color when exposed to light, but reverted to their original colors when left in the dark. He noticed that the coloration reaction only occurred for fulgides with aryl substituents, but never for completely aliphatic systems. Initially, he believed that the color change could only takes place in the crystalline phase and ascribed it to a crystal effect. At a later stage, he observed the photochromism in solution as well and then postulated that the color change was the result of E/Z-isomerization. Schönberg, instead, ascribed this phenomenon to a mechanism involving a biradical species.

The coloration mechanism was reinvestigated with new techniques in the 1960s. Initial studies supported the hypothesis that the E/Z isomerization caused the color change. It was not until 1968 that the mechanism responsible for the photochromism of fulgides was correctly identified. Several groups had reported that arylmethylene succinic anhydrides could be converted to naphthalene derivatives by the action of heat or light, but Santiago and Becker were the first to realize that this reaction was connected with the photocoloration process. They proved that the color change was in fact the result of the 6π-electrocyclization of a fulgide to a dihydronaphthalene succinic anhydride-type structure that could be reverted thermally or photochemically to the original fulgide, or could be oxidized to a naphthalene succinic anhydride (see Scheme 1.6). Hart and Heller showed that the photoinduced process obeys the Woodward-Hoffmann rules. In 1984, Kaftory obtained a crystal of the colored form of a fulgide and studied it by X-ray diffraction, thereby determining the structure of the cyclized molecule unequivocally.

When neither of the two substituents at the methyldiene opposite to the aryl group is a hydrogen, and hydrogen abstraction is therefore not possible, [1,5]-H or [1,3]-H shifts can occur instead, creating more stable aromatic structures (see Scheme 1.7).
In attempts to overcome these undesirable side-reactions, Heller et al. designed mesitylfulgide $\text{G6E}$ (see Chart 1.6).\textsuperscript{137} As there are no hydrogens on either of the carbons involved in the formation of the new bond, the abovementioned side reactions cannot occur. An additional advantage of this design turned out to be that in the closed form the steric repulsion between the methyl groups on both sides of the new bond prevents the disrotatory thermal ring-opening process, making it the first example of a fulgide for which the cyclized form is thermally stable at room temperature. The main disadvantage of this system was the slow photocyclization. This problem was overcome by replacing the mesityl by a dimethylfuryl group and by the introduction of an additional methyl group, forming fulgide $\text{G7E}$ (see Chart 1.6).\textsuperscript{138} This molecule has all the advantages of $\text{G6E}$, but in addition it undergoes significantly faster cyclization.

![Chart 1.6.](image)

Heller et al. also introduced the class of so-called fulgimides, which are structurally similar to fulgides, but contain a succinimide group instead of a succinic anhydride. One of the first fulgimides they studied, $\text{G8Z}$, is depicted in Chart 1.7.\textsuperscript{139} The photochemical behavior of these molecules strongly resembles that of the fulgides. Their properties will therefore not be discussed separately, unless there is a specific reason to do so.

![Chart 1.7.](image)

Dozens of fulgides and fulgimides have been studied in the past three decades, the vast majority of them containing a heterocyclic aryl substituent at one of the methyldiene carbons and two methyls at the other one. Due to the latter substitution with two identical groups, only three isomers exist for these molecules, viz. the $E$-, $Z$- and c-forms, where c refers to the cyclized structure (see Chart 1.8).
1.5.1 Electronic Absorption Properties

In general, E- and Z-fulgides absorb at significantly shorter wavelengths than their corresponding c-forms. X-ray crystallographic data and UV-vis studies of fulgides and related compounds indicate that fulgides can be considered as containing two largely independent acrylic acid-type chromophores (see Chart 1.9).

The UV-vis absorption spectrum of a fulgide closely resembles the combination of the spectra of these two chromophores, rather than that of the corresponding butadiene. The absorption spectra of the E- and Z-forms generally do not differ significantly. The UV-vis absorption spectra of G7E and G7c are displayed in Figure 1.8.

![Figure 1.8](image_url)
Due to steric hindrance in $E$- and $Z$-fulgides, the rings twist out of plane, thereby reducing the $\pi$-conjugation over the molecule. In the closed form the molecule adopts a more planar structure, which increases the $\pi$-conjugation and shifts the absorption into the visible region.$^{143,144}$

Substitution can have a strong effect on the electronic absorption spectra of fulgides. In the following discussion, the indicated locations of atoms, bonds or substitution positions refer to Chart 1.10. It is important to note, however, that the general structure displayed in Chart 1.10 is intended solely for clarification and does not necessarily represent the exact structures that were investigated in the studies discussed below.

