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# Photochromism of a Novel Class of Spiroindolines: 6-Aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2′-indolines]

**Ortwin Brede, Leonie Goebel, and Thomas Zimmermann***

*Max Planck Society, Research Unit Time-Resolved Spectroscopy at the University of Leipzig, Permoserstrasse 15, D-04303 Leipzig, Germany*

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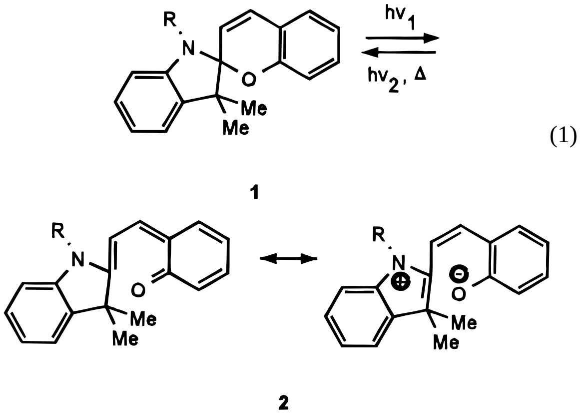
The photochromism of a new class of spiro compounds (spiro[cyclohexadieneindolines) has been studied by UV and visible stationary photolysis and laser flash photolyis ($\lambda$ = 266, 353, and 532 nm). In analogy to spiropyrans, isomerization to ring-opened compounds (merocyanines) and formation of spiro compound triplets has been found. Visible light illumination of the red merocyanines regenerates the original spiro compound. Since in liquid solutions decomposition reactions compete with the recyclization, under these conditions only three switching cycles could be verified. In the case of spiroindolines embedded in a polyethylene matrix after five cycles, no decomposition has been observed. The photoisomerization process has been found to proceed via the first excited singlet states of the spiro compounds and merocyanines, respectively. Quantum yields of all reactions and spectra and extinction coefficients of the spiro[cyclohexadieneindolines] and of their isomerization products (merocycanines) are given.

## Introduction

Photochromism is a phenomenon which is of great interest because of its manifold technical applications.[1,2,3] For about the last 40 years, 2*H*-1-benzopyrans, *spiro* condensed with another heterocycle in position 2, have been known to undergo a reversible photoisomerization and have been intensely studied.[4,5] In the case of the spiro[indoline-2*H*-1-benzopyrans] **1** where this heterocycle is an indoline system, the UV irradiation gives the colored merocyanine **2** which can be recyclized with visible light or with heat to the original spiro compounds (eq 1).[2,6,7]

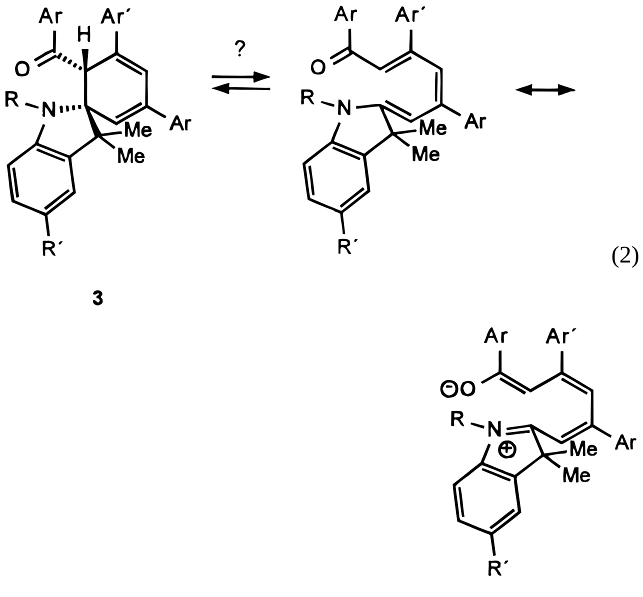


(1)

**1**

**2**

Recently a novel class of spiroindolines, the 6-aroyl-3,5-diarylspiro[cyclohexa-2,4-diene-1,2′-indolines] **3**, were synthesized by diastereoselective ring transformation of 2,4,6-triarylpyrylium salts with 2-methyleneindolines.[8] Their electrocyclic ring opening should lead to the merocyanines **4** which are vinylogs of the merocyanines **2** (cf. eq 2). Hence the hypothesis arose that the spiro[cyclohexadieneindolines] **3** should also exhibit photochromic properties.



(2)

**3**

**4**

To prove this hypothesis, laser photolysis and stationary photolysis experiments with the spiro[cyclohexadieneindolines] **3** has been performed.[9,10] In this paper we report the photochromic properties of these compounds in detail.

## Experimental Section

The photolysis experiments were carried out at (293 ± 1) K with $N_2$-saturated solutions, which in the case of pulsed photolysis were continuously flowing through the sample cell.

**Stationary Photolysis.** The samples were illuminated with intense light of a Xenon high-pressure lamp (XBO 450 W, Osram). Ultra violet and visible spectral ranges were selected by using a bandwidth filter UG11 ($\lambda$ = 250−390 nm, maximum at 340 nm) and an edge filter BG23 (>450 nm). After the photolysis, the quartz cells containing the samples were directly positioned in the UV−vis spectrometer (Shimadsu UV-2101).

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[*] Institute of Organic Chemistry, University of Leipzig, Permoserstrasse 15, D-04303, Leipzig, Germany.

