Pergamon

Tetrahedron: *Asymmetry* 10 (1999) 4677–4687

TETRAHEDRON: *ASYMMETRY*

# 1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline]: its thermal enantiomerization and the equilibration with its merocyanine†

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Received 6 October 1999; accepted 25 November 1999

**Abstract**

The enantiomers of the title compound, the important photochromic material (*RS*)-**1b**, have been enriched semipreparatively by liquid chromatography. As a consequence, we were able to determine the barrier of the thermal interconversion (*R*)-**1b**⇌(*S*)-**1b** via time-dependent polarimetry, amounting to $\Delta G^{\neq}$=85.9 kJ/mol at 22.0°C in $d^6$-DMSO (Table 2). The thermal equilibration of the corresponding merocyanine **2b** was monitored in $d^6$-DMSO by time-dependent $^1$H NMR, resulting in $\Delta G_1^{\neq}$=102.8 and $\Delta G_2^{\neq}$=92.0 kJ/mol at 22°C (Table 1). This means that, starting from (*RS*)-**1b**, the opened isomer **2b** is attained by a slow reaction ($\Delta G_1^{\neq}$=102.8 kJ/mol, Fig. 4). Therefore, the merocyanine **2b** cannot be identified with the intermediate required for the fast process of C($sp^3$)–O bond cleavage ($\Delta G^{\neq}$=85.9 kJ/mol) upon the above enantiomerization of (*RS*)-**1b**. Apparently, these two thermal isomerizations (Fig. 4) are independent of each other. The structure of the unknown intermediate of the interconversion (*R*)-**1b**⇌(*S*)-**1b** must therefore differ from the known one of merocyanine **2b**. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Many derivatives of 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] **1a** (Scheme 1) are of interest because of their photochromism.[2] The parent molecule **1a** can be transformed photochemically into the merocyanine **2a** which isomerizes thermally with a very high rate back to **1a**.[3] Therefore, unsubstituted **1a** has no practical value with respect to photochromism. This situation changes upon the introduction of a nitro group into the 6-position: the title compound **1b** has probably been cited in the literature most often among all photochromic materials. The corresponding merocyanine **2b** is obtained by irradiation and reverts to the equilibrium mixture (Scheme 1) consisting predominantly of the spiro

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† Chiral 2*H*-pyrans, Part 10. Part 9: Ref. 1.

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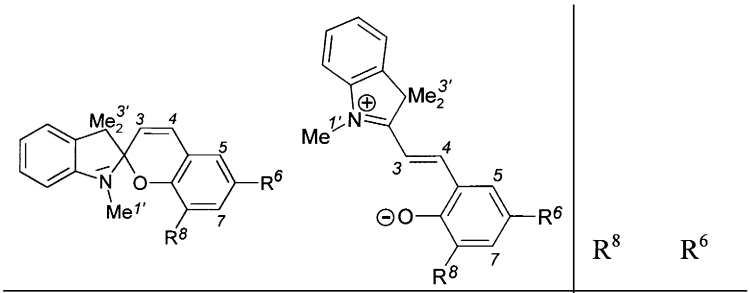
*PII:* S0957-4166(99)00538-8

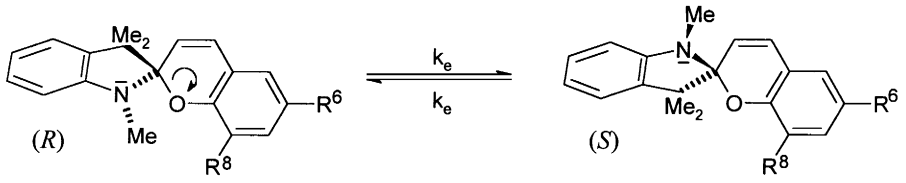
compound **1b**. The rate of isomerization of **2b** is much lower than that of the **2a**→**1a** reversal.[3–8] Although analogs have now been found which are more stable to light than **1b**, the latter has been significant for the development of practical applications of photochromism and continues to be significant for basic research,[2,9,10] e.g. with respect to **1b** chemically bonded to another molecule. A further nitro group in the 8-position again changes the properties: only a very small amount of the spiro compound **1c** appears in the thermal equilibrium[11,12] (Scheme 1) in dipolar aprotic solvents, which means that the observed photochromism is a reversible one with limited applicability.




| | | | $R^8$ | $R^6$ |
|---|---|---|---|---|
| (*RS*)-**1a** | ⇌ | **2a** | H | H |
| (*RS*)-**1b** | ⇌ | **2b** | H | $NO_2$ |
| (*RS*)-**1c** | ⇌ | **2c** | $NO_2$ | $NO_2$ |

Scheme 1. Thermal equilibria between spiro compounds and merocyanines. The positional numbers given in the formula of the merocyanines **2** do not correspond to their systematic names but to the ones of the spiro compounds **1**

