Chiroptical molecular switches

de Lange, Ben

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CHAPTER 2

CHIROPTICAL MOLECULAR SWITCH: CONCEPTS AND SYNTHESIS

2.1 Introduction

Photochemically switchable bistable molecules have recently attracted considerable attention due to possible applications in reversible optical data storage.\(^1\)\(^2\) The use of organic molecules in this field has been stimulated by a number of important advantages: (i) the large increase in information storage density, theoretically to the molecular level and, (ii) the large variety of photophysical properties, which might be achieved by introducing small changes in the molecular structure. So far, research has mainly been focused on cis-trans isomerizations of azobenzenes and reversible photocyclization reactions. Detection of both bistable states has been limited to the observation of differences in UV/Vis spectra, although recently some approaches have been reported using other -less destructive- read-out procedures. Apart from the frequently observed low thermal stability of one of the two isomers, an important restriction for these reported methods is the simultaneous use of different physical techniques for the writing/reading/erasing cycle, as has been discussed in Chapter 1.

This thesis deals with the development of molecular optical switches, where the bistability is based on the chirality of two enantiomeric forms of an organic molecule. In this chapter the principles and synthesis of the molecular components of a chiroptical molecular switch will be presented. The envisaged molecular switch is the result of a photochemical interconversion of two chiral isomers $P$ and $M$ by the use of circularly polarized light (cpl, Figure 2.1).\(^3\)

\[
P \xrightleftharpoons{r\text{-cpl}} \quad M
\]

\[
(+) \quad (-)
\]

*Figure 2.1. Schematic representation of a chiroptical molecular switch.*

2.2. Circularly Polarized Light

Optical activity of molecules is detected by the difference in interaction of one enantiomer with right- or left-handed circularly polarized light (r- or l-cpl). This difference in interaction is revealed in two phenomena: (i) circularly birefringence, i.e.


\(^3\) In Chapter 6, a chiroptical molecular switch based on a stereospecific photoisomerization of M-cis $\rightarrow$ P-trans using two different wavelengths of *linearly* polarized light is described.
2. Chiroptical Molecular Switch: Concepts and Synthesis.

The refractive index for the right-handed circularly polarized component of a linearly polarized light beam passing through an optically active medium, will be different from the left-handed component. This leads to differences in light velocities between the two components ($\lambda$- and $\tau$-cpl) of the beam and upon emerging from the optically active medium, a rotation of the plane of linearly polarized light of the resulting vector sum is observed and, (ii) differences in absorption, i.e. in the region of an absorption band, the optically active compound has an unequal molar absorption coefficient $\varepsilon$ for $\tau$- and $\lambda$-cpl. These interactions can be measured by optical rotation dispersion (ORD) and circular dichroism (CD), giving the molar rotation ($\Theta$) and the molar ellipticity ($\Phi$), respectively.

The difference in absorption by irradiation of a racemic compound with either $\tau$- or $\lambda$-cpl can lead to different concentrations of the two enantiomers in a photochemical induced reaction and the chiral information of the irradiating light can be transformed into chiral information stored in the molecules. The methodology to obtain optically active molecules by irradiation with circularly polarized light without the use of external chiral auxiliaries or sensitizers has been referred to as absolute asymmetric photochemistry. Three approaches to achieve asymmetric induction via this method can be distinguished:

- Asymmetric photosynthesis: the photochemical induced formation of new chemical bonds. An example is the asymmetric synthesis of helicenes by ring closure of diarylethlenes using circularly polarized light reported by Kagan and Calvin, where enantiomeric excesses of 0.5-0.7% were found.

- Asymmetric photodestruction: the selective decomposition of one of the enantiomers of a molecule.

- Photoenantiomerization: the direct conversion of one enantiomer of a racemic compound into the other by irradiation with $\lambda$- or $\tau$-cpl, for example, by a selective isomerization procedure (i.e. deracemization). This process has only been demonstrated in the asymmetric rearrangement of octahedral transition-metal complexes with bidentate ligands like the Cr(ox)$_3^-$ ion and Cr(acac)$_3$.

For reviews see:


Recently, Schuster and Zhang tried to achieve a conversion in the liquid crystalline phases of 4-cyano-4'-n-pentylbiphenyl by a cpl-induced photoresolution of a small amount of an added 1,1'binaphthyl derivative. Although photochirality by iod of 5% dissolved optically pure 1,1'binaphthyl compound caused the transition from the cholesteric to the nematic phase, the reverse process by irradiation with cpl, leading to enantiomeric enrichment, failed. Schuster, G.B.; Zhang, M. J. Phys. Chem. 1992, 96, 5063.


A photoenantiomerization process will be the basis for the molecular switch described in the following sections.

### 2.3 Chiroptical Molecular Switch

#### 2.3.1 The Molecules

The bistability of the molecular switch is based on the two enantiomeric forms of inherently disymmetric alkenes, i.e. alkenes which can exist in optically active stereoisomers, without the presence of a stereogenic centre. In 1977, Feringa and Wynberg reported the first resolution of sterically overcrowded alkenes resulting in thermally stable optically active stereoisomers. A representative of this type of molecule is shown in Scheme 2.1.

![Scheme 2.1](image)

Scheme 2.1. The two chiral forms P and M of sterically overcrowded alkene 1.

Molecule 1 consist of an upper tetrahydrophenanthrene part connected via a central double bond to a fluorene moiety. The successful resolution of this alkene is due to the special structural features of the tetrahydrophenanthrene unit. The tetrahydrophenanthrene part is bulky enough to inhibit fast racemization by movement of the aromatic moieties of upper and lower halves through the mean plane of the molecules, but has sufficient conformational flexibility to prevent excessive distortion of the central olefinic double bond leading to rapid racemization by rotation of the double bond. The two chiral forms of these helically shaped molecules are denoted P and M, respectively for a right-handed and a left-handed helix. This olefin shows structural resemblance with helicenes and can be compared with a hexahellicene functionalized with an additional annulated phenyl ring.

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12 Extended NMR studies of the conformations of symmetrically overcrowded bifluorenylidene, bianthrones, biacridanes and bixanthylidene have indicated the chirality of these compounds, but no resolution was reported. See Chapter 4 "Sterically Overcrowded Bistri cyclic Ethylenes" for a literature survey on this subject.

13 These molecules are denoted by the helicity rule, with P (plus) for a right handed-helix and M (minus) for a left-handed helix. See: Cahn, R.S.; Ingold, C.K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* 1966, 5, 385.

2.3.2 Optical Enrichment by Circularly Polarized Light

Photochemical switching between the P and M form will be achieved by the use of right- or left-handed circularly polarized light (r- or l-cpl). Upon irradiation with non-polarized light or linearly polarized light, a rapid equilibrium process between the two forms can occur, due to photochemically induced rotation of the central double bond (formally a cis/trans isomerization), leading to a photostationary state consisting of equal amounts of the two enantiomers (Scheme 2.1). By irradiation of a racemic mixture with r- or l-cpl light, we expect to obtain a small enrichment in one of the two enantiomers, by an enantioselective cis-trans isomerization process. As indicated in Chapter 2.2, the P-isomer will absorb r-cpl to a different extent than the M-isomer, leading to a photostationary state with a slight enantiomeric excess of one of the two isomers. This small enantiomeric excess can be detected by the use of linearly polarized light, due to the large optical rotations and molar ellipticities of these helicene type molecules. Using l-cpl a slight enantiomeric excess of the other enantiomer is expected. A negative sign of the optical rotation can be considered as a zero and a positive sign as a one (or vice versa), so a binary optical data storage system or a molecular switch will be obtained based on these bistable organic molecules.