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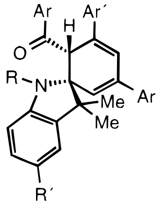
**TABLE 1: Structure and UV−vis Spectral Data of the Spiro[cyclohexadieneindolines] Taken in Cyclohexane**



**3**

| 3 | Ar | Ar′ | R | R′ | $\lambda_{max}$/nm | $\epsilon_3$/dm$^3$ mol$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|---|---|
| **a** | Ph | Ph | Me | H | 311, 323 | 9 500, 35 900 |
| **b** | Ph | 4-MeO−$C_6H_4$ | Me | H | 315, 266 (sh), 257 (sh), 249 | 13 100, 31 000, 34 300, 37 400 |
| **c** | Ph | Ph | Me | $NO_2$ | 400 (sh), 389, 338 (w), 257 | 8 600, 10 100, 5 100, 16 800 |
| **d** | Ph | 4-Br−$C_6H_4$ | Me | H | 316, 257 | 11 300, 36 000 |
| **e** | 4-Br−C6H4 | Ph | Me | H | 310, 262 | 10 900, 56 700 |
| **f** | Ph | Ph | Me | Br | 316, 263 (sh), 255 | 9 200, 28 800, 34 500 |
| **g** | Ph | Ph | Ph | H | 314, 290, 252 | 20 000, 25 000, 47 200 |

**Laser Flash Photolysis.** Experiments were carried out with a perpendicular probe excitation arrangement. The solutions were photolysed in a full quartz system using the different harmonics ($\lambda$ = 266, 355, and 532 nm) of a Quanta Ray GCR-11 $Nd^{3+}$:YAG laser (Spectra Physics, Inc.). The optical detection system consisted of a pulsed 900 W Xenon lamp (XBO 900, Osram), a Spectra Pro-500 monochromator (Action Research Corp.), a 1P28 (RCA) photomultiplier, and a TDS 640 (500 MHz) Tektronix digitizing oscilloscope; details are given in ref 11. The overall time resolution of the system was 5 ns.

**Actinometry.** The following substances were used as references for the actinometry for the stationary, as well as for pulsed, photolysis:

$$\lambda = 266\text{ nm},\quad \text{aqueous KI},\quad \Phi = 0.22,^{12}$$
$$\epsilon_{578}(e_{solv}^{-}) = 10\,600\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1\ 13}$$
$$\epsilon_{400}(e_{solv}^{-}) = 2200\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1\ 14}$$

$$\lambda = 355\text{ nm},\quad \text{benzophenone},\quad \Phi = 1,^{15}$$
$$\epsilon_{530}(^1\text{T}) = 7220\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1\ 16}$$

$$\lambda = 532\text{ nm},\quad \text{Ru(bpy)}_3\text{Cl}_2,\quad \Phi = 1,^{17}$$
$$\epsilon_{366}(^1\text{T}) = 17\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1\ 17}$$
$$\epsilon_{390}(^1\text{T}) = 1850\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$$

The extinction coefficients were determined by relative actinometry, i.e., by comparing with similar absorptions of the references. In some cases $\epsilon$ was determined from the photonity dependence in case of saturation behavior.[18] The laser photonity was measured by an appropriate device.

**HPLC Separations.** The chromatographic separations were made at a Hewlett Packard HP 1050 machine with detection by UV−vis spectroscopy. Using a silica gel column (LiChroCART 250−4 HPLC cartridge LiChrospher Si 60.5 $\mu$m, Merck). A mixture of *n*-heptane and tetrahydrofurane (4:1, v:v), with addition of 0.5% dichloromethane, served as a mobile phase.

**Chemicals.** The solvents cyclohexane, acetonitrile, ethanol, *n*-heptane, and tetrahydrofurane were used in spectroscopic quality (Aldrich). Actinometer standards were of p.a. quality. A nonstabilized polyethylene of LDPE type (Mirathen Al 23KA, Leuna) was used as a solid matrix. The spiro[cyclohexadieneindolines] **3** were synthesized as described in a previous paper.[8]

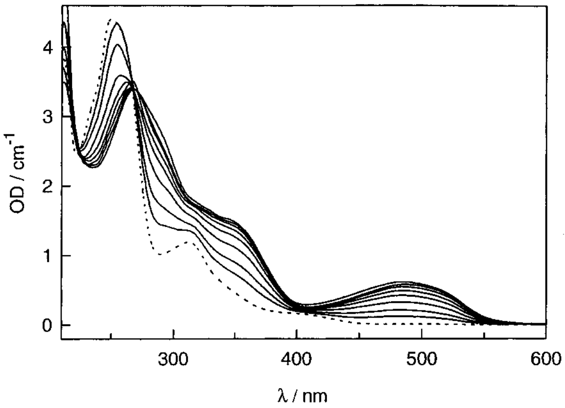


**Figure 1.** Development of absorption spectra during UV illumination of a 0.1 mM solution of **3a** in cyclohexane: dashed line, original spectrum of **3a**; full lines, illumination effect. The time dependence is demonstrated in the left part of Figure 2.

## Results and Discussion

The spiro[cyclohexadieneindolines] **3** given in Table 1 were used for our photochromism studies.

Except for the nitro-substituted compound **3c**, the spiro[cyclohexadieneindolines] have similarly shaped optical absorption spectra. Figure 1 (dashed line) shows the absorption spectrum of **3a**. The spectroscopic data of the other substances used are given in Table 1.

**Stationary Photolysis.** When a very dilute solution of **3a** was illuminated in cyclohexane with UV light, the original spectrum of the spiro compound (Figure 1, dashed line) changes by shifting to the visible range. After illumination of **3a** for 60 min, an equilibrium between **3** and **4** is reached in which a red colored compound dominates, the possible merocyanine **4a**. This spectral change is shown in Figure 1, whereas Figure 2 illustrates the time dependence of the illuminations. After reaching the equilibrium state, the sample was illuminated with visible light, and hence, the starting spectrum of **3a** has been mainly reproduced (Figure 2, right part), slightly superimposed with the spectrum of a side product. After repeating the UV and visible illumination cycles three times, the red absorption of **4a** is reduced to about a third of the original value.

