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A tolan substituted optically active spiropyran

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Abstract

A substituted optically active spiropyran with a tolan group in the 6′-position is described. Both the parent spiropyran and its derivative were separated by chiral HPLC and characterized by CD spectroscopy. There is a 'diastereomeric switch' at temperatures below −30°C , but the compound does not show liquid crystalline properties.

1. Introduction

The development of technologies for the non-destructive readout of photochromic bistable molecules — one of the requirements for their use as rewritable optical memory devices[1] — continues to command attention in materials research. One possible approach is the use of optically active molecules with switchable optical activity, so-called chiroptical switches,[2] another is the use of achiral photochromic compounds to control the pitch or phase of a liquid crystal.[3] Optically active molecules have also been used to switch between liquid crystalline phases.[2] Light of two different wavelengths is used to write and erase the information, whereas the information is read with light of a wavelength that does not affect the organic compound photochemically. Recently, we demonstrated that the optically active spiroindolinopyran **1** is capable of functioning as a chiroptical molecular switch (Scheme 1). The UV/vis induced photochromic switch between the closed spiro and the open merocyanine form was followed by CD (circular dichroism) spectroscopy. In addition, we found a second switch probably based on the temperature-dependent inversion of the diastereomeric composition ('diastereomeric switch'). The information is photochemically permanent but can be erased simply by heating. The disadvantage for this switching is the limitation to temperatures below −40°C.

The combination of photochromic and liquid crystalline properties in one compound is of great technical interest, e.g. in display technology.[4] The synthesis of a copolymer with spiroindolinopyran and mesogenic side groups gave a light switchable liquid crystal, which, however, operated only

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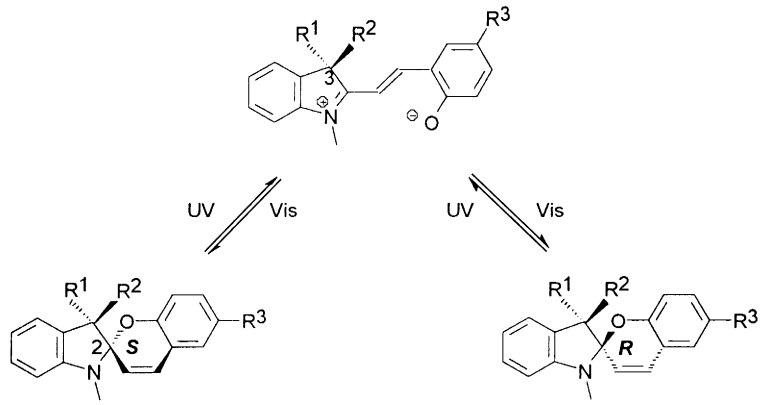


1 $R^1 = CH_3$; $R^2 = C_3H_7$; $R^3 = NO_2$
2 $R^1 = C_3H_7$; $R^2 = CH_3$; $R^3 = C{\equiv}CPh$

Scheme 1.

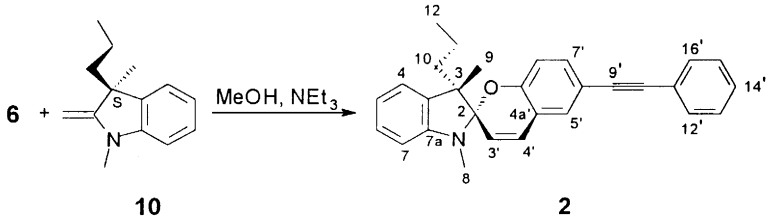
below −10°C or required temperature change.[4,5] Attempts to attach mesogenic groups directly to a spiroindolinopyran resulted in a material which exhibited some features of liquid crystals but did not show photochromism ('quasi-liquid crystals').[3,6]

In the following we describe the synthesis of **2**, a compound with a mesogenic group attached to the benzopyran moiety of the spiropyran, as a first attempt to raise the temperature of the diastereomeric switch to ambient temperature and to improve the photostability of the spiropyran. Also, we describe the preparation and the chiroptical properties of the diastereomers resulting from the ring closure of the optically active spiropyrans **1** and **2**.

2. Results and discussion

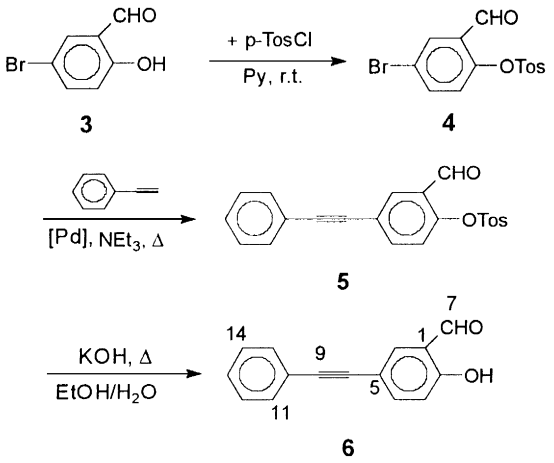
*2.1. Synthesis of the optically active spiropyran derivative **2***