The principle of such an optical data storage device is depicted in Figure 2.2, which demonstrates the writing, reading and erasing cycle. In the unwritten state a racemate (MP) is present. Writing can occur by irradiation with (left or right) circularly polarized light (cpl, for instance at $\lambda = 333 \text{ nm}$) to give a local excess of the P (or M) isomer. Reading can be performed by the use of linearly polarized light (lpl, i.e. by means of the optical rotation) at another wavelength without interfering with the written information or at the same wavelength with very low light intensity avoiding to influence the stored data. Erasing of the information can occur with linearly polarized light of high intensity at the same wavelength used for writing.

\[ \text{CPL 333 nm} \]
\[ \text{MP MP MP MP} \]
\[ \text{unwritten} \]
\[ \text{LPL} \]
\[ \text{MP PP PP MP} \]
\[ \text{write} \]
\[ \text{LPL 333 nm} \]
\[ \text{MP PP PP MP} \]
\[ \text{read} \]
\[ \text{MP MP MP MP} \]
\[ \text{erase} \]

Figure 2.2. Proposed writing, reading and erasing cycle for a chiroptical molecular switch.

For trans-4-(1',2',3',4'-tetrahydrophenanthrene-4'-ylidene)-1,2,3,4-tetrahydrophenanthrene, a structural comparable compound in these series, large molar rotations and molar ellipticities were reported: [94]$_{202.5}$ -88.080 and [91]$_{195}$ -71.000. Feringa, B.L. Asymmetric oxidation of phenols, Ph.D. Thesis, Groningen, 1978, p 69.
The nowadays highly desired direct writing after reading procedure\(^1\) can also be applied by using directly circularly polarized light in the "read state", leading to a new photostationary state with again a small excess of one of the two isomers, depending on the use of either l- or r-cpl.

By applying this cpl-induced optical enrichment method, we might be able to construct a **chiroptical molecular switch**, a photochemical (optical) switch based on the chirality of two enantiomeric forms of one molecule. Before a chiroptical molecular switch can be realized in practice, many fundamental questions have to be answered, the requirements for the switch defined and a flexible synthetic route has to be developed.

### 2.3.3 The Requirements for a Chiroptical Molecular Switch

The molecules, which form the basis for the chiroptical molecular switches must meet some important requirements to be suitable for a practical switching device:\(^{16}\)

- Thermal stability of both isomers; this means that no racemization of the two forms should occur at normal working temperatures (e.g. -20 – 50 °C).
- Readily photochemical interconversion of the P into the M isomer and vice-versa; the photostationary state should be reached in a short time.
- Large anisotropy factor \(g\); this value quantifies the chiral recognition of a molecule by circularly polarized light.\(^{17,18}\)
- Large molar rotations allowing detection of even very small enantiomeric excesses of one of the isomers.
- Photochemical stability; the photochemical switching cycle should be repeatable many times, without the formation of any side-products.
- All these properties should remain in a macromolecular system for instance by embedding the compounds in a polymer matrix, necessary to improve the material properties of the organic molecules.

### 2.3.4 Molecular Design

After the description of the basic structure, the principles and important requirements for the chiroptical molecular switch in the previous sections, the challenge in organic chemistry is the synthesis of these sterically overcrowded alkenes. Our aim is to develop a synthetically flexible route, with the ability to introduce different functional groups to tune the properties of the molecules in the required direction. A typical target molecule 2 is drawn in Figure 2.3:

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\(^{16}\) See also Chapter 1, Section 1.3 and 1.9, for a discussion on this subject.

\(^{17}\) The anisotropy factor \(g\) is defined as \(\Delta e/e\), where \(\Delta e\) is the difference in molar absorption coefficients for left and right cpl \((\Delta e = e_l - e_r)\) obtained from the CD spectrum and \(e\) is the extinction coefficient obtained from the UV spectrum. The \(g\) factor can be considered as the fraction of one enantiomer of a racemic compound, which will be excited more than the other. The maximum optical yield for a photoenantiorimerization process is \(g \times 100\%\) as given by Stevenson: Stevenson, K.L.; Verdieck, J.F. Mol. Photochem. 1969, 1, 271.

\(^{18}\) Anisotropy factors of a similar order of magnitude as have been reported for helicenes are expected \((g = 0.01)\).\(^2\) These \(g\) values were sufficiently large to allow easy determination of the optical activity induced by circularly polarized light in the synthesis of helicenes using optical rotation measurements.\(^{6,7}\)
2. Chiroptical Molecular Switch: Concepts and Synthesis.

![Structure](image)

**Figure 2.3. Basic structure of target molecules.**

- **F** = functional groups introduced for the attachment of these alkenes to polymeric backbones to improve the material properties. Hydroxyl or carboxylic acids functionalities are typical examples of useful groups for this approach.
- **X,Y** = CH₂, S, O, N-R etc. The introduction of various (hetero) atoms might have a profound influence and could provide answers about important structural factors controlling the properties of the alkenes.
- **A,D** = acceptor and donor groups for directing the electronic properties of the molecules. These functionalities can also be important for obtaining macroscopic structures by dipole-directed alignment of the molecules via the application of an external electric field.

2.4 Synthesis, Introduction and Initial Attempts

2.4.1 The McMurry Coupling

The first objective in the synthesis of these overcrowded alkenes, is the formation of the central, sterically demanding, double bond. Synthetic methodologies to obtain olefinic bonds include Wittig-type reactions, Peterson olefination procedures and McMurry coupling reactions.

In 1977, a synthetic route to some members of this class of alkenes was reported by Feringa and Wynberg using a low-valent titanium mediated McMurry coupling between two different ketones as a key step to form the central double bond. The

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19 The introduction of a substituent (for example an acceptor group A) in the lower part of alkenes 2 leads to the formation of unsymmetrically substituted ethylenes. A chiroptical molecular switch based on a stereospecific cis-trans isomerization of these molecules is described in Chapter 6.


reaction between 1,2,3,4-tetrahydrophenanthrene-4-one (3) and 9H-fluorene-9-one (4), as shown in Scheme 2.2, leads to a variety of products 1, 5a,b and 6 via a non-selective coupling procedure. Although the direct cross-coupling of ketones is an advantage, some major difficulties using this route are:

- The selectivity, as mixtures of alkenes are obtained which are difficult to separate (two chromatographic separations were necessary, including a laborious preparative TLC procedure).
- Low yield; only by the use of a large excess of fluorenone, a reasonable yield of 1 was obtained (25%). The fourfold excess of one of the reagents will be a limiting factor, when using other less accessible substituted ketones as starting materials.
- The strong reducing power of the titanium reagent will prevent the introduction of various groups, e.g. nitro or carboxylic acid functionalities.
- Environmental pollution (i.e. waste problems) by the large amounts of titanium salts necessary for the coupling reaction; the isolation of only 0.25 gram of alkene required no less than 6.5 gram TiCl₄.