A formal analysis of the time dependence of the VIS photolysis part in Figure 2 results in two exponential time laws, $k_{4,brutto} = 1.6 \times 10^{-2}$ s$^{-1}$ and $k_{5,brutto} = 3.5 \times 10^{-3}$ s$^{-1}$. We

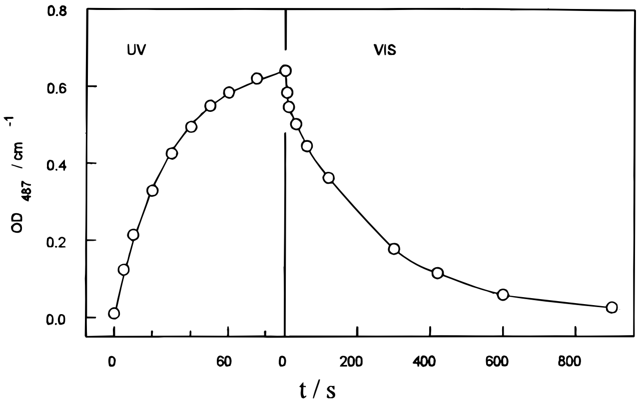


**Figure 2.** Time dependent changes of the 480 nm band: left part, UV light illumination of 0.1 mM solution of **3a** in cyclohexane (spectral effects, see Figure 1); right part, bleaching of the merocyanine by visible light illumination.

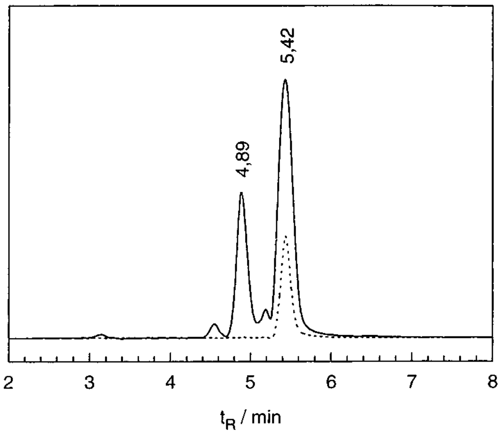


**Figure 3.** HPLC chromatogram of an UV-illuminated (60 min) sample of **3d** detected at $\lambda = 255$ nm (full line) as well as at $\lambda = 500$ nm (dashed line): 4.89 peak due to **3d**, 5.42 due to **4d**.

explain these time constants as being caused by the reconversion reaction 3 and the decomposition reaction 4 of **4a**.

The described photobehavior of the spiroindoline/merocyanine pair **3a**/**4a** has been observed also for the other compounds listed in Table 1. Only **3g** differs a bit. Here, visible light causes primarily red coloration with subsequent complete decomposition.

$$\mathbf{4} + h\nu_{\mathrm{vis}} \rightarrow \mathbf{3} \qquad (3)$$

$$\rightarrow \text{products} \qquad (4)$$

Generally, distinctively from spiropyrans, all the studied spiroindolines **3** exhibit no thermal back-reaction analog to reaction 3, at least not measurable in liquid solution. In solid solution as, for example, in polyethylene matrix, the photochromic behavior of the spiro[cyclohexadieneindolines] was found to be quite similar to that of those in liquid samples. The back-reaction 3, however, proceeds photolytically as well as thermally, in the latter case over a time period of days. Distinctively from liquid samples, after five illumination cycles no decomposition reaction 4 has been observed.

Despite the relative instability of the merocyanines, in most cases it was possible to separate the components of the illuminated samples of **3** or **4** by the HPLC technique. In our system, the spectral detector enabled detection at different wavelengths as well as recording of the whole UV−vis spectra. Figure 3 shows a HPLC analysis of a (60 min) UV-illuminated **3d** sample. Here, the peaks of residual and nonconverted **3d** (4.89) and that of **4d** (5.42) can be well distinguished. Furthermore, the clear separation enables the recording of the spectra of the merocyanines and the determination of optical data (extinction coefficients and quantum yields), conversion rates, and the characterization of byproducts.

**TABLE 2: Retention Times $t_R$ of the Corresponding Spiro and Merocyanine Forms**

| spiroindoline | $t_R$/min | merocyanine | $t_R$/min |
|---|---|---|---|
| **3a** | 5.55 | **4a** | 5.73 |
| **3b** | 8.06 | **4b** | 8.10 |
| **3c** | 10.40 | **4c** | 8.30 |
| **3d** | 4.89 | **4d** | 5.42 |
| **3e** | 4.31 | **4e** | 4.46 |
| **3f** | 5.76 | **4f** | 5.66 |
| **3g** | 6.46 | **4g** | 6.83 |
| | | **4g′** | 6.29 |