In addition to the above transformations between constitutional isomers (e.g. Scheme 1), recently a second thermal process was investigated: the enantiomerization,[13] i.e. the interconversion of the enantiomers (*R*) and (*S*) of the spiro compounds **1** with the rate constant $k_e$ according to Scheme 2. The methods used in this case were temperature-dependence measurements of $^1$H NMR signals[13] of suitable diastereotopic groups or time-dependent polarimetry at constant temperature.[13] The latter technique is much more generally applicable; however, it requires an enrichment of one of the enantiomers which was accomplished recently by liquid chromatography[13–15] on nonracemic sorbents. In the case of (*RS*)-**1c** (Scheme 2), $^1$H NMR showed the interconversion of the enantiomers to be very fast.[11,16,17] No information about the enantiomerization of (*RS*)-**1a** was available; our corresponding results[12] will be briefly mentioned below. (*RS*)-**1b** was investigated[16,18] via the coalescence of $^1$H NMR signals at 138°C (80 MHz; d$^6$-DMSO) and at 205°C (no transmitter frequency given; biphenyl). However, our intention was to compare the rate of the (*R*)-**1b**⇌(*S*)-**1b** process (Scheme 2) with that of the **2b**→(*RS*)-**1b** isomerization (Scheme 1) which cannot be monitored at such high temperatures. Therefore, we needed to enrich the unknown enantiomers of **1b** and to measure their interconversion at lower temperatures, e.g. by time-dependence polarimetry.




| | $R^8$ | $R^6$ |
|---|---|---|
| **1a** | H | H |
| **1b** | H | $NO_2$ |
| **1c** | $NO_2$ | $NO_2$ |

Scheme 2. Thermal enantiomerizations of spiro compounds

## 2. Equilibration of the merocyanine 2b with the spiro compound (*RS*)-1b

The preparation[19–23] of the merocyanine results in a mixture of **2b** and **1b**, in our case in a ratio of 75:25, estimated from $^1$H NMR in $CD_2Cl_2$ at −90°C. Apparently, the pure solid **2b** is not known. The stereoisomer depicted is assumed[17,24–26] to be the preferred one in solution and is consistent with our $^1$H NMR results. Formula **2b** is one of several resonance structures.

Rates of the thermal **2b**→**1b** transformation (Scheme 1) have been measured several times[3–8] by monitoring the UV band around 560 nm after irradiation of the spiro compound **1b**, without isolation of **2b**. In order to have conditions comparable with the ones of our measurement of enantiomerization of (*R*)- and (*S*)-**1b** (see Section 4 below), we had to monitor the **2b**→**1b** isomerization in the same solvent at the same temperature. For this purpose, we chose $^1$H NMR with its narrow linewidths, a method which can compare the decrease of signals of **2b** quantitatively with the increase of signals of **1b** (Fig. 1). Isolation and characterization of enriched merocyanine **2b** (Fig. 1; 0 min) offers a more reliable basis for kinetics than use of a less characterized solution. The presence of a very small amount of **2b** in the equilibrium mixtures has been stated.[3,5,26] No signals of the aromatic protons of **2b** are visible at lower concentration (e.g. Fig. 1; ~24 h). The solution of the spiro compound **1b** in d$^6$-DMSO is slightly yellow for a very short time, whereas the equilibrated one looks violet. At a concentration of 0.09 mol/l, an equilibrated solution of **1b** in d$^6$-DMSO showed signals of 1.2% of **2b** (cf. Experimental), in addition to the absorptions of **1b**. The $CMe_2$ peaks at $\delta$=1.10 and 1.20 for **1b** and the $CMe_2$ signal at $\delta$=1.73 for **2b** were chosen to determine the equilibrium constant K=[**2b**]:[**1b**]=0.012 and the free enthalpy difference $\Delta G$=+10.8 kJ/mol at 22.1 °C (Table 1). The equilibrium was attained from both sides. The experimental data (cf. Fig. 1) were treated as a reversible first-order reaction[40] with no intermediates, resulting in $\Delta G_1^{\neq}$=102.8 and $\Delta G_2^{\neq}$=92.0 kJ/mol. Our data are in approximate agreement with the ones calculated from literature results[3–8] which were obtained by UV photometry in solvents other than d$^6$-DMSO.

## 3. Preparative separation and characterization of the enantiomers of the spiro compound (*RS*)-1b

The enantiomers were enriched semipreparatively by liquid chromatography (LC) in heptane:2-propanol, 9:1, on tris(3,5-dimethylphenylcarbamoyl)cellulose/$SiO_2$ at 3 bar. The samples obtained were characterized by analytical LC (Fig. 2) under conditions similar to the ones given above. A novel, highly sensitive UV–circular dichroism (CD) detector[27–30] was used for LC measurements. The enantiomeric purity (P) obtained[28,31–33] served to correct the experimental CD spectra for P=100% (Fig. 3). In