![Chart 1.10](image)

A significant change in the electronic absorption spectrum of the c-form can be achieved by varying the aryl group of a fulgide ($Y = O$). Replacement of 3-furyl ($X = O$) by 3-thienyl ($X = S$) or 3-pyrrolyl ($X = NR$) groups causes a large red shift of the visible absorption maximum.$^{145}$

Another way to shift the absorption of the c-form to longer wavelengths is the introduction of donor substituents on the aryl group.$^{146-150}$ Often - but not always - these substitutions cause a red shift of the absorption maxima of the $E$- and $Z$-forms as well, although less pronounced in comparison with the c-form.

In the case of fulgimides ($Y = NR$), the imidic nitrogen can also be substituted. Upon introduction of an electron-withdrawing group on this nitrogen, the absorption maxima of the $E$-, $Z$- and c-forms all exhibit a bathochromic shift.$^{151}$

Tomoda et al. concluded that the electronic transitions in the c-forms of fulgides involve an intramolecular electron migration from the aryl group to the carbonyl groups.$^{152}$ The introduction of an electron-donating group on the aryl ring therefore stabilizes the excited state and shifts the absorption maximum to lower energy.$^{149}$ This trend was later confirmed by theoretical calculations.$^{153}$ It is reasonable to assume that the introduction of an electron-withdrawing group on the imidic nitrogen of a fulgimide will have a similar stabilizing effect.

A red shift of the visible absorption of the c-form can also be achieved by introducing bulky groups on either side of the new bond that is formed upon cyclization (positions $R_2$ and $R_3$).$^{154,155}$ The exact reason for this phenomenon remains unclear. The electronic absorption spectra of the $E$- and $Z$-forms are not significantly affected by these substitutions. The introduction of bulky groups at position $R_1$ does not have a strong influence on the absorption spectra of the $E$-, $Z$-, and c-forms.$^{155,156}$
1.5.2 Luminescence Properties

No emission has been detected at room temperature for the $E$-, $Z$- or c-forms of any of the fulgides described in the literature so far.\textsuperscript{157,158}

1.5.3 Photoreactivity

In $E$-fulgides, two competing photochemical processes can occur, viz. photocyclization and $E/Z$-isomerization. Ring-closure results in a color change, whereas $E/Z$-isomerization does not. The latter process is therefore generally regarded as an undesirable side-reaction.

Substitution of a fulgide can have a strong effect on the photoreaction quantum yields. The most efficient way to increase the efficiency of the photocyclization and suppress the $E/Z$-isomerization is the introduction of a bulky substituent at position $R_1$ (see Chart 1.10).\textsuperscript{154,156,159-165} With a large enough substituent it is possible to reduce the quantum yield of $E/Z$-isomerization ($\varphi_{EZ}$) to virtually 0. The decoloration quantum yield $\varphi_{CE}$ is not affected significantly by these substitutions.

Ilge and Colditz\textsuperscript{163} calculated that increasing the steric hindrance by the introduction of bulky substituents in the $R_1$ position causes a twist of the single bond $\alpha$, which in turn results in an increased bond order for bond $\beta$ in both the ground and excited states, thereby effectively blocking rotation and reducing the quantum yield $\varphi_{EZ}$. At the same time, the interaction between carbon atoms $a$ and $b$, which form the new C-C bond upon cyclization, is increased and $\varphi_{EC}$ rises consequently. Yokoyama et al. provided a different explanation. They attributed the decrease of $\varphi_{EZ}$ to the steric hindrance between the bulky substituent and the methylidene group, making rotation around the bond $\beta$ to create the $Z$-form energetically very unfavorable.\textsuperscript{154} The increase in $\varphi_{EC}$ was explained by assuming the existence of two important conformations for the $E$-isomer, one reactive and the other unreactive. A bulky substituent should increase the relative representation of the reactive conformation, thereby promoting the cyclization.\textsuperscript{156}

Even though NMR experiments\textsuperscript{166} and theoretical calculations\textsuperscript{144,166} have confirmed the existence of two conformations, it did not follow from the calculations that the relative representation of one of the two conformations increased when a bulky substituent was introduced.\textsuperscript{166,167} The calculations did show, however, that the introduction of bulky substituents changed the relative positions of the carbon atoms $a$ and $b$, thereby increasing their mutual through-space bonding interaction. This finding supports the theory of Ilge and Colditz described above.\textsuperscript{163}