**TABLE 3: UV−vis Spectral Data of the Merocyanines 4**

| compound | $\lambda_{max}$/nm | $\epsilon_4$/dm$^3$ mol$^{-1}$ cm$^{-1}$ |
|---|---|---|
| **4a** | 493 | 7 600 |
| | 330 (sh) | 13 200 |
| | 272 | 22 900 |
| **4b** | 490 | 7 350 |
| | 355 (sh) | 15 400 |
| | 315 | 20 000 |
| | 267 | 29 200 |
| **4c** | 406 | 15 500 |
| | 358 | 12 800 |
| | 295 (sh, w) | 12 400 |
| | 260 | 21 400 |
| **4d** | 503 | 5 000 |
| | 335 (sh) | 9 300 |
| | 310 (sh, w) | 10 500 |
| | 273 | 17 400 |
| **4e** | 506 | 7 900 |
| | 342 | 14 200 |
| | 275 | 31 100 |
| **4f** | 487 | 5 800 |
| | 323 | 14 000 |
| | 285 | 19 400 |
| | 270 (sh) | 19 200 |
| **4g** | 475 | 5 500 |
| | 342 | 17 100 |
| | 272 | 36 300 |
| **4g′** | 475 | 15 000 |
| | 350 (sh, w) | 14 000 |
| | 275 | 35 000 |

Table 2 shows the retention times of the spiro[cyclohexadieneindolines] **3** and of the merocyanines **4**. Table 3 presents the characteristics of the UV−vis spectra of the merocyanines. In the case of **3g**, two isomeric merocyanines **4g** and **4g′** with different HPLC retention times but very similar UV−vis spectra seem to exist.

**Laser Flash Photolysis.** To learn more about the mechanism of the photoisomerization of the spiro[cyclohexadieneindolines], we performed UV (266 and 355 nm) and visible (532 nm) laser flash photolysis experiments with detection by time-resolved optical spectroscopy. Generally, no fluorescences could be observed in the nanosecond time range, which is analogous to the spiropyrans.[19,20]

Through absorption spectroscopy, it has been found that all observed signals were formed within the time resolution of the laser system of about 5 ns. But there is a marked influence of different solvents on the transient spectra. Hence, by flashing compounds **3** with cyclohexane as the solvent, the pure merocyanine **4** spectra are detected that were already known from the steady-state experiments. This can be seen for the example of **3a** in Figure 4a. In acetonitrile solution, however, a completely different spectral shape appears (Figure 4b). The time behavior of the spectral signals, shows, as expected, that

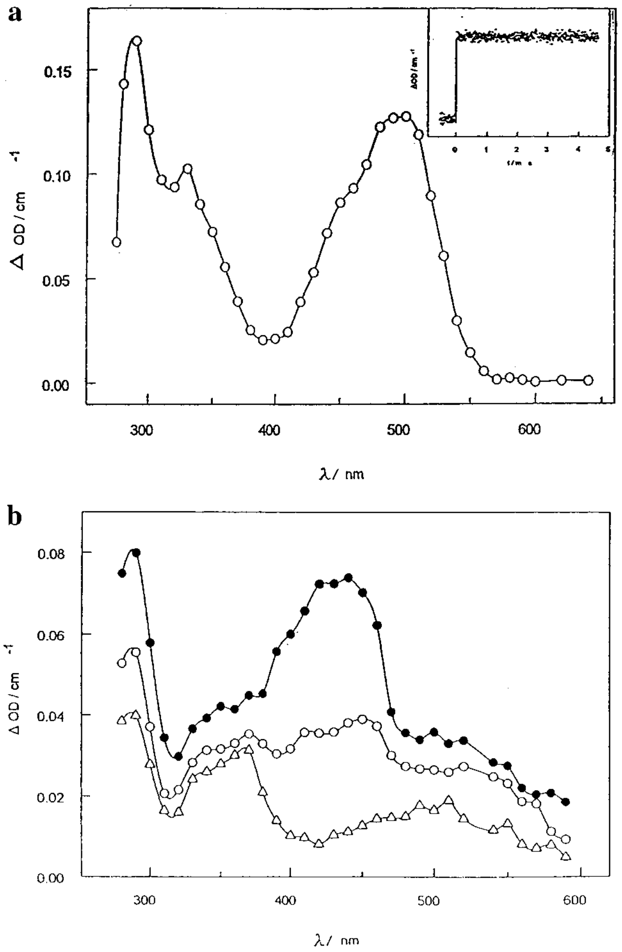


**Figure 4.** a) Optical absorption spectrum recorded in the 266 nm laser photolysis of a deaerated 0.06 mM solution of **3a** in cyclohexane (0.20 ns after the pulse). The inset shows the time profile at $\lambda = 500$ nm. (b) Transient absorption spectra taken in the 266 nm laser photolysis of a 0.06 mM deaerated solution of **3a** in acetonitrile: (●) immediately (10 ns) after the pulse and after 5 $\mu$s (○) and (△) $\mu$s, respectively.

the merocyanine absorption with a characteristic maximum at $\lambda = 500$ nm is formed rapidly, but remaines stable (Figure 4a). In acetonitrile another transient dominates the spectrum, having a characteristic absorption maximum at $\lambda = 440$ nm and decays with a half-life time of 3.7 $\mu$s. In the longer time range a small absorption of the merocyanine **4a** remains. Because of its lifetime, its reaction with oxygen, and its relaxation to the singlet ground state (without any product formation), we assign this species to the first excited triplet state of the spirocompounds **3** formed by competition to the isomerization to **4**. This mechanism can be imagined to proceed via a short-lived first excited singlet state of **3**.

$$\mathbf{3}(\mathrm{S0}) + h\nu \rightarrow \mathbf{3}(\mathrm{S1}) \rightarrow \mathbf{4} \qquad (2)$$

$$\rightarrow \mathbf{3}(\mathrm{T1}) \qquad (5)$$

Except for **3c**, all other spiroindolines show a quite similar laser photolysis behavior as that of **3a**. The nitro-substituted derivative **3c** exhibits an opposite behavior. It forms predominantly the triplet in cyclohexane solution, superimposed to the merocyanine **3c** background (cf. Figure 5a). In acetonitrile the pure merocyanine spectrum has been observed (Figure 5b) that agrees well with that obtained in the steady-state experiments.