These disadvantages in the McMurry coupling method, in particular as applied to cross-couplings, strongly indicated the need for a novel mild and selective synthetic procedure, where it is possible to differentiate between the upper and lower part of the molecule.

Scheme 2.2. McMurry coupling between tetrahydrophenanthrene (3) and fluorenone (4).

2.4.2 Wittig Type-Reactions and Peterson Olefination Procedures

Initial attempts to find a selective method for constructing the central olefinic double bond were focused on Wittig-type procedures, starting from the fluorene derived phosphorane 7 and ketone 3 as depicted in Scheme 2.3. However, this reaction failed

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to give any of desired alkene and only some starting material was isolated. A reason for this negative result might be the large sterical hindrance in the formation of the intermediate betaine or oxaphosphetane. The problems associated with obtaining tri-or tetrasubstituted alkenes via the Wittig reaction are already known from the literature.\textsuperscript{28}

![Scheme 2.3. Wittig reaction between phosphorane 7 and ketone 3.](image)

The Peterson olefination procedure, starting from the trimethylsilyl derivative of fluorene 8, did not provide the required product either (Scheme 2.4).\textsuperscript{25}

![Scheme 2.4. The Peterson olefination procedure and the "Brouwer" method.\textsuperscript{26}](image)

In a later stage of this research an attempt was performed, to achieve a direct coupling between the anion of fluorene and the ketone to afford a hydroxy intermediate 10, which should then be dehydrated to alkene 1 (Scheme 2.4).\textsuperscript{26} This reaction failed to give any hydroxy adduct. Another problem in this procedure (if any adduct was isolated) would be the dehydration step, which can also lead to the formation of the probably less sterically demanding endocyclic double bond, via elimination of the $\alpha$-hydrogen in the tetrahydrophenanthrene part.

Similar problems were expected when the tetrahydrophenanthrene unit should be functionalized with phosphine or trimethylsilyl groups to perform the reverse Wittig reaction or Peterson olefination. Although these reactions have not been investigated extensively, the encountered and expected problems have turned our attention to a more appropriate and successful synthetic route.

\textsuperscript{25} In Chapter 4, the successful coupling of 10N-methyl-9H-acridine and 2-methyl-9H-thioxanthene-9-one via a one-pot Peterson olefination is described.

\textsuperscript{26} The work was based on the coupling of (thio)xanthenes and adamantone via this procedure as reported by Brouwer in our laboratory: Brouwer, A.C. Exploring the synthesis of functionalized 9-adamantrylideneanthene dioxetanes, research report, Groningen, 1988.
2.5 Synthesis, the Diazo-Thioketone Coupling Method

2.5.1 Introduction, Mechanism and (Retro)Synthetic Scheme

An useful strategy to prepare extremely hindered alkenes is a two-fold extrusion reaction as schematically drawn in Figure 2.4. The rationale for this approach is the fact that intermolecular reactions are more strongly influenced by steric hindrance than intramolecular processes. Construction of a molecule such as A would keep steric interactions to a minimum in the intermolecular step. Consecutive extrusions of X and Y allows the introduction of the sterically strained double bond in alkene B.

\[ \begin{array}{c}
\text{A} \\
\text{X} \\
\text{Y} \\
\text{B} \\
\text{X} \\
\text{Y} \\
\end{array} \]

Figure 2.4. Schematic representation of a two-fold extrusion process for the preparation of sterically strained double bonds.

The 1,3,4-thiadiazoline system (X = N=N, Y = S) proved to be particularly useful for the synthesis of sterically hindered alkenes. After the discovery of the formation of episulfides in the reaction between diazoalkanes and thioketones by Staudinger and the extensive studies of Schönberg et al., the great value of this synthetic methodology was recognized by Barton and Kellogg. The method is based on a 1,3-dipolar cycloaddition between a diazo compound 11 and a thioketone 12 to give a thiadiazoline 13 as an intermediate (Scheme 2.5). In most cases, this thiadiazoline readily loses nitrogen by a thermal extrusion process to form the thiirane structure 14. This episulfide can be desulfurized by several methods to alkene 15. Typical procedures for the elimination of sulfur are refluxing of the episulfide in a high boiling solvent in the presence of a slight excess of copper powder or a phosphine. Although very hindered alkenes have been obtained via this method, the synthesis of the extremely sterically hindered tetra-t-butyl ethylene has failed so far.

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27 E. Schudde is gratefully acknowledged for performing some initiating experiments related to the diazo-thioketone method in the early stages of this project on chiroptical molecular switches.
35 See e.g.: Seitz, O.; Hoffmann, H. Synthesis, 1977, 201.
By using this methodology for the synthesis of our target molecules, two possible routes can be followed. In principle, the "upper" phenanthrene part can be introduced in the molecule by using a diazo compound 16, which can react with the thioketone derivative 17 of the lower part of the molecule (process A, Scheme 2.6). The second approach is the reverse reaction by using the thioketone derived from the phenanthrene 18 and the diazo compound obtained from the fluorene moiety 19 (process B). The use of route B will be limited due to the rapid conversion of the thioketone 18 into the enol form, which can easily dimerize with concomitant elimination of hydrogen sulfide.37 In the following sections, the formation of alkenes, based on process A, will be described.

The "Upper" Part of the Molecule

The synthesis of 1,2,3,4-tetrahydrophenanthrene-4-one (3) required a 7 steps synthesis as is shown in Scheme 2.7 starting from tetraline (20, 1,2,3,4-tetrahydronaphthalene) and is based on a literature procedure described by Dillenschneider et al.38 After a Friedel-Crafts acylation of 20 with succinic anhydride, a Wolff-Kishner reduction, an esterification, dehydrogenation, saponification and a Friedel-Crafts ring closure of the acid chloride of 25, ketone 3 was obtained in an overall yield of 17% as a slightly grey coloured solid.

38 Dillenschneider, J.P.; Maire, J.C. Bull. Chim. Soc. Fr. 1964, 10, 2506. Because of the rather short description in the literature, full experimental details are given in Section 2.7, including $^1$H NMR data.
The next step is the conversion of ketone 3 into a diazo precursor. Diazo compounds have been obtained by a variety of methods, for example, base-catalyzed decomposition of tosylhydrazones (Bamford-Stevens reaction)\(^3^9\) or N-alkyl, N-nitroso derivatives\(^4^0\) and oxidation of hydrazones with lead(IV)acetate, mercury(II)oxide or silver(I)oxide.\(^4^1\) This last method was chosen, because the oxidation of hydrazones by silver(I)oxide was reported to occur very rapidly at low temperatures,\(^4^1\) an important advantage for the formation of usually unstable aliphatic diazo derivatives (see Scheme 2.12).

Ketone 3 was transformed into 1,2,3,4-tetrahydrophenanthrene-4-one hydrazone (26) by refluxing in ethanol with a five-fold excess of hydrazine hydrate according to standard procedures described in the literature for the preparation of hydrazones.\(^4^2\) After crystallization from ethanol, 26 was obtained as slightly yellow coloured small needles in 90% yield (Scheme 2.8).