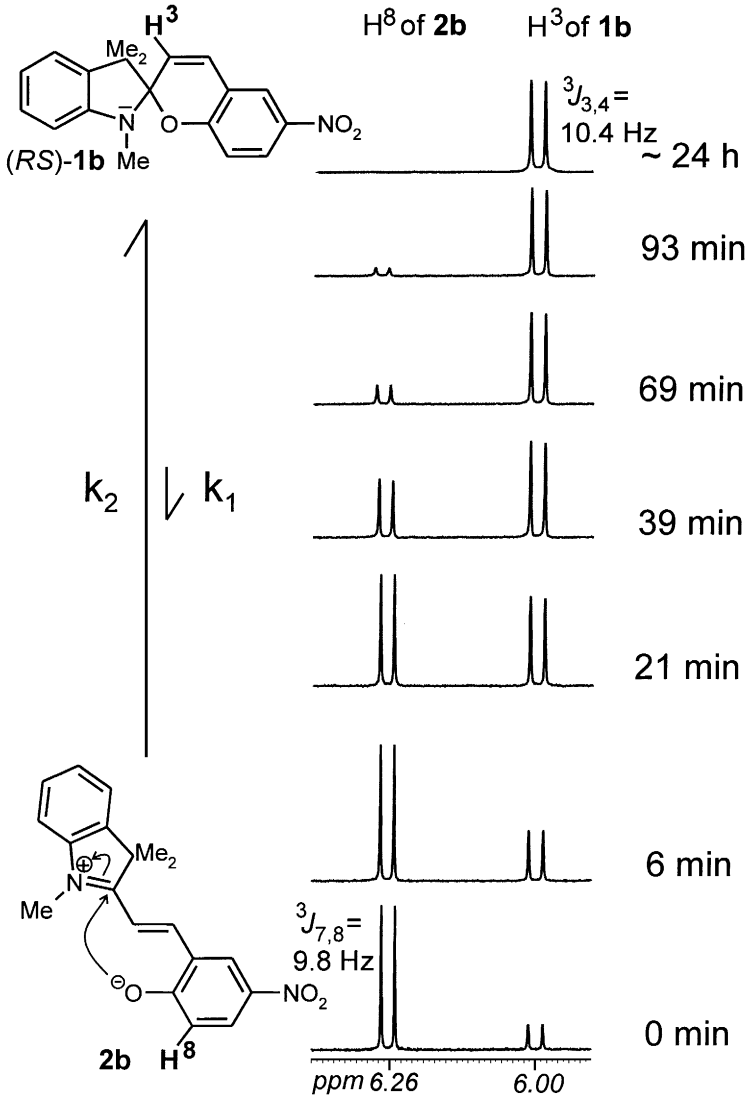


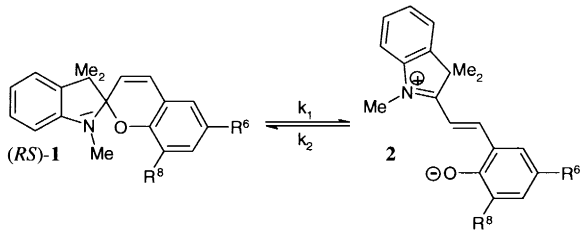

Fig. 1. $^1$H NMR of protons H-8 of **2b** and H-3 of (*RS*)-**1b** in d$^6$-DMSO at 400 MHz. Equilibration of the merocyanine **2b** with the spiro compound (*RS*)-**1b** at 22.1°C in the absence of light. Times of measurement of enriched **2b** are given. See text for the presence of **2b** after the end of the reaction

agreement with the CD spectra of other 6-substituted [2*H*-1-benzopyran-2,2′-indolines][15,34] and with the 6-unsubstituted **1a**,[12] the enantiomers of **1b** show an intense band around 250 nm and a weaker one around 290 nm with unequal signs.

## 4. Enantiomerization of the spiro compounds (*R*)- and (*S*)-1b

At 22.0°C, $(+)_{436}$- and $(-)_{436}$-**1b** racemize in d$^6$-DMSO. The plot of ln α versus t (α being the polarimetric angle of rotation at 436 nm) is linear during four half-life periods. We treated our kinetic data as a reversible first-order reaction.[35] For the enantiomerization via an unknown intermediate (or

Table 1
Equilibration between spiro compounds (*RS*)-**1** and merocyanines **2** at 22°C, measured by time-dependent UV absorptions[3] for (*RS*)-**1a** **2a** and by time-dependent $^1$H NMR intensities for the other compounds




| | | $R^8$ | $R^6$ | Solvent | $k_1$ $s^{-1}$ | $\Delta G_1^{\neq}$ kJ/mol | $k_2$ $s^{-1}$ | $\Delta G_2^{\neq}$ kJ/mol | K[a] | $\Delta G^b$ kJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| (*RS*)-**1a** | **2a** | H | H | 1- and 2-propanol[c] | $7.5\cdot10^{-6}$ | 101.2 | 0.18 | 76.5 | $0.42\cdot10^{-4}$ | +24.7 |
| (*RS*)-**1b** | **2b** | H | $NO_2$ | $d^6$-DMSO | $3.9\cdot10^{-6}$ | 102.8 ± 0.9 | $320\cdot10^{-6}$ | 92.0 ± 0.7 | $120\cdot10^{-4}$ | +10.8 ± 0.2 |
| (*RS*)-**1c** | **2c** | $NO_2$ | $NO_2$ | $d^7$-DMF | $7.4\cdot10^{-6}$ | 101.3 ± 0.7 | $0.14\cdot10^{-6}$ | 111 ± 1[11] | 51 | -9.6 ± 0.4 |

[a] Equilibrium constant K = [**2**] : [(*RS*)-**1**].
[b] Calculated by ΔG = - RTlnK.
[c] The proportion of the two alcohols is not given in ref. 3.

unknown intermediates), a statistical factor[13] of 2 was applied, i.e. $k=2k_e$. We obtained $t_{0.5}$=2.9 min, $k=3.94\cdot10^{-3}$ $s^{-1}$ and the $\Delta G^{\neq}$ value in Table 2 for the enantiomerization‡ of the widely used (*RS*)-**1b**.