The quantum yield of the photochemical cycloreversion can be increased for fulgides by introducing a bulky substituent in the $R_2$ position.\textsuperscript{154,155,162,164,168} This substituent has to be rather large, as anything smaller than adamantane does not have a significant effect. In the case of furylfulgides this substitution does not affect the efficiency of the other processes,\textsuperscript{154,162} but for thienylfulgides\textsuperscript{164} and indolylfulgides\textsuperscript{155} a decrease in $\varphi_{EC}$ and increase in $\varphi_{EZ}$ were observed.
Substitution of the aryl ring with an electron-donating group causes a sharp decrease in the cycloreversion quantum yield, while the introduction of an electron-withdrawing substituent has the opposite effect. When the imidic nitrogen of a fulgimide is substituted with an electron-withdrawing group, however, the cycloreversion quantum yield decreases. As already mentioned, the introduction of an electron-donating substituent at the aryl group or an electron-withdrawing substituent at the imidic nitrogen of a fulgimide causes a stabilization of the polar excited state of the c-form. This stabilization is also considered to be responsible for the reduction of the cycloreversion quantum yield.

Several groups have studied the effect of electron-withdrawing or -donating substituents on the cyclization quantum yield of fulgides and fulgimides. No correlation has been found to date, however.

1.5.4 Electrochemistry

In 1984 Fox and Hurst reported that for some fulgides cyclization occurs upon one-electron reduction. They ascribed this phenomenon to a flattening of the π-system caused by the added electron, which increases the overlap between the orbitals on the reactive carbon atoms a and b (see Chart 1.10).

In some cases the reductive cyclization does not take place. This behavior is attributed to the presence of either an electron acceptor substituent that is capable of trapping the added negative charge, or to a bulky substituent preventing the π-system from flattening. These fulgides form stable radical anions.

1.5.5 Energetics

The photochemical conversions of fulgides are primarily singlet-state processes. Ilge et al. performed triplet-quenching and -sensitization experiments on fulgides. Using triplet sensitizers, it was possible to observe E/Z- and Z/E-isomerizations from the triplet state of a fulgide, but cyclization never occurred. They found that triplet quenchers had no effect on the reactivity of the fulgides, which proved that no intersystem crossing (ISC) took place. In a series of studies Fan et al. showed, however, that ISC may occur for the class of pyrryl fulgides, and that their cyclization takes place from both the singlet and triplet states.

Using transient absorption techniques, Ilge et al. determined that the E/Z- and Z/E-isomerizations occur with a time constant $\tau < 5$ ps, and the cyclization reaction with $\tau = 6$ ps. From these data they concluded that the excited state pathways for these reactions are barrierless.
By applying transients absorption techniques with femtosecond time resolution, Handschuh et al. succeeded to study the cyclization reaction in more detail. They found that the photocyclization follows two parallel pathways, one direct with $\tau = 2.5$ ps and the other one involving an intermediate state from which the cyclized molecule is formed with $\tau = 33$ ps. The intermediate has not been identified. When the fulgides are incorporated in a polymeric matrix, the latter two-step process is inhibited and only the direct cyclization pathway operates.

### 1.6 Luminescence Switching

Photochromic molecules are believed to have great potential for optical data storage. Such an application, however, requires several conditions to be met. One of them is the ability to read out the data in a non-destructive way. The method of choice to establish the state of a photochromic molecule is UV-vis absorption. This technique, however, involves the electronic excitation of the photochromic molecules by the sample beam, which can result in their partial conversion to the other form. A way around this is to combine the photochromic moiety with a remote probe that is sensitive to the state of the system. By measuring the response of this probe, rather than that of the photochromic species, the data can be read out without affecting the system.

Although diverse probes can be employed for this purpose, for practical applications it is also important that the readout of the data is straightforward. The detection of light is a sensitive, quick and cheap technique, and therefore many studies focus on probes exhibiting luminescence when the photochromic structure is in one form, but cease to emit after the conversion to the other form. In such a system, the state of the photochromic moiety dictates whether the probe converts the absorbed energy to emitted light or dissipates it non-radiatively. This process can be referred to as "luminescence switching".

There are certain problems associated with this approach. First of all, it is hard to create a system in which the chromophore can be selectively excited, that is, to find a wavelength range where only the chromophore absorbs, but the two forms of the photochromic system do not. Also, in most systems, the luminescence of the chromophore is quenched in one of the states by energy transfer to the photochromic moiety, which may trigger its undesired conversion to the other form. These problems must be overcome before a usable device can be constructed using these materials.