The best kinetic distinction and identification of the triplet states of **3** is the quenching with oxygen.[36] This reaction proceeds for all spiroindoline triplets with $k_7 = (1.9 + 0.1) \times 10^9$ dm$^3$ mol$^{-1}$s$^{-1}$.

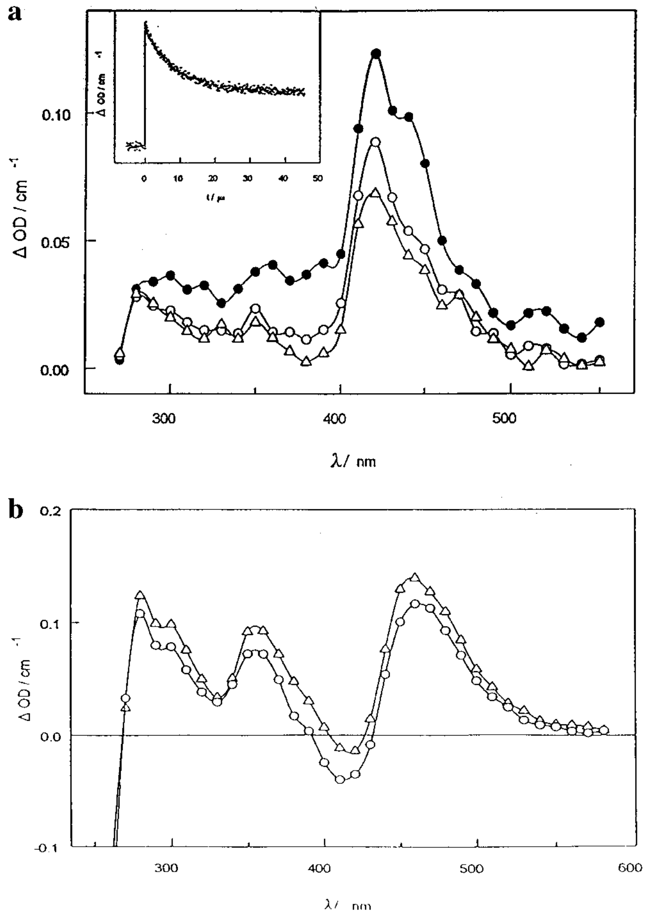


**Figure 5.** (a) Transient absorption spectra taken in the 266 nm laser photolysis of a 0.05 mM solution of **3c** in cyclohexane: 10 ns (●), 8 $\mu$s (○), and 16 $\mu$s (Δ) after the pulse. The inset shows a time profile at $\lambda = 420$ nm. (b) Optical absorption spectra recorded in the 266 nm laser photolysis of a deaerated 0.1 mM solution of **3c** in acetonitrile: (Δ) 10 ns and (o) 40 $\mu$s after the pulse.

**TABLE 4. Extinction Coefficients of the First Excited Triplet States of the Spiro[cyclohexadieneindolines ] 3(T1) Taken in Acetonitrile or Cyclohexane**

| compound | $\epsilon_{\mathrm{T1}}$/dm$^3$ mol$^{-1}$ cm$^{-1}$ | $\lambda_{\max}$/nm |
|---|---|---|
| **3a** | 2550 | 420[a] |
| **3b** | 1350 | 430[a] |
| **3c** | 2500 | 420[b] |
| **3d** | 4400 | 420[a] |
| **3e** | 1850 | 420[a] |
| **3f** | 5400 | 420[a] |
| **3g** | 2350 | 420[a] |

[a] Acetonitrile. [b] Cyclohexane.

$$\mathbf{3}(\mathrm{T1}) + \mathrm{O}_2 \rightarrow \mathbf{3}(\mathrm{S0}) + \mathrm{O}_2 \qquad (6)$$

The maximum triplet extinction coefficients have been determined from the photonity dependence of the triplet occupation. Using the border line value of photolytic saturation (variation of the laser energy till effect saturation) along with known photon fluxes, the triplet extinction coefficients could be determined.[18] Table 4 gives the experimental determined $\epsilon$ values.

The same procedure has been used for the determination of some of the extinction coefficients (for **4d,f**) of the merocyanine formed. Here, the values calculated from steady-state experiments (cf. Table 3) could be confirmed.

The laser photolysis at 532 nm of merocyanine **4a** solution in cyclohexane, prepared by stationary photolysis results in a spectrum that demonstrates the depletion of **4a**, i.e., its conver-

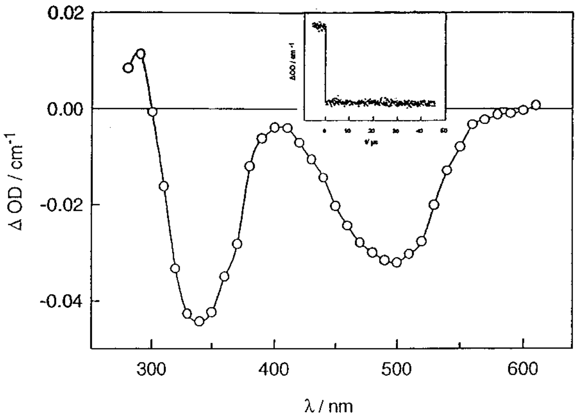


**Figure 6.** Optical absorption spectrum taken in the 532 nm laser photolysis of a merocyanine **4a** solution in cyclohexane. The solution has been prepared by 60 min. UV illumination of a 0.1 mM solution of **3a**. The inset shows a time profile at $\lambda = 490$ nm.