The polarimeter cell was protected from external light. Under our usual experimental conditions, a significant photochemical contribution of the light of the polarimeter lamp to the decrease of the rotation angle had been excluded earlier.[13] A similar experiment for $(-)_{436}$-**1b** in heptane:2-propanol, 9:1, at 436 nm with the usual continuous irradiation resulted in $\Delta G^{\neq}$=97.1±0.3 kJ/mol at 34.1°C. The reading of the transmission through the cell was strongly reduced by a shutter and the angle was measured periodically in 20 second intervals. This reduced irradiation resulted in $\Delta G^{\neq}$=97.2±0.3 kJ/mol at 33.8°C. The spiro compound **1b** shows very weak absorption at λ=405 nm but no significant ones at 436 and 546 nm (cf. Fig. 3). Racemizations at these wavelengths with the usual continuous irradiation did not show any dependence upon λ which might have occurred by eventual photoreactions. From the above experiments, we conclude that the decrease of the rotation angle is effected thermally.

‡ In the above section on equilibration of the merocyanine **2b** the very small amount of **2b** in the equilibrium with **1b** has been mentioned. This means that the spiro compounds (*R*)- and (*S*)-**1b** react mainly by enantiomerization but, in addition, do so by formation of the merocyanine **2b**, with a very small probability. This formation of **2b** contributes to the decrease of the angle of rotation, but this decrease is mainly caused by the interconversion of (*R*)- and (*S*)-**1b**. Our calculations,[36] including equilibrium constants between merocyanines and spiro compounds, showed that, for all molecules in Table 2, the contributions of the formation of merocyanines to the decrease of the angles of rotation are within the experimental errors. Therefore, the data given in Table 2 represent the true enantiomerization processes of the spiro compounds via an intermediate.