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41 See e.g. (a) Schroeder, W.; Katz, L. *J. Org. Chem.* 1954, 19, 718. (b) The oxidation of 1-indanone, hydrazone to 1-diazoindane with Ag\(_{2}\)O was completed within 15 min at -15 °C; Moss, R.A.; Funk, J.D. *J. Chem. Soc.* 1967, 2026.
2.5.3 *The "Lower" Part of the Molecule*

The chemical conversion of ketones to thioketones can be accomplished by various methods. A very convenient procedure is refluxing the ketone with a slight excess of phosphorous pentasulfide in a high boiling solvent, like toluene or xylene. More recently Lawesson’s reagent has been developed as a mild reagent for this conversion (schema 2.9).

The synthesis of 9H-xanthene-9-thione (30), 9H-thioxanthene-9-thione (31) and 10N-methyl-9H-acridane-9-thione (32) has been performed by both methods. These reactions can be easily monitored by the rapidly changing colour of the solution. Thioketones exhibit fascinating colours, from deep blue to dark green, due to the thiocarbonyl chromophore.

```
27 Y = O
28 Y = S
29 Y = NCH₃
4 Y = -
```

```
Lawesson’s reagent = HCO-Ph₃P-S-P-S-Ph₃O
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Scheme 2.9. *Synthesis of thio ketones.*

The use of phosphorous pentasulfide for the synthesis of 30, 31, and 32 was preferred, because no "smelly" chromatographic step was needed, which was necessary in order to remove the remaining salts, when applying the Lawesson’s reagent procedure. It is essential to run the conversion of the ketone to the thio ketone to completion, as indicated by thin-layer chromatography, because separation of starting material from the thio ketone proved to be very difficult. Via this method 9H-xanthene-9-thione (30), 9H-thioxanthene-9-thione (31) and 10N-methyl-9H-acridane-9-thione (32) were obtained in yields varying between 60-80% as beautiful dark violet, small green or red sparkling crystals, respectively. These thio ketones were stable in air and no oxidation or dimerization (vide infra) was observed.

In some cases, these thio ketones were a little smelly due to small traces of remaining phosphor-sulfur salts after crystallization, which could be removed by a rapid filtration of the compounds dissolved in dichloromethane over a short silica gel column.

9H-Fluorene-9-thione (17), which has been described as a rather unstable green solid, could not be obtained by the phosphorous pentasulfide method. The instability is due to the facile formation of a dimeric structure as shown in Scheme 2.10.

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The initial reaction of fluorenone with Lawesson's reagent at 80 °C in toluene or benzene afforded the dark green thio-ketone, but after standing overnight the colour had changed to yellow. The formation of the dimeric structure 34 was confirmed by an X-ray analysis determination as was performed by Lawesson et al.\textsuperscript{37} Although the isolation of pure 9H-fluorene-9-thione 17 using Lawesson's reagent has been reported,\textsuperscript{7} several attempts to reproduce these results were unsuccessful. The solution of ketone 4 in toluene in the presence of 33 rapidly turned dark-green, indicating formation of the required thio-ketone. However, after evaporation of the solvent in order to isolate the thio-ketone, the colour changed to brown-yellow. In some cases, this decomposition was already observed during the reaction. Based upon these encountered difficulties, it was decided to use the thio-ketone without further purification for the coupling method described in the next section. After an almost complete conversion of the ketone as indicated by TLC analysis, the dark green solution was rapidly cooled to room temperature and, after a fast filtration on a silica gel column, was added to the diazo compound (see Experimental Section).

**2.5.4 The Coupling Method**

1,2,3,4-Tetrahydrophenanthrene-4-one hydrazone (26) was oxidized to the unstable deep purple diazo compound 16 with silver(I) oxide (1.5 equiv.) in ether at -10 °C, using magnesium sulfate as a desiccant (Scheme 2.11). After filtration of the salts, the appropriate dark green thio-ketones were subsequently added to the cold solution of the diazo compound. Evolution of nitrogen was observed until the dark red colour of the solution had faded away. The formed episulfides precipitated from the solution as slightly yellow solids and were easily isolated as nearly pure compounds by filtration in yields varying from 52-94%. The intermediate thiadiazoline structures were not detected, indicating a rapid decomposition to the much more stable thiiranes. The episulfides could be easily desulfurized with copper in boiling xylene\textsuperscript{34} to afford alkenes 38, 39 and 1 in 78-82% yield as crystalline compounds after crystallization from ethanol (Scheme 2.11). Unfortunately, the red 10N-methyl-9H-acridane-9-thione (32) refused to react with the diazo compound. Upon slowly heating of the mixture of 32 and the diazo compound 16 to room temperature, to initiate the reaction, only decomposition of the diazo compound to an azine was observed (Scheme 2.12).\textsuperscript{47}
2. Chiroptical Molecular Switch: Concepts and Synthesis.

![Diagram](image)

Scheme 2.11. The diazo-thioketone coupling.

**General remarks:**

- The oxidation step seemed to be dependent on the quality of the silver(I) oxide used. In some cases, the oxidation of the hydrazone proceeded very slowly and more silver(I) oxide had to be used, in order to obtain the purple solution of the diazo compound. Essential differences between silver(I) oxide from several suppliers (Fluka, Aldrich, Janssen Chimica) were not observed and an exact explanation for this phenomenon cannot be given at this moment.

- In some experiments, the episulfides did not precipitate from the solution. In those cases, the solvent was removed and the residue crystallized from ethanol.