**TABLE 5: Quantum Yields of the Merocyanine Formation Reaction 2, of its Photobleaching Reaction 3 taken in Cyclohexane, and of the Spirocompound Triplet Population in Reaction 5 taken in Acetonitrile**

| compound | $\Phi_{3\to4}$/266 nm | 355 nm | $\Phi_{4\to3}$/532 nm | $\Phi_{T1}$/266 nm | 355 nm |
|---|---|---|---|---|---|
| **3a** | 0.020 | 0.15 | 0.12 | 0.25 | 0.20 |
| **3b** | 0.026 | 0.13 | 0.071 | 0.49 | 0.58 |
| **3c** | 0.11[a] | 0.053[a] | | 0.24[b] | 0.56[b] |
| **3d** | 0.077 | 0.24 | 0.21 | 0.26 | 0.46 |
| **3e** | 0.056 | 0.12 | 0.097 | 0.20 | 0.31 |
| **3f** | 0.065 | 0.17 | 0.15 | 0.46 | 0.75 |
| **3g** | 0.045 | 0.048 | 0.017 | 0.72 | 0.93 |

[a] Acetonitrile. [b] Cyclohexane.

sion mainly to **3a** (cf. Figure 6). This spectrum looks like the mirror-inverted merocyanine spectrum of the UV laser photolysis of **3a** (cf. Figure 4a).

The laser photolysis of compounds **3** at 355 nm gave similar results as the 266 nm experiments, at least from the qualitative point of view. The quantum yields differ markedly. For the main reactions studied in this paper, quantum yields have been determined by laser photolysis: formation of merocyanines (reaction 2) and spiro[cyclohexadieneindoline] triplets (reaction 5) at $\lambda = 266$ and 355 nm and decoloration of the merocyanine at $\lambda = 532$ nm. As standards for the actinometry the potassium iodide, the benzophenone and the Ru(bpy)$_3$Cl$_2$ actinometer have been used (see Experimental Section). The determined values are given in Table 5.

**Two-Color Flash Photolysis.** To demonstrate the connection between the UV light induced isomerization of **3** to merocyanines **4** and its reconversion to **3** by photobleaching with visible light (switching cycles), we undertook a two-color experiment. With the fourth harmonic (266 nm) of the Nd:YAG laser the spirocompound **3** was isomerized to **4**. About 15 ns later, with a blanked-out pulse of the second harmonic (532) which has been sent delayed to the sample, **4** has been photobleached. This is demonstrated on the example of **3a** in cyclohexane solution. Figure 7a shows the sequence of the laser pulses by measuring of scattered light; Figure 7b shows the generation reaction 2 and the photobleaching reaction 4. For technical reasons, the latter process is not very intense, but is clearly resolved. Analogous experiments with spiropyrans resulted only in a merocyanine isomerization, and no reconversion of the spiro form has been found.[21,22]

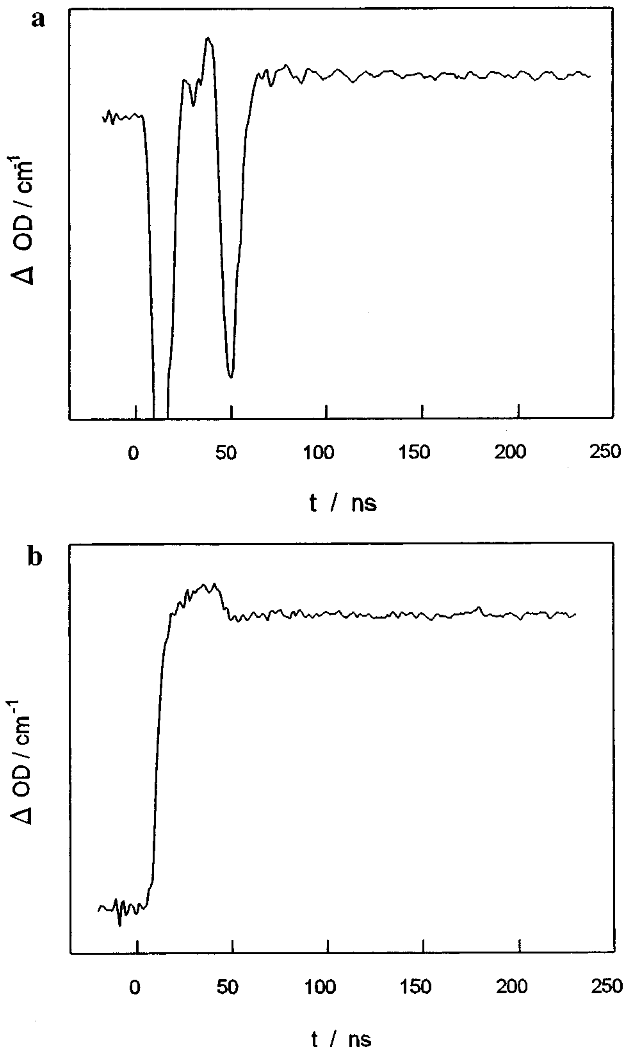
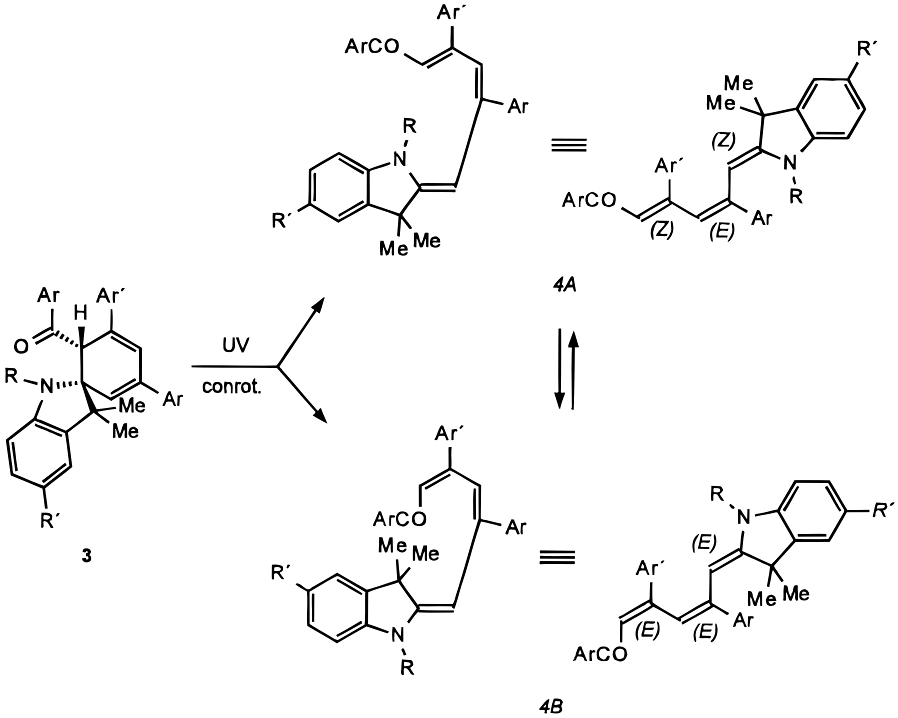