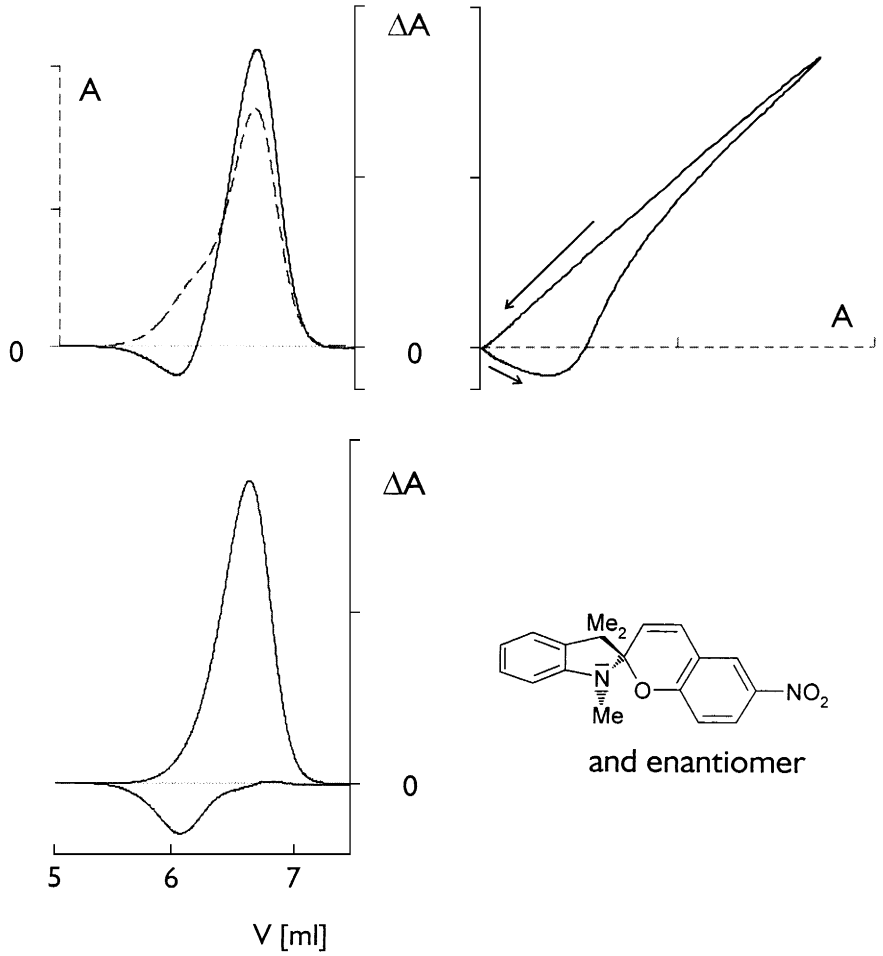



Fig. 2. Liquid chromatography of ~4 μg of enriched $(+)_{436}$-**1b** in heptane:2-propanol, 9:1, on tris(3,5-dimethylphenylcarbamoyl)cellulose/$SiO_2$. Absorbance A and differential absorbance ΔA at 250 nm. Top left: experimental chromatograms A(V) and ΔA(V). Top right: experimental ΔA(A) diagram, resulting in a slope ΔA/A. Bottom: computer deconvolution[28] of the experimental chromatogram ΔA(V) by using the ΔA/A value obtained. Electronic integration results in the retention factors k′=0.8 and 1.0 as well as an enantiomeric purity of 71±2%, determined in spite of the peak overlap

## 5. Discussion of the two different isomerizations investigated

The cleavage of the C($sp^3$)–O bond of the spiro compound is the essential prerequisite of both the enantiomerization and the formation of the merocyanine(s). We have represented the transition states of the enantiomerization by the structures[13,37] (*R*)- and (*S*)-(*Z*)-**TS** in Fig. 4, right side, on the basis of ab-initio calculations[38] and several other theoretical approaches cited in a review.[13] Very little is known about the central area of the reaction profile (Fig. 4, right side). At least one intermediate, lower in energy than (*R*)- and (*S*)-(*Z*)-**TS**, is postulated for symmetry reasons. With reference to the necessary calculations concerning this intermediate (or these intermediates), we prefer to postpone the discussion of detailed structure(s).

The merocyanine **2b** cannot be identified with this intermediate (or these intermediates) because **2b** is attained by a slow isomerization of (*RS*)-**1b** ($\Delta G_1^{\neq}$=102.8 kJ/mol, Table 1; Fig. 4, left side) which apparently is kinetically independent of the fast enantiomerization of (*RS*)-**1b** ($\Delta G^{\neq}$=85.9 kJ/mol, Table

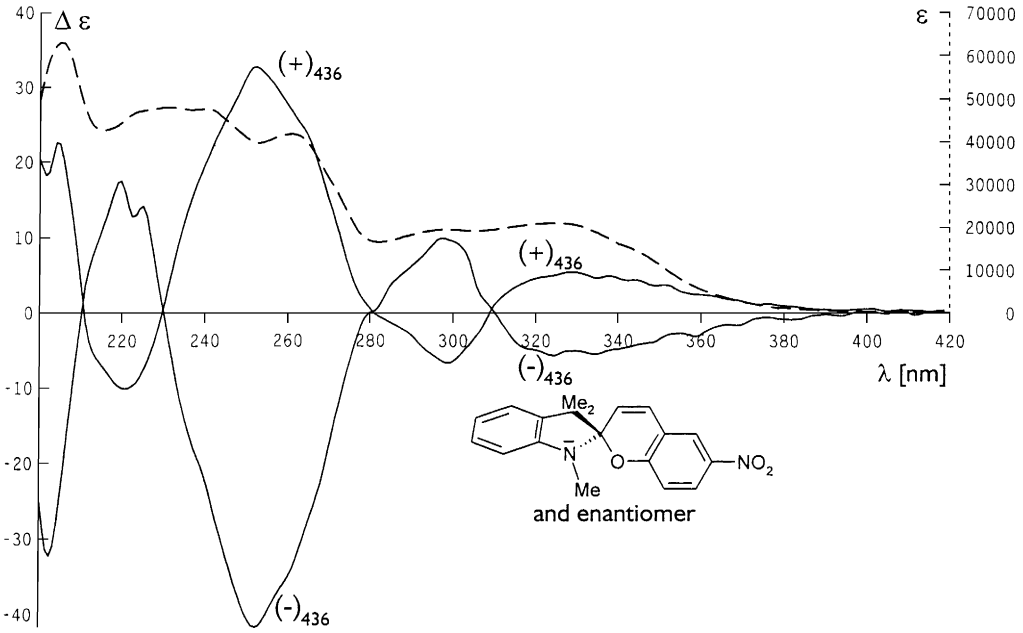



Fig. 3. Circular dichrograms $\Delta\varepsilon(\lambda)$ of $(+)_{436}$- and $(-)_{436}$-**1b** and ultraviolet spectrum $\varepsilon(\lambda)$ of (±)-**1b** in heptane:2-propanol, 9:1. $\Delta\varepsilon$ and $\varepsilon$ in l mol$^{-1}$ cm$^{-1}$, corrected for an enantiomeric purity of 100%. The signs $(+)_{436}$ and $(-)_{436}$ refer to polarimetry

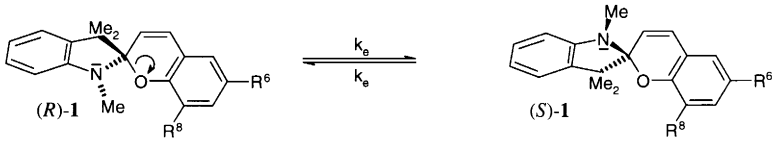
2), a fact which we had already mentioned in a review article.[13] The unknown intermediate(s) of the latter process must therefore have a structure different from **2b**. The same conclusion can be drawn for the analogs (*RS*)-**1c**/**2c**, bearing two nitro groups,[11,17] as well as for (*RS*)-**1a**/**2a**, bearing no nitro group.[3,12] The corresponding $\Delta G^{\neq}$-values have been included in Tables 1 and 2.