- The fluorene functionalized episulfide 37 was contaminated with an azine derivative (< 10%), which was formed by the decomposition of one molecule of the diazo compound reacting with a second diazo molecule (Scheme 2.12). These orange coloured compounds could not be removed by crystallization or chromatography from the episulfide. After conversion to the alkene, however, separation was accomplished by a single crystallization from hexane.

![Diagram](image)

Scheme 2.12. Formation of azines 41.

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The structures of the episulfides and alkenes were confirmed by consistent NMR data and elemental analysis. Some typical NMR characteristics are (for numbering scheme, see Figure 2.5):

- The two aliphatic protons at C-1, C-2 and C-3 (upper half) show chemical shift non-equivalence in the $^1H$ NMR spectrum, a clear evidence for the presence of chirality in the molecules.
- An upfield shift was observed for the protons at C-6', C-7' and C-8' in the lower part of the molecules due to the shielding by aromatic rings in the upper half.
- In the $^{13}C$ NMR spectra of the episulfides, two characteristic peaks are found between 50 and 60 ppm, which can be assigned to the quarternary thirane carbon atoms. These absorptions are shifted to the aromatic part of the spectrum upon formation of the central olefinic bond.
- Another typical absorption for the episulfides is found around 9.5 ppm in the $^1H$ NMR spectrum. This absorption can be ascribed to the proton at the C-5 carbon in the phenanthrene part of the molecule, shifted downfield due to the close proximity of the electron withdrawing sulfur atom of the three-membered ring.

In Chapter 3, the structures of some of these alkenes are established unequivocally by X-ray analysis of related derivatives.

2.6 Conclusions

In this chapter, the conditions for application of sterically overcrowded alkenes as models for binary molecular optical storage devices have been outlined and the principles and basic structure of the envisaged chiroptical molecular switch have been described. An efficient and selective synthetic route to these olefins was found based on a diazo-thioketone coupling method. Further studies on the feasibility of these alkenes to function as molecular switches are described in Chapter 3 and 6.\(^{48}\)

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2. Chiroptical Molecular Switch: Concepts and Synthesis.

2.7 Experimental Section

General Methods

All reactions were magnetically stirred and performed under an inert atmosphere of nitrogen unless stated otherwise. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone. Toluene was distilled from Na/benzophenone and stored over 4Å sieves. Dichloromethane (CH₂Cl₂), ether (Et₂O), pet-ether 60-40 and hexane were distilled from P₂O₅ and stored over 4Å sieves. Dichloromethane (CH₂Cl₂), ether (Et₂O), pet-ether 60-40 and hexane were distilled from P₂O₅ and stored over 4Å sieves. Dichloromethane (CH₂Cl₂), ether (Et₂O), pet-ether 60-40 and hexane were distilled from P₂O₅ and stored over 4Å sieves. Methanol and ethanol were distilled from Mg and stored over 4Å sieves. All commercially available chemicals were obtained from Janssen Chimica, Aldrich or Fluka and were used without further purification.

Melting points (uncorrected) were determined on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. ¹H NMR spectra were recorded on a Hitachi Perkin Elmer R-24B spectrometer (at 60 MHz), a Nicolet NT-200 spectrometer (at 200 MHz) or on a Varian VXR-300 spectrometer (at 300 MHz). The chemical shifts are denoted in δ units (ppm) relative to tetramethylsilane (TMS) as an internal standard at δ = 0.00 ppm. Splitting patterns are designated: s (singlet), bs (broad singlet), d (doublet), dd (double doublet), ddd (double double doublet), t (triplet), q (quartet), m (multiplet). ¹³C NMR spectra were recorded on a Varian VXR-300 spectrometer (at 75.43 MHz). The chemical shifts are denoted in δ units (ppm) with the solvent as an internal standard and converted to the TMS scale using δ (CDCl₃) = 76.91 ppm. The spectra were recorded in the APT (Attached Proton Test) mode with a positive value for the C and CH₃ peaks and a negative value for the CH and CH₂ peaks. For convenience and a more easy comparison with other data the splitting patterns are still designated as in coupled ¹³C NMR spectrum: s (singlet, C), d (doublet, CH), t (triplet, CH₂), q (quartet, CH₃). The recording of the spectra using the Nicolet NT-200 and Varian VXR-300 spectrometer was performed by the NMR service team of the Organic Chemistry Department of the University of Groningen. The NMR spectra were recorded in CDCl₃ unless stated otherwise. Infrared Spectra were recorded on a Perkin Elmer 841. High Resolution Mass Spectra (HRMS) were obtained on an AEI MS-902 spectrometer by Mr A. Kieviet. Elemental analyses were performed in the Microanalytical Department of the University of Groningen. The average values of duplo determinations are reported. The X-ray analyses were performed by Mr. F van Bolhuis and Drs. A.M. Meetsma.

4-Oxo-4-[2-(5,6,7,8-tetrahydronaphthyl)butanoic acid (21)

A mixture of benzene (350 mL), 1,2,3,4-tetrahydronaphthalene (20, 66.0 g, 0.50 mol) and succinic anhydride (50.0 g, 0.50 mol) was mechanically stirred and cooled to 0 °C, whereupon it became very viscous. To this slurry was slowly added AlCl₃ (88 g, 0.66 mol) in 90 min, taking care to keep the inner temperature below 5 °C. The cooling bath was removed and the mixture stirred for 18 h. The red-brown slurry was cooled to 0 °C and 10% aqueous HCl (300 mL) was added slowly to decompose the formed salts while keeping the temperature below 25 °C. Benzene (1 x 200 mL) was added, the organic layer separated and the water layer extracted with benzene (1 x 200 mL). The combined organic layers were washed with H₂O (1 x 200 mL), brine (1 x 200 mL), dried (Na₂SO₄) and after evaporation of the solvent under reduced pressure, acid 21 was obtained as a yellow solid (47.9 g, 0.21 mol, 41.3%). This compound proved to be > 95% pure by ¹H NMR analysis and was used in the following step without further purification: mp 113.6-116.0 °C (lit: mp 115.5 °C); ¹H NMR (60 MHz) δ 1.56-1.95 (m, 4H), 2.50-2.94 (m, 6H), 3.21 (t, J = 6.0 Hz, 2H), 6.92-7.78 (m, 6H).