**Figure 7.** (a) Laser pulse sequence in the two-color experiment: first pulse with 266 nm, second one with 532 nm light. (b) Time profile of the 266 nm induced merocyanine **4a** formation and its photobleaching with a delayed 532 nm pulse.

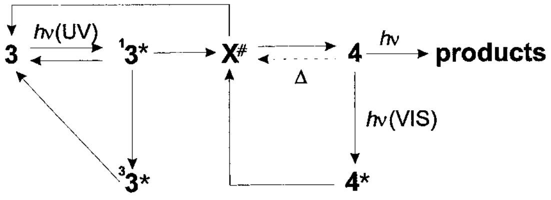
**Structure of the Merocyanines.** The ring opening of cyclohexadienes to hexatrienes is well-established.[23] If it is assumed that by UV illumination an electrocyclic reaction takes place then the stereochemistry of the merocyanines formed can be predicted by the Woodward–Hoffmann rules.[24,25,26] Starting from the spiro[cyclohexadieneindolines] **3**, the structure of which was unequivocally deduced from a X-ray analysis,[8] by conrotatory ring opening via the first excited singlet state a merocyanine with a (*Z*),(*E*),(*Z*)-configuration of the double bonds (**4A**) (clockwise rotation) and another with an (*E*),(*E*),(*E*)-configuration (**4B**) (anticlockwise rotation) can be formed (Scheme 1). For the merocyanines **4a–f** obtained by UV illumination of **3a–f** as the single products, the structure **4A** seems to be more likely since the reaction which proceeds via an approximation of the less bulky substituents (H,R = CH$_3$) should have a lower activation energy then that one which proceeds via the approximation of the more bulky substituents (COAr and CMe$_2$) and should so be favored.

If the *N*-methyl group is substituted by a phenyl ring (compound **3g**) possessing a higher steric demand, obviously both rotation directions are possible, and hence both merocyanines (**4g** and **4g′**) are obtained simultaneously. Since the charge delocalization in merocyanines usually leads to low barriers of (*E*)/(*Z*)-isomerization[27] an interconversion of the two merocyanines should also be considered. This is really observed for the merocyanines **4g** and **4g′** where a photoisomerization could be detected by HPLC analytics.

**SCHEME 1**



**SCHEME 2**



**Mechanism of the Photoreactions of 3 and 4.** The reaction scheme 2 of the mechanism of the studied photoreactions will be discussed. The formation of the merocyanines happens via an intermediate first excited singlet state **$^1$3***. This is in agreement with the Woodward–Hoffmann rules[24–26] predicting that such electrocyclic, conrotatory reactions proceed via the first excited singlet state. This state is very short-lived (ref 35, 5 ps). The reaction shows no influence of oxygen, even in high concentrations. This behavior can be purely seen in cyclohexane.

In acetonitrile as solvent, merocyanine **4** and spiro[cyclohexadieneindoline] triplets $^3$**3*** are formed, the latter ones in higher yield. It is obvious that the triplet generation reduces the merocyanine yield, i.e., the singlet state is a common intermediate.

Support for this partially speculative argumentation is given by very recent ultrafast fluorescence spectroscopy, exciting the spiroindolines **3** with 253 nm quanta.[35] Hence, fluorescence of the spirocompounds 3 itself ($\lambda = 350$ nm, $\tau = 5$ ps), as well as of the photoactive ring deconvolution of the polarized primary ring opened structure (red spectral range, $\tau$ between 10 ps and 1 ns, in dependence on the solvent polarity), is symbolized with X# in the center of Scheme 2.