The barriers $\Delta G_1^{\neq}$ in Table 1 do not depend significantly upon the substituent pattern. Apparently, the ground states of the merocyanines **2** are stabilized by nitro groups (ΔG-values in Table 1). Therefore, $\Delta G_2^{\neq}$ increases appreciably in the order **2a**→**2b**→**2c** reflecting the different thermodynamic stabilities of the opened isomers **2**. It appears that the experimental overall barriers $\Delta G_1^{\neq}$, e.g. 102.8 kJ/mol for (*RS*)-**1b**→**2b** (Fig. 4, left side), comprise the cleavage process for the C($sp^3$)–O bond in **1** and, in addition, subsequent *E*/*Z*-isomerizations around the partial double bonds, required for attaining the merocyanine **2**.

The barrier between (*RS*)-**1b** and **2b** has been symbolized by a simple curve in Fig. 4, left side, although this interconversion should consist of several steps. This assumption has been confirmed by calculations of Abe, Nakao, Horii, Okada and Irie.[24] A corresponding calculation[39] for the interconversion of (*R*)- and (*S*)-**1b** could contribute to answer the question of the structure of the unknown intermediate(s). In addition, calculations may solve another remaining problem: at which molecular state, e.g. at which point of the reaction coordinates (horizontal lines) in both parts of Fig. 4 do the two isomerizations, e.g. (*R*)-**1**→**2b** and (*R*)-**1**→(*S*)-**1b**, start to use different pathways?

Further work should show whether the different isomerizations described in Fig. 4 are a general phenomenon of 2-donorsubstituted 2*H*-1-benzopyrans and also of the corresponding benzo-1,4-oxazines.

Table 2
Enantiomerization of spiro compounds (*R*)- and (*S*)-**1**, measured by time-dependent polarimetric rotation angles and, for **1c,** by temperature-dependent $^1$H NMR spectra[11]




| | $R^8$ | $R^6$ | Solvent | T °C | $t_{0.5}$[a] | $k_e$[b] $s^{-1}$ | k[c] $s^{-1}$ | $\Delta G^{\neq c}$ kJ/mol |
|---|---|---|---|---|---|---|---|---|
| **1a** | H | H | 1- and 2-propanol[d] | 22.1 | 5.2 h | $1.84\cdot10^{-5}$ | $3.68\cdot10^{-5}$ | 97.4 ± 0.3[12] |
| **1b** | H | $NO_2$ | $d^6$-DMSO | 22.0 | 2.9 min | $197\cdot10^{-5}$ | $394\cdot10^{-5}$ | 85.9 ± 0.3 |
| **1c** | $NO_2$ | $NO_2$ | $d^7$-DMF | 23 | $4\cdot10^{-3}$ s | 78 | 156 | 60.1 ± 0.5[11] |

[a] Experimental half-life for **1a** and **1b**. $t_{0.5}$ for **1c** is calculated from the experimental $k_e$ value.[11]
[b] Rate constant for the enantiomerization without an intermediate; see text.
[c] Rate constant and free enthalpy of activation for the enantiomerization via an intermediate; see text.
[d] We used a 1:1 mixture of propanols. Their proportion is not given in ref. 3.

## 6. Experimental

### *6.1. General methods*

Melting points were determined on a Büchi SMP-530 apparatus and are not corrected. $^1$H NMR spectra were recorded on a Bruker ARX-400 (400 MHz) spectrometer using tetramethylsilane ($\delta$=0 ppm) as standard. The temperature of 22°C was determined by a sample of methanol. Compound **2b** was equilibrated in the NMR probe in $d^6$-DMSO in the absence of light (Fig. 1). Our unpublished program DIASTER was used for evaluation of the data on the basis of a reversible first-order reaction.[40] All $^1$H NMR analyses included intensities; no decomposition products were detected. IR spectra were measured on a Beckman Acculab 1, the mass spectra on a Varian MAT 331A (70 eV) spectrometer. A Hitachi U 2000 instrument was used for UV spectroscopy. CD spectra were recorded on a Jasco J-710 dichrograph. A mixture of heptane:2-propanol, 9:1, was used as solvent because the barrier to racemization is strongly solvent dependent ($d^6$-DMSO, $\Delta G^{\neq}$=85.9 kJ/mol at 22.0°C, $t_{0.5}$=3 min; heptane:2-propanol, 9:1, $\Delta G^{\neq}$=97.2±0.3 kJ/mol at 34.1°C, $t_{0.5}$=74 min). Differential absorption coefficients $\Delta\varepsilon$ of the maxima were given after correction for enantiomeric purities (P) of 100%. Our computer program CDUV F. WINDOWS served for plotting and smoothing the spectra (e.g. Fig. 3). The enrichments and analyses of enantiomers were performed[37,41] by liquid chromatography (LC) on a tris(3,5-dimethylphenylcarbamoyl)cellulose/$SiO_2$ (Chiralcel OD) analytical column, length 25 cm, diameter 4.6 mm. The novel Jasco CD-995 instrument[42] was used for combined UV/CD detection of LC and for determination[28] of P. Our computer program SEPP F. WINDOWS served to record the chromatograms and to process the LC data (e.g. Fig. 2).[28] For the thermal racemizations of the enriched enantiomers, the cell of a Perkin–Elmer 241 polarimeter was thermostated, e.g. to 22.0°C, and the decrease of the angle of rotation, e.g. at 436 nm, was monitored. On this occasion, $(+)_{436}$- and $(-)_{436}$-**1b** were distinguished, (+) and (−) standing for the signs in polarimetry, [+] and [−] for the signs in CD. The contents of a fresh phial of $d^6$-DMSO (99.8%; Deutero GmbH,