Arguably, the first example of luminescence switching by energy transfer was presented by Tsivgoulis and Lehn in 1995. They studied diarylethenes substituted with oligothiophenes (including G90, see Chart 1.11) and found that their luminescence was quenched upon conversion to the closed form. The presented data suggests that this behavior is due to energy transfer from the excited luminophore to the closed diarylethene species. Unfortunately, the authors made no attempt to determine the exact source of the fluorescence, or explain its quenching.
Since then, several luminescence switching systems consisting of a photochromic molecule substituted with a luminophore have been synthesized and studied for their potential in non-destructive readout. These systems have been rather diverse: diarylethenes\textsuperscript{182-184} and spirooxazines\textsuperscript{185} substituted with rhenium tricarbonyl bipyridine complexes, diarylethenes with porphyrin,\textsuperscript{186} triphenylimidazole,\textsuperscript{187} and bis(phenylethynyl)anthracene\textsuperscript{188,189} substituents, and a spiropyran substituted with (metallo)porphyrins.\textsuperscript{190} The structures of some of these systems are displayed in Chart 1.12.

\textbf{Chart 1.12.} Several examples of published luminescence switching systems. $\textbf{G10o}$ described in ref. 182, $\textbf{G11o}$ in ref. 184, $\textbf{G12c}$ in ref. 185 and $\textbf{G13o}$ in ref. 187.
The first example of intermolecular luminescence switching by energy transfer, using separate photochromic and luminescent molecules in solution, was not demonstrated until 2001, despite the fact that such systems are easier to construct than their intramolecular counterparts. For intermolecular luminescence switching, the state of the system can also be determined using emission lifetime measurements.

In a luminescence switching system, the luminophore does not necessarily have to be a molecular species. The same principle has been proven for quantum dots substituted with spiropyrans. The emission of these systems can be reversibly switched ON and OFF by converting the photochromic moieties.

The possibility to achieve luminescence switching by energy transfer in the solid state was first demonstrated in 1999. Kawai et al. copolymerized diarylethenes with fluorenes, and consequently spin-coated the polymer onto glass or quartz plates. The emission of the resulting film could be switched ON and OFF by conversion of the photochromic moiety. Another example of a copolymer of a diarylethene with a fluorophore that exhibits luminescence switching was published in 2002. In that same year luminescence switching of bis(phenylethynyl)anthracene-substituted diarylethenes embedded in a polymer film was observed on the single-molecule level.

In the solid state, like in solution, a covalent link between the chromophore and the photochromic species is not a requirement to achieve luminescence switching by energy transfer. It was shown that this process can also occur intermolecularly, with the chromophore and photochromic species present as separate species in a film, or even in two separate polymeric layers.

Besides application in data storage, it has been suggested that photochromic molecules may be used for fluorescence resonance energy transfer (FRET) measurements. FRET involves non-radiative energy transfer from a donor to an acceptor molecule via intermolecular long-range dipole-dipole coupling. It is frequently used in biology and biochemistry to study the interaction between two biomolecules, one substituted with a donor, the other with an acceptor group. One factor complicating FRET measurements is that in order to evaluate the results, they must be compared to a situation where the acceptor is absent. This is achieved by either performing a separate control experiment, or by photobleaching the acceptor after some time. As biochemical processes can be rather complex and time-dependent, a method by which the acceptor could be removed and reintroduced at any given time would have considerable advantages. Using model systems, spiropyrans and diarylethenes have been shown to be promising candidates for this application.
1.7 Energy Transfer Switching

Other, more sophisticated applications can be envisaged for photochromic system. One possibility would be to use a photochromic moiety as a bridge between an energy donor and acceptor, switching the energy transfer ON and OFF by reversibly converting the bridge. If a luminescent acceptor is used, the state of the photochromic bridge can be distinguished by changes in the emission. In this Thesis, this type of system will be referred to as an "energy transfer switch".

Prior to the investigations described in this Thesis, one attempt to create such a system had been reported in the literature. It involves an anthracene energy donor and a Coumarin energy acceptor linked by a photochromic fulgide bridge (G14E, see Chart 1.13). This donor-bridge-acceptor (DBA) system is based on the principle that in its open form the energy levels of the photochromic system lie in between those of the donor and the acceptor, thereby facilitating the energy transfer. In its closed form, the energy levels of the photochromic unit are below those of the termini, so that excitation energy is transferred to the photochromic bridge and no emission from the acceptor is observed.