The solvatochrome influence of the solvents on the fluorescence of X# and the polarity effects on the fluorescence life time observed in ultrafast spectroscopy[35] give information on the stability of the intermediate X#, the probability of reformation of **$^1$3*** and, therefore, also for the formation of the triplets **$^3$3***. This recent results are presented elsewhere.[35]

Analogous to the spiropyrane literature,[28,29] the photoreaction 2 of the spiro[cyclohexadieneindolines] should take place via a barrier-less photoisomerization on the energy hyper face of the first excited singlet state. The ring opening should be an electrocyclic reaction, as discussed in the foregoing paragraph. After bond clevage the free molecule ends can rotate, and under rearrangement of the methine chain a stable merocyanine structure can be generated. The photobleaching of the merocyanines **4** should proceed via the already mentioned (s)cis-isomer, but probably in a more step mechanism envolving an intermediate excited singlet **$^1$4***. The triplet **$^3$3*** seems to relax only. Decomposition products are formed probably via a competing channel to the photoreaction of **4**. The activation barrier for the thermal back-reaction 3 is very high, and therefore, the reaction rate is very slow.

**Role of Solvents and of Solid Matrices.** As experimentally demonstrated in the foregoing paragraphs, the solvents strongly influence the photoreaction of the spiro[cyclohexadieneindolines]. Except for **3c**, in cyclohexane all spirocompounds **3** rearrange to merocyanines **4.** In acetonitrile the formation of triplets **$^3$3*** dominates. In ethanol both processes take place with comparable intensity.

The merocyanines have a weak polar carbonyl function, and therefore, in the polar solvent acetonitrile after photolytic cyclohexadienyl ring opening an immediate ring reclosing (reproduction of **3**) can be imagined, reducing the yield of **4**. Furthermore, the marked triplet **$^3$3*** formation in acetonitrile should be explained by another reason, namely by the change of the relative position of the singlet and triplet energy levels by this solvent. Hence, a lowering of the **$^3$3*** level in respect to **$^1$3*** would enlarge the intersystem crossing rate and, therefore, increase the triplet yield. Because of the identity of the shape of the absorption spectra of the spiro[cyclohexadieneindoline] spectra in the different solvents used, we interpret the observed solvent dependent different triplet yields by the mentioned change in the energy level scheme.[33,34] This argumentation should be supplemented by the data of picosecond spectroscopy mentioned in the foregoing chapter.[35]

In the case of the nitro-substituted compound **3c**, the observed phenomena are completely inverted: dominating triplet formation in cyclohexane is observed, whereas in acetonitrile only merocyanine has been observed. The introduction of the nitro group within the molecule effects additional energy levels of $n\pi^*$ character. Hence, changes of solvent influenced altitude of these levels and changes in the triplet population efficiency may be understood.

In the polyethylene matrix the spiro compounds **3** are distributed, but no solvation can take place. The transients are formed within the laser pulse time resolution as in the liquid phase. A part of the species decay in some microseconds, interpreted as $^{3}\mathbf{3^*}$, the remaining absorption remains stable (assigned to merocyanines). Unfortunately, because of accumulating photolysis effects we could not record exact spectra, but the roughly taken spectra aggree with those of liquid phase. The thermal back-reaction (see Scheme 2) is very slow ($k_{3,\mathrm{therm.}} = 5.2 \times 10^{-6}\ \mathrm{s}^{-1}$, corresponding with a lifetime of 2 days) and follows first-order kinetics.

Distinctively from the polyethylene (PE) matrix, in course of heating up in liquid phase no thermal back-reaction has been observed. These obviously different findings may be explained due to the temperature dependence of the activation barriers of the deconvolution of the intermediate X# to the relaxed merocyanine **4**, and on the other hand due to the reformation of this highly ordered transition state X#, necessary for recyclization.

## Conclusions

The spiro[cyclohexadieneindolines] **3** studied in this paper show a photochromic conversion to red colored merocyanines **4** (cf. reaction 2), which is photolytically reversible and thermally retarded. Particularly in the laser flash photolysis experiments, a strong influence of the solvent nature on the reaction channel has been observed. Hence, in cyclohexane photoisomerization reaction 2 to **4** takes place, whereas in acetonitrile triplet formation reaction 6 of **3** dominates.

The quantum yields of the photoisomerization reaction 2 in cyclohexane depend on the laser wavelength and quantum yield amounts ranging from amount $\Phi_{266\mathrm{nm}} = 0.02-0.08$ and $\Phi_{315\mathrm{nm}} = 0.15$. The photoinduced back-reaction 3 has a quantum yield of $\Phi_{532\mathrm{nm}} = 0.1-0.2$. All these reactions proceed within subnanosecond times. The thermal back-reaction 3, however, is a very slow one (needs days) and could be observed only in a polyethylene matrix.

In acetonitrile, spiro[cyclohexadieneindoline] triplets $^{3}\mathbf{3^*}$ are characterized by their transient spectra, extinction coefficients, and quantum yields.

For a comparison with the known spiropyrane and spirooxazine systems, the spiro[cyclohexadieneindolines] show agreement in the following points: (i) rapid (<1 ns) formation of the merocyanines, (ii) positive solvatochromism of the merocyanines, (iii) similar quantum yields of photoisomerization, dependent on the excitation wavelength, and (iv) photochromism also in solid matrices.

The following significant distinctions of the spiro[cyclohexadieneindoline] system should be mentioned: (i) a very slow thermal backreaction from **4** to **3**, (ii) relatively high quantum yields of the photoinduced backreaction from **4** to **3**, (iii) the extinction coefficients of the merocyanines are relatively small, and (iv) no involvement of triplet states in the merocyanine formation, the process of photoisomerization proceeds only via the excited first singlet $^{1}\mathbf{3^*}$. The characteristics of the liquid state photochromism of the spiro[cyclohexadieneindolines] show decomposition of the system within some switching cycles. Their behavior in solid matrix (PE) may be more useful.

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