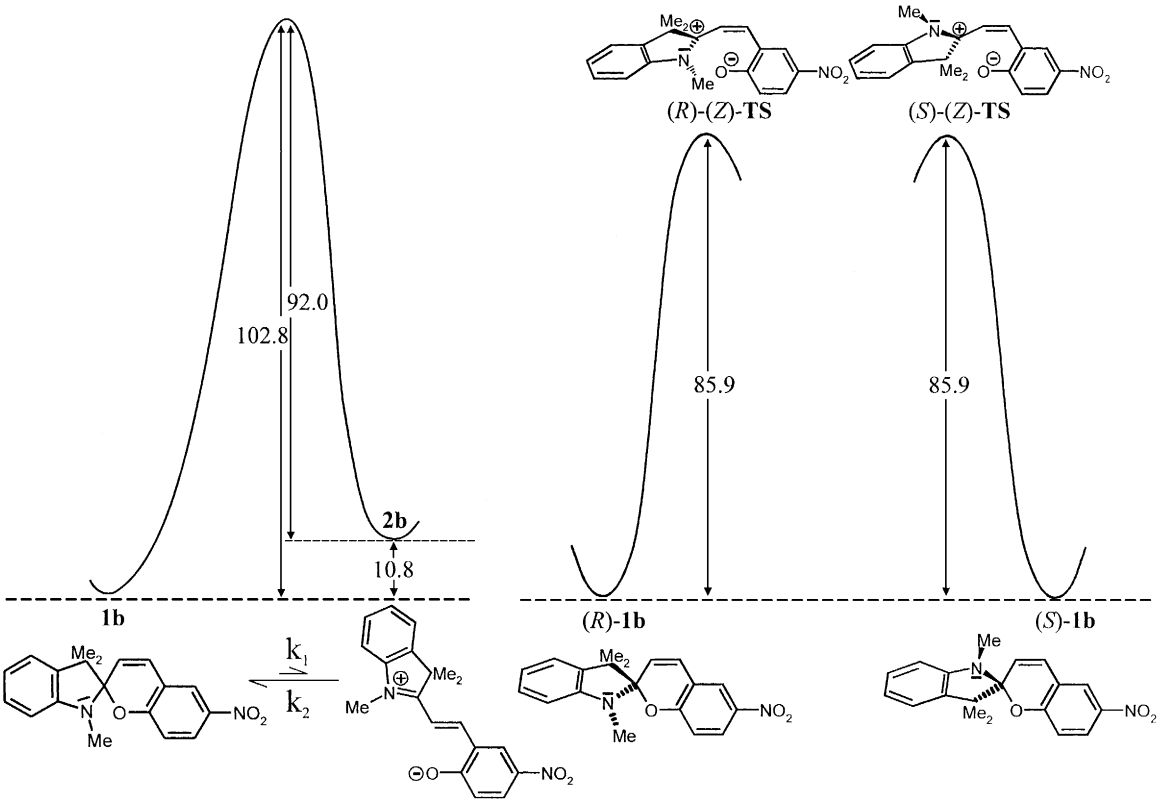



Fig. 4. Schemes of free enthalpy changes (kJ/mol) in d$^6$-DMSO at 22°C. Left side: equilibration of spiro compound **1b** and merocyanine **2b**; a simple overall curve has been drawn which does not show individual reaction steps. Right side: enantiomerization of spiro compounds (*R*)- and (*S*)-**1b** (see Section 4). (*R*)- and (*S*)-(*Z*)-**TS** are the transition states for the cleavage process of the C($sp^3$)–O bonds. These structures are symbolized by only one of the possible resonance formulae

Kastellaun, Germany) was used as a solvent for polarimetric and $^1$H NMR kinetics. The racemizations were measured during two to three half-life periods. The data were treated by first-order kinetics and corrected for an intermediate, as described in Section 4 on enantiomerization of the spiro compounds. The results (Table 2) for the two enantiomers agreed within error limits.