This system is not a true energy transfer switch, in the sense that the photochromic unit does not simply influence the rate of energy transfer between the energy donor and acceptor, but instead it becomes the energy acceptor in its closed form.

Chart 1.13.

A better, and generally more elegant solution concerns the creation of a donor-switch-acceptor triad in which energy transfer from the donor to the acceptor occurs only when the system is in one of its two forms. When converted to the other form, the energy transfer process should be inhibited, or at least become considerably less efficient. Such a system would be a true energy transfer switch.

One way to achieve this goal would be to create a system where in one state the energy levels of the photochromic bridge lie above those of both the donor and acceptor, and energy transfer, if any, takes place by means of a superexchange mechanism. In the other state, the levels of the bridge should move in between those of the donor and acceptor, resulting in a hopping mechanism for the energy transfer (see Figure 1.9).
Figure 1.9. Simplified energy diagrams for the proposed switchable donor-bridge-acceptor (DBA) system. Left: long-range energy transfer occurs between the donor (D) and acceptor (A). The bridge (B) does not facilitate the process. Right: efficient energy transfer occurs between D and A through B.

The state of the system is then determined by monitoring the emission of the acceptor upon excitation of the donor with light of sufficiently high energy. In such a system the bridge never becomes an energy trap and, hence, excitation of the donor will not strongly affect the state of the switch. Ideally, one would like the excited state of the bridge mediating the energy transfer to be non-reactive. Conversion of the bridge should then be achieved by direct excitation to a different, higher-lying excited state. For example, the energy transfer could be a triplet-triplet process, while the reaction only takes place from the singlet-excited state of the photochromic unit. Only then true non-destructive readout can be achieved.

1.8 Scope of This Thesis

The aim of the work presented in this Thesis was the development of a true photochromic energy transfer switch. \([\text{Ru(bpy)}_3]^2+\) and \([\text{Os(bpy)}_3]^2+\) complexes (bpy = 2,2'-bipyridine) were employed as the energy donor and acceptor moieties, respectively. These coordination compounds were selected because of their photochemical stability, reversible redox behavior, long emission lifetimes - which makes the detection of energy transfer relatively straightforward - and for the vast experience with donor-bridge-acceptor systems containing such complexes, also in the Amsterdam research group. The suitability of diarylethenes, spiropyrans and fulgimides to act as switchable bridges for the envisaged system was evaluated. Several triad systems were investigated. A number of model systems, consisting of a photochromic molecule either attached to a single metal complex or bridging two identical ones, was also studied in order to better understand the electronic interactions between the different components.
In Chapter 3 of this Thesis, two novel model systems, consisting of a diarylethene-based ligand bridging either two [Ru(bpy)$_3$]$^{2+}$ or two [Os(bpy)$_3$]$^{2+}$ moieties, are investigated. The interaction between the Ru and Os metal complexes and the diarylethene is described and a previously unknown triplet-sensitized cyclization pathway of the diarylethene is identified.

In Chapter 4 the corresponding Ru/Os heterodinuclear diarylethene complex is described. It is found that the properties of the heterodinuclear system can be understood in depth on the basis of the experimental data obtained for the model homodinuclear systems in Chapter 3.

In Chapter 5, mononuclear nitrospiropyran complexes, containing either a [Ru(bpy)$_3$]$^{2+}$ or an [Os(bpy)$_3$]$^{2+}$ moiety, are investigated. The interaction between the Ru and Os metal complexes and the nitrospiropyran is studied, and an electrochemical ring-opening mechanism for the nitrospiropyran is described. This mechanism had been previously identified by others, but it is shown here that their description was incomplete.

Chapter 6 deals with several disubstituted spiropyran systems, both homo- and heterodinuclear. It is found that replacing the nitro group in the model systems described in Chapter 5 by a metal complex inhibits both the photochemical and the electrochemical ring-opening process.

In Chapter 7 fulgimides monosubstituted with a [Ru(bpy)$_3$]$^{2+}$ or an [Os(bpy)$_3$]$^{2+}$ group are investigated. A peculiar equilibration phenomenon between the $E$- and $Z$-forms of the metal-fulgimides is observed.

In Chapter 8, the results from the preceding Chapters 3-7 are compared and the prospects of the different photochromic systems for the envisaged photochromic energy transfer switch are evaluated. Several suggestions for further research are made.
Chapter 1

1.9 References


Introduction


Chapter 1