4-[2-(5,6,7,8-Tetrahydronaphthyl)]butanoic acid (22)
Keto-acid 21 (44.0 g, 0.19 mol), KOH (37.0 g, 0.66 mol), H₂O (25 mL) and NH₂NH₂H₂O (23.5 mL, 24.2 g, 0.44 mol) were successively added to magnetically stirred diethylene glycol (250 mL). The mixture was refluxed for 4 h, whereupon the colour changed to dark-brown. The excess of NH₂NH₂H₂O and the formed H₂O (± 50 mL) were slowly removed by distillation (60 min) until the inner temperature of the flask reached 200-210 °C. After stirring at this temperature for 4 h, the black solution was cooled to 60 °C and H₂O (300 mL) was added. After cooling to room temperature 20% aqueous HCl (300 mL) was slowly added and the water layer extracted with CH₂Cl₂ (3 x 250 mL). The combined organic layers were washed with H₂O (1 x 100 mL), dried (Na₂SO₄) and after evaporation of the solvent in vacuo, acid 22 was obtained as a dark-brown solid (39.5 g, 0.18 mol, 95.6%). This compound proved to be > 90% pure by ¹H NMR analysis and was used in the next step without further purification: mp 39.5-42.8 °C (lit. mp 49.5 °C); ¹H NMR (60 MHz) δ 1.58-2.12 (m, 6H), 2.15-2.90 (m, 8H), 6.67-7.15 (m, 3H), 10.88 (bs, 1H).

Methyl 4-[2-(5,6,7,8-tetrahydronaphthyl)]butanoate (23)
Acid 22 (36.0 g, 0.17 mol) was stirred and refluxed with MeOH (200 mL) and concentrated H₂SO₄ (1 mL) for 18 h. The dark brown solution was then cooled to room temperature and H₂O (300 mL) was added. The methanol was removed under reduced pressure and the resulting water layer extracted with CH₂Cl₂ (4 x 150 mL). The combined brown organic layers were washed with saturated aqueous NaHCO₃ (2 x 100 mL), H₂O (1 x 100 mL) and brine (1 x 100 mL), dried (Na₂SO₄) and after evaporation of the solvent a brown oil was obtained. This viscous oil was purified by bulb to bulb distillation (160-170 °C, 2.0 mmHg) to afford pure 23 as a clear oil (32.0 g, 0.14 mol, 83.5%): ¹H NMR (60 MHz) δ 1.55-2.15 (m, 6H), 2.20-2.90 (m, 8H), 3.60 (s, 3H), 6.70-7.15 (m, 3H).

Methyl 4-(2-naphthy1)butanoate (24)
Methylester 23 (30.0 g, 0.13 mol) and 5% Pd/C (1.0 g) were stirred and heated slowly to 140 °C when evolution of H₂ was observed. The temperature was slowly raised to 250 °C in 30 min and stirred at 250-260 °C for 4 h. ¹H NMR analysis showed that no starting material was left. The mixture was cooled and CH₂Cl₂ (150 mL) was added. After filtration and removal of the solvent under reduced pressure a slightly blue shining oil was obtained. This oil was purified by bulb to bulb distillation (160-170 °C, 1.0 mmHg) to provide pure 24 as a clear oil (26.0 g, 0.11 mol, 88.2%): ¹H NMR (60 MHz) δ 1.70-2.45 (m, 4H), 2.75 (t, J = 7.0 Hz, 2H), 3.58 (s, 3H), 7.10-7.88 (m, 7H).

4-(2-Naphthyl)butanoic acid (25)
To ester 24 (24.0 g, 0.11 mol), dissolved in absolute ethanol (100 mL) was added a solution of KOH (15.0 g, 0.27 mol) in H₂O (100 mL) and the resulting mixture subsequently stirred and refluxed for 90 min. After cooling to room temperature H₂O (150 mL) was added to the clear brown solution and the ethanol was removed under reduced pressure. The water layer was cooled to 0 °C and 20% aqueous HCl (200 mL) was added slowly. The acid separated as a white solid, which was isolated by filtration. The wet acid was dissolved in CH₂Cl₂ (± 500 mL), dried (Na₂SO₄) and after evaporation of the solvent, 25 was obtained as a white powder (20.6 g, 0.10 mol, 91.4%). This compound proved to be > 95% pure by ¹H NMR analysis and was used
in the next step without further purification: mp 97.4-99.2 °C (lit:38 mp 98.5 °C); 1H NMR (60 MHz) δ 1.65-2.50 (m, 4H), 2.75 (t, J = 7.0 Hz, 2H), 7.05-7.90 (m, 7H).

1,2,3,4-Tetraphenanthrene-4-one (3)
A solution of acid 25 (5.0 g, 23.4 mmol), SOCl₂ (5 mL, 8.2 g, 68.9 mmol) and pyridine (0.5 mL) in dry THF (50 mL) was stirred at 20 °C for 90 min. The THF was removed under reduced pressure and the brown residue stripped with benzene (50 mL). The brown oil was dissolved in benzene (50 mL) and after cooling to 5 °C, SnCl₄ (5.0 mL, 11.1 g, 42.7 mmol) was added in 15 min at such a rate that the temperature did not rise above 20 °C. The cooling bath was removed and the mixture was stirred for 18 h. The viscous mixture was slowly poured into ice/water (approximately 250 g) and 20% aqueous HCl was added until pH 1 was reached. This mixture was extracted with Et₂O (3 x 100 mL) and the combined Et₂O layers were washed with saturated aqueous NaHCO₃ (1 x 100 mL) and brine (1 x 100 mL). After drying (Na₂SO₄) and evaporation of the solvent under reduced pressure, a light brown oil was obtained which slowly solidified upon standing. Recrystallization from ethanol provided 3 as a slightly grey coloured solid (4.8 g, 22.9 mmol, 89.8%): mp 122.2-122.9 °C;

General procedures for the synthesis of thioketones:

a) Lawesson's reagent

9H-Xanthene-9-thione (30)
To a stirred solution of ketone 27 (3.00 g, 15.3 mmol) in toluene (25 mL) was added Lawesson’s reagent 33 (3.11 g, 7.7 mmol). This mixture was stirred and heated to 110 °C. After 3 h TLC analysis (hexane/Et₂O, 90:10, SiO₂, starting material Rₜ = 0.26, product Rₜ = 0.54) showed no starting material left. The green mixture was cooled, filtered, the residue washed with CH₂Cl₂ (50 mL) and the solvents evaporated under reduced pressure. The smelly residue was purified by chromatography (SiO₂, pet-ether 60-40/CH₂Cl₂, 90:10). The thio ketone was crystallized from CH₂Cl₂/Et₂O (30 mL, 4:1) to provide 30 in two fractions as small dark violet crystals (1.87 g, 8.8 mmol, 57.5%), giving a green colour in solution: mp 155.3-156.2 °C (lit:37 157 °C); 1H NMR (200 MHz) δ 2.82 (dd, J = 6.7, 6.6 Hz, 2H), 7.25 (d, J = 8.5 Hz, 1H), 7.43 (ddd, J = 8.5, 7.8, 1.1 Hz, 1H), 7.60 (ddd, J = 8.5, 7.8, 1.5 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 9.42 (dd, J = 8.8, 1.5 Hz, 1H); 13C NMR δ 22.63 (t), 31.15 (t), 40.70 (t), 125.37 (d), 126.25 (d), 126.59 (d), 126.69 (s), 127.90 (d), 128.36 (d), 130.95 (s), 132.33 (s), 133.73 (d), 146.37 (s), 199.96 (s, C=O).