### *6.2. (±)-6-Nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]* ***1b***[43]

A solution of 0.54 g (3.23 mmol) of 2-hydroxy-5-nitrobenzaldehyde and 0.52 g (3.00 mmol, d=0.98, 0.53 ml) of 2-methylene-1,3,3-trimethylindoline in 10.0 ml of ethanol (99%) was heated at reflux for 2 h. Upon cooling, yellow crystals precipitated from the deep coloured reaction mixture and were filtered off. Recrystallization from ethanol afforded (±)-**1b** as yellow needles (0.75 g, 2.33 mmol, 78%), mp 172–174°C. UV, see Fig. 3. IR (KBr) cm$^{-1}$: 2970, 1650, 945; $^1$H NMR (d$^6$-DMSO): $\delta$=1.12/1.22 (3H/3H, s/s, C($CH_3$)$_2$), 2.68 (3H, s, $NCH_3$), 6.00 (1H, d, $^3J$=10.4 Hz, H-3), 6.62 (1H, d, $^3J$=7.3 Hz, H-7′), 6.81 (1H, m, H-5′), 6.89 (1H, d, $^3J$=8.9 Hz, H-8), 7.14 (2H, m, H-4′ and H-6′), 7.23 (1H, d, $^3J$=10.4, H-4), 8.00 (1H, dd, $^3J$=8.9 Hz, $^4J$=2.8 Hz, H-7), 8.22 (1H, d, $^4J$=2.8 Hz, H-5). MS, *m/z* 322 ($M^+$), 159. Anal. calcd for $C_{19}H_{18}N_2O_3$ (322.4): C, 70.79; H, 5.63; N, 8.69. Found: C, 70.76; H, 5.62; N, 8.69.

### 6.3. $(+)_{436}$-6-Nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] **1b**

Semipreparative enrichment was performed by LC on Chiralcel OD, heptane:2-propanol, 9:1, flow rate 0.5 ml/min, 3 bar. A total amount of 10 mg of (±)-**1b** was injected in several portions, yielding two fractions. The one at k′=1.0 represented a pale yellow solid, mp 175–176°C. P=71±2% (Fig. 2). CD (heptane:2-propanol, 9:1, 21°C) $\lambda_{max}$/nm ($\Delta\varepsilon$): 220 (−10), 253 (+33), 298 (−6.6), ~332 (+4.7).

### 6.4. $(-)_{436}$-6-Nitro-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] **1b**

The semipreparative enrichment described for $(+)_{436}$-**1b** yielded a fraction at k′=0.8, representing a pale yellow solid, mp 172–174°C. P=57±2%. CD (heptane:2-propanol, 9:1, 21°C) $\lambda_{max}$/nm ($\Delta\varepsilon$): 220 (+17), 253 (−41), 298 (+9.6), ~332 (−5.7).

### 6.5. 4-Nitro-2-[(E)-2′-(1′′,3′′,3′′-trimethyl-3H′′′-2′′-indoliumyl)-1′-ethenyl]-1-phenolate **2b**[19]

Compound (±)-**1b** (0.35 g, 1.09 mmol) in 100 ml of *n*-hexane was irradiated with UV-light (30 min, Heraeus TQ 150). The pale yellow solution turned blue and a brownish solid precipitated which was filtered off and vacuum dried. 0.21 g (0.65 mmol, 59%) of a mixture of **2b** and (±)-**1b** was obtained as a red brown powder, mp 134–165°C (lit.[19] 150–175°C). IR (KBr) $cm^{-1}$: 2970, 1617; $^1$H NMR ($d^6$-DMSO, 75% **2b**, 25% **1b**): The positional numbers in the following assignments do not correspond to the above systematic name of **2b** but to the numbers given in its structural formula in Scheme 1. $\delta$=1.74 (6H, s, $C(CH_3)_2$), 3.85 (3H, s, N–$CH_3$), 6.26 (1H, d, $^3J$=9.8 Hz, H-8), 7.46/7.53 (1H/1H, ddd, $^3J$=7.9 Hz, $^3J$=7.5 Hz, $^4J$=2.6 Hz, H-5′ and H-6′), 7.70/7.76 (1H/1H, d, $^3J$=7.9 Hz/$^3J$=7.5 Hz, H-4′ and H-7′), 7.81 (1H, dd, $^3J$=9.8 Hz, $^4J$=3.1 Hz, H-7), 8.33–8.45 (2H, m, H-3 and H-4), 8.68 (1H, d, $^4J$=3.1 Hz, H-5). MS, *m/z* 323.3 ($MH^+$). Anal. calcd for $C_{19}H_{18}N_2O_3$ (322.4): C, 70.79; H, 5.63; N, 8.69. Found: C, 70.95; H, 5.66; N, 8.71.

## Acknowledgements

We are grateful to Dr. T. Burgemeister, Dipl.-Chem. M. Hofweber and Mr. F. Kastner for careful spectral measurements. Dr. Y. Abe, Sakai, Japan and Dr. M. Frieser, Regensburg, contributed considerably to the discussion of mechanisms. Mr. R. Würdinger, Jasco Deutschland GmbH, Groß-Umstadt, kindly gave access to the CD-995 detector. Support of the present work by Fonds der Chemischen Industrie is acknowledged.

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