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MHz) δ 7.37 (dd, J = 8.1, 7.0, 1.0 Hz, 2H), 7.50 (d, J = 8.8, 7.0, 1.5 Hz, 2H), 8.74 (dd, J = 8.1, 1.5 Hz, 2H); 13C NMR δ 118.10 (d), 124.56 (d), 128.85 (s), 129.68 (d), 134.69 (d), 150.30 (s), 204.73 (s, C=S).

9H-Xanthene-9-thione (30) was also prepared by the use of P2S5 in toluene as described for 31. Starting from 9H-xanthene-9-one (27, 12.3 g, 62.8 mmol) and P2S5 (27.9 g, 125.5 mmol, 2 equiv.) followed by crystallization from CH2Cl2/Et2O (150 mL, 1:1) furnished 30 (10.3 g, 48.5 mmol, 77.3%).

b) P2S5

9H-Thioxanthene-9-thione (31)
To a stirred solution of 9H-thioxanthene-9-one (28, 8.0 g, 37.7 mmol) in toluene (200 mL) was added P2S5 (16.7 g, 75.4 mmol). After refluxing for 4 h TLC analysis (SiO2, hexane/Et2O 90:10, starting material Rf = 0.31, product Rf = 0.53), showed no starting material left. The dark green mixture was cooled, filtered and the smelly residue washed with hot toluene (2 x 100 ml) and CH2Cl2 until the washings were only slightly green. The toluene and CH2Cl2 were removed under reduced pressure and the brown-green mass recrystallized from xylene (150 mL) to afford in two fractions 7.2 g of small dark green needles (31.6 mmol, 82.6%): mp 172.1-173.9 °C; (lit:49 mp 170 °C); 1H NMR (200 MHz) δ 7.10-7.64 (m, 6H), 8.94 (dd, J = 8.8, 1.1 Hz); 13C NMR δ 125.98 (d), 126.97 (d), 131.63 (d), 131.92 (s), 133.32 (d), 137.53 (s), 211.62 (s, C=S).

10N-Methyl-9H-acridane-9-thione (32)
This compound was prepared as described for 31. Starting from 10N-Methyl-9H-acridane-9-one (29, 2.09 g, 10.0 mmol, SiO2, hexane/Et2O 70:10, starting material Rf = 0.09, product Rf = 0.17) and P2S5 (4.45 g, 20 mmol, 2 equiv.) followed by crystallization from CH2Cl2 (50 mL) afforded 32 as red small needles (1.65 g, 7.9 mmol, 78.9%); mp 256.1-257.9 (lit:50 mp 258-260 °C); 1H NMR (300 MHz) δ 3.98 (s, 3H), 7.33 (ddd, J = 8.3, 6.8, 1.2 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.74 (ddd, J = 8.8, 6.8, 1.7 Hz, 2H), 9.18 (dd, J = 8.3, 1.7 Hz, 2H); 13C NMR δ 34.63 (q), 115.25 (d), 122.82 (d), 122.88 (s), 131.86 (d), 133.89 (d), 137.75 (s), C=S was not observed due to the very low solubility of this compound.

General procedure for the synthesis of episulfides:

Dispiro[1,2,3,4-tetrahydrophenanthrene-4, 2'-thiirane-3', 9''-(9''H)-xanthene] (35)
A stirred solution of hydrazone 26 (270 mg, 1.29 mmol) in dry Et2O (20 mL) was cooled to -10 °C, whereupon MgSO4 (approximately 500 mg), Ag2O (447 mg, 1.93 mmol, 1.5 equiv.) and a saturated KOH solution in methanol (1 mL) were successively added. The mixture turned orange, then red and after 30 min a deep purple solution of the diazo compound was obtained. In some cases when only a orange or red colour was observed, some more Ag2O (116 mg, 0.5 mmol) and saturated KOH (1 mL) was added, the temperature allowed to rise to 0 °C and the mixture stirred for another 60 min. The deep purple solution was filtered into another ice-cooled bulb and the remaining residue was washed with cold Et2O (10 mL). To this clear solution was added the dark green 9H-xanthene-9-thione (30) in small portions. Evolution of

nitrorgen was observed and the deep purple colour slowly disappeared. The thiokeitone was added until the evolution of nitrogen had ceased and the colour of the solution had become light yellow. A total amount of 230 mg (1.09 mmol, 0.8 equiv.) was necessary. After stirring for 60 min at 0 °C, the Et₃O was removed under reduced pressure and the green-brown residue (500 mg) crystallized from absolute ethanol (100 mL) to provide episulfide 35 as small white needles (400 mg, 1.02 mmol, 94.1%), based on added thiokeitone. In most experiments a white precipitate of pure episulfide 35 was obtained, which was isolated by filtration: mp 175.9-176.4 °C; ℎ NMR (300 MHz) δ 1.21-1.39 (m, 2H), 2.25-2.35 (m, 2H), 2.37-2.46 (m, 1H), 2.51-2.63 (m, 1H), 6.23 (dd, J = 8.5, 7.9, 1.5 Hz, 1H). 6.73 (dd, J = 7.9, 1.5 Hz, 1H). 6.84 (dd, J = 8.2, 7.0, 1.5 Hz, 1H). 6.86-6.89 (m, 1H). 6.93 (d, J = 7.9 Hz, 1H). 7.19 (d, J = 7.9 Hz, 1H). 7.21-7.23 (m, 1H). 7.34-7.42 (m, 2H). 7.47 (d, J = 8.2 Hz, 1H). 7.55 (dd, J = 8.8, 8.2, 1.5 Hz, 1H). 7.72 (dd, J = 8.2, 0.6 Hz, 1H). 7.84 (dd, J = 8.5, 1.2 Hz, 1H). 9.24 (d, J = 8.5 Hz, 1H); 13C NMR δ 20.48 (t), 28.90 (t), 32.59 (t), 51.73 (s), 58.60 (s), 115.28 (d), 116.25 (d), 121.35 (s), 121.93 (d), 122.02 (s), 122.66 (d), 122.85 (d), 124.04 (d), 124.57 (d), 124.51 (d), 124.73 (d), 127.05 (d), 127.50 (d), 127.97 (d), 128.46 (d), 128.61 (d), 129.47 (d), 131.36 (s), 132.40 (s), 132.46 (s), 140.33 (s), 153.18 (s), 154.37 (s); HRMS Calcd for C₁₂H₉O: 392.120, found 392.122; Anal. Calcd for C₁₂H₉O: C, 82.62; H, 5.14; S, 8.17. Found: C, 82.10; H, 5.13; S, 8.27.

**Disspiro[1,2,3,4-tetrahydrophenanthrene-4, 2'-thirane-3', 9''-(9''H)-thioxanthene] (36)**

This compound was prepared following the procedure described for 35. Starting from hydrazine 26 (500 mg, 2.36 mmol) and thiokeitone 31 (450 mg, 1.97 mmol), episulfide 36 was obtained as a light yellow crystalline solid (570 mg, 1.40 mmol, 69.9%) after crystallization from ethanol (± 150 mL): mp 165.3-164.5 °C; ℎ NMR (300 MHz) δ 1.34-1.56 (m, 2H), 1.92-2.01 (m, 1H), 2.40-2.48 (m, 1H), 2.59-2.68 (m, 1H), 3.56-3.67 (m, 1H). 6.38 (dd, J = 8.8, 7.8, 1.5 Hz, 1H). 6.70 (dd, J = 8.8, 7.8, 1.5 Hz, 1H). 6.97 (d, J = 8.8 Hz, 1H). 6.99 (d, J = 8.8 Hz, 1H). 7.26-7.33 (m, 4H). 7.35 (d, J = 8.8 Hz, 1H). 7.41 (d, J = 7.8 Hz, 1H). 7.45 (dd, J = 8.3, 6.8, 1.5 Hz, 1H). 7.55 (d, J = 7.8 Hz, 1H). 8.00 (dd, J = 7.8, 1.5 Hz, 1H). 9.51 (d, J = 8.8 Hz, 1H); 13C NMR δ 20.87 (t), 29.85 (t), 34.79 (t), 59.60 (s), 61.13 (s), 123.73 (d), 123.91 (d), 124.37 (d), 124.74 (d), 125.16 (d), 126.14 (d), 126.29 (d), 126.30 (d), 127.21 (d), 127.22 (d), 127.88 (d), 129.35 (s), 130.26 (d), 130.99 (d), 132.18 (s), 132.79 (s), 133.07 (s), 133.22 (s), 135.45 (s), 140.94 (s); HRMS Calcd for C₁₂H₉O: 408.101, found 408.100; Anal. Calcd for C₁₂H₉O: C, 79.39; H, 4.94; S, 15.67. Found: C, 79.73; H, 5.01; S, 15.69.

**Disspiro[9H-fluorene-9, 2'-thirane-3', 4''-(1''-2''-3''-4''-tetrahydrophenanthrene)] (37)**

To a stirred solution of 9H-fluorene-9-one (4, 360 mg, 2.00 mmol) in toluene (10 mL) was added Lawesson’s reagent 33 (662 mg, 1.50 mmol). This mixture was stirred and heated to 80 °C. After 2 h the green mixture was rapidly cooled (under an inert atmosphere of nitrogen) and immediately poured onto a column of SiO₂. After rapid chromatography (hexane/CH₂Cl₂, 90:10, was used as an eluens), the green fluid from the column was directly added to a stirred deep purple solution at -10 °C of diazo compound 16 (prepared from hydrazine 26 (210 mg, 1.00 mmol), as described for 35). The colour of the solution changed to brown. When the addition was complete, the mixture was stirred for 30 min. The solvents were removed in vacuo and the brown residue (600 mg) crystallized from absolute ethanol (200 mL) to furnish episulfide 37 as an orange powder (194 mg, 0.52 mmol, 51.8%). This compound was contaminated by small amounts of an orange substance (some azine, = 10%), which could not be removed at this stage by chromatography or crystallization: mp 147.3-
8.50. Found: episulfide 37 (140 mg, 0.37 mmol), crystallization from n-hexane.

This compound was prepared following the procedure described for 38. Starting from 4(9'H-Fluorene-9'-ylidene)-1,2,3,4-tetrahydmphenanthne (39).

To a stirred solution of episulfide 36 (120 mg, 0.29 mmol) in xylene (10 mL) was added Cu-bronze powder (64 mg, 1.00 mmol). After refluxing for 2 h the mixture was cooled to room temperature. The brown coloured copper residue was removed by filtration, the salts washed with CH$_2$Cl$_2$ (20 mL) and the solvents removed under reduced pressure to afford a slightly yellow solid. After crystallization from absolute ethanol (± 25 mL) 38 was obtained as small white shining needles (68 mg, 0.19 mmol, 82.2%): mp 205.8-206.8 °C; $^1$H NMR (300 MHz) δ 1.95-2.05 (m, 1H), 2.11-2.26 (m, 1H), 2.30-2.44 (m, 1H), 3.00-3.18 (m, 2H), 3.52-3.59 (m, 1H), 6.22-6.25 (m, 2H), 6.85-6.90 (m, 1H), 6.98 (ddd, J = 8.2, 6.7, 1.2 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.18 (ddd, J = 7.9, 6.7, 0.9 Hz, 1H), 7.23-7.25 (m, 1H), 7.31-7.34 (m, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.65 (dd, J = 7.6, 1.5 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H); $^{13}$C NMR δ 22.03 (t), 28.54 (t), 28.60 (t), 115.98 (d), 116.59 (d), 122.08 (d), 122.75 (d), 122.80 (s), 123.70 (s), 124.28 (d), 124.95 (d), 125.07 (d), 125.38 (s), 126.26 (s), 126.45 (d), 127.12 (d), 127.13 (d), 127.24 (d), 127.58 (d), 127.67 (d), 127.79 (d), 131.97 (s), 133.04 (s), 137.56 (s), 137.86 (s), 135.25 (s), 154.53 (s); HRMS Calcd for C$_{27}$H$_{28}$O: 360.151, found 360.149; Anal. Calcd for C$_{27}$H$_{28}$O: C, 89.96; H, 5.60. Found: C, 90.15; H, 5.63.

General procedure for the synthesis of alkenes:

9-(1',2',3',4'-Tetrahydmphenanthrene-4'-yldiene)-9H-thioxanthene (39)

This compound was prepared following the procedure described for 38. Starting from episulfide 36 (120 mg, 0.29 mmol), alkene 39 was obtained as a slightly green crystalline solid (90 mg, 0.24 mmol, 81.4%) after crystallization from ethanol (25 mL): mp 181.1-182.7 °C; $^1$H NMR (300 MHz) δ 1.97-2.07 (m, 1H), 2.11-2.21 (m, 1H), 2.34-2.44 (m, 1H), 3.04-3.23 (m, 2H), 3.34-3.42 (m, 1H), 6.36 (ddd, J = 7.8, 1.5 Hz, 1H), 6.41 (ddd, J = 8.8, 7.0, 1.5 Hz, 1H), 6.78 (ddd, J = 8.8, 7.8, 1.5 Hz, 1H), 6.99 (ddd, J = 8.3, 6.8, 1.5 Hz, 1H), 7.15 (d, J = 8.3, 6.8, 1.5 Hz, 1H), 7.27 (ddd, J = 8.8, 7.3, 1.5 Hz, 1H), 7.33-7.39 (m, 3H), 7.53 (d, J = 8.3 Hz, 1H), 7.58-7.64 (m, 3H), 7.68 (d, J = 8.3 Hz, 1H); $^{13}$C NMR δ 22.34 (t), 28.14 (t), 28.72 (t), 124.16 (d), 124.92 (d), 125.04 (d), 125.20 (d), 125.81 (d), 125.90 (d), 126.09 (d), 126.39 (d), 126.45 (d), 127.24 (d), 127.33 (d), 127.34 (d), 127.61 (s), 127.91 (d), 128.55 (d), 131.82 (s), 131.97 (s), 134.05 (s), 134.69 (s), 135.45 (s), 136.46 (s), 136.58 (s), 137.86 (s), 138.38 (s); HRMS Calcd for C$_{27}$H$_{28}$S: 376.129, found 376.127.

4-(9'H-Fluorene-9'-yldiene)-1,2,3,4-tetrahydmphenanthre (1)

This compound was prepared following the procedure described for 38. Starting from episulfide 37 (140 mg, 0.37 mmol), crystallization from n-hexane (± 30 mL) furnished alkene 1 as a yellow solid (100 mg, 0.29 mmol, 78.1%), traces of azine were removed.
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at this stage): mp 237.6-238.9°C (lit.\textsuperscript{11a} mp 236-238 °C); \textsuperscript{1}H NMR (300 MHz) δ 1.48-1.60 (m, 1H), 2.21-2.31 (m, 1H), 2.58-2.66 (m, 1H), 2.80-2.88 (m, 1H), 3.05-3.12 (m, 1H), 3.80-3.93 (m, 1H), 6.05 (dd, J = 7.9, 0.7 Hz, 1H), 6.58 (ddd, J = 7.9, 1.0 Hz, 1H), 7.05 (ddd, J = 8.5, 7.0, 1.0 Hz, 1H), 7.18-7.47 (m, 5H), 7.63 (d, J = 8.8 Hz, 1H), 7.79-7.91 (m, 3H), 7.99 (d, J = 8.8 Hz, 1H), 8.04-8.10 (m, 1H); \textsuperscript{13}C NMR δ 21.67 (t), 30.16 (t), 31.25 (t), 118.66 (d), 119.42 (d), 124.40 (d), 124.77 (d), 125.26 (d), 125.87 (d), 125.92 (d), 126.26 (d), 126.39 (d), 126.51 (d), 126.57 (d), 127.12 (d), 128.58 (d), 130.82 (d), 131.03 (s), 132.24 (s), 133.81 (s), 135.24 (s), 137.64 (s), 138.36 (s), 138.72 (s), 139.28 (s), 140.17 (s), 140.77 (s); HRMS Calcd for C\textsubscript{27}H\textsubscript{20}: 344.156, found 344.157.