The tolan group is a simple but convenient mesogenic group. As R^3 in **2**, the phenylethynyl moiety becomes part of the benzopyran chromophore of the spiropyran molecule, with possible steric and electronic effects. The key intermediate for the synthesis of **2** is the tolanaldehyde **6**, which, after condensation with the suitable Fischer base, should give the desired product (Scheme 2). Compound **6** was obtained by starting from the salicylaldehyde **3**, which was tosylated and then reacted with phenylethyne in triethylamine in the presence of CuI and $PdCl_2(PPh_3)_2$ (Hagihara variant[7] of the Heck reaction[8]) to give **5** in 86% yield (Scheme 3). Detosylation was effected in low yield (32%) with potassium hydroxide in boiling aqueous ethanol.



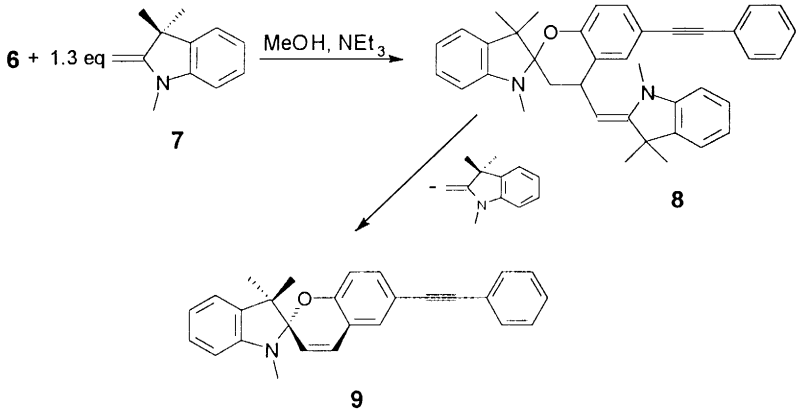
10 **2**

Scheme 2.



Scheme 3.

To test the feasability of the condensation reaction **6** was reacted with the commercially available achiral Fischer base **7**. In order to achieve complete conversion, an excess of the base was employed, but the result was, not unexpectedly,[4] the bicondensation product **8** (identified by ^{1}H NMR and mass spectroscopy). The formation of this product is favored when substituents render the pyran electron-rich. However, the second Fischer base could be cleaved off and removed by distillation at 150°C under reduced pressure to yield the simple spiropyran **9** (Scheme 4).



Scheme 4.

Based on this result the successful synthesis of the chiral spiropyran **2** was effected in 76% yield by condensing a 1.37-fold molar excess of the tolanaldehyde **6** with the chiral Fischer base **10**.

2.2. HPLC analysis and spectroscopic (CD) assignments

In the closed spiro form **2**, as with the parent compound **1**, there is a mixture of diastereomers: with the configuration at C(3) of the starting Fischer base known to be *S* (*R* in the case of **1**) the new stereogenic center C(2) can be either *R* or *S*. These diastereomers equilibrate via the open merocyanine form of the spiropyran, which is accessible photochemically. HPLC separation was achieved using a Chiralpak OT+ column. Irradiation with visible light before separation effected maximum conversion into the closed spiro form. On the chiral column, rather than two peaks being detected, two pairs of peaks, two intense ones and two less intense, were observed. The ee of the chiral Fischer base **10** used for the synthesis of **1**

and **2** was 80%,[9] and these four peaks represent all possible stereoisomers. In *n*-hexane:*i*-propanol, 9:1, the diastereomeric equilibrium at 5°C is close to unity as determined from the relative areas of the two intense peaks. This equilibrium is strongly solvent dependent: in $CDCl_3$ it is 1:1.6 for **1** and 1:1.7 for **2** at 24°C determined by ^1H NMR. The two fractions corresponding to the two intense peaks were collected and the CD spectra obtained. Fig. 1 shows the spectra of **1**, Fig. 2 those of **2**. The spectra are very similar, displaying a prominent band at 255 nm and a second one of lower intensity and opposite sign at 300 nm. Since the fractions shown in Figs. 1 and 2 are diastereomers rather than enantiomers, their spectra are not mirror-images, although they very nearly are. The contribution of the different alkyl groups at the stereogenic center C(3) to the spectra is very small, as was tested for the chiral Fischer bases **10** which show Cotton effects $\Delta\varepsilon$ of ± 1. On the basis of NOE data, the configuration of **1** has been determined to be (2*R*,3*R*) for the first fraction with the positive CD at 255 nm and (2*S*,3*R*) for the second fraction.[9] In accord with these data, the first eluting fraction of **2** has a negative CD at 255 nm and its configuration should be (2*S*,3*S*) while that of the second fraction is positive and the configuration (2*R*,3*S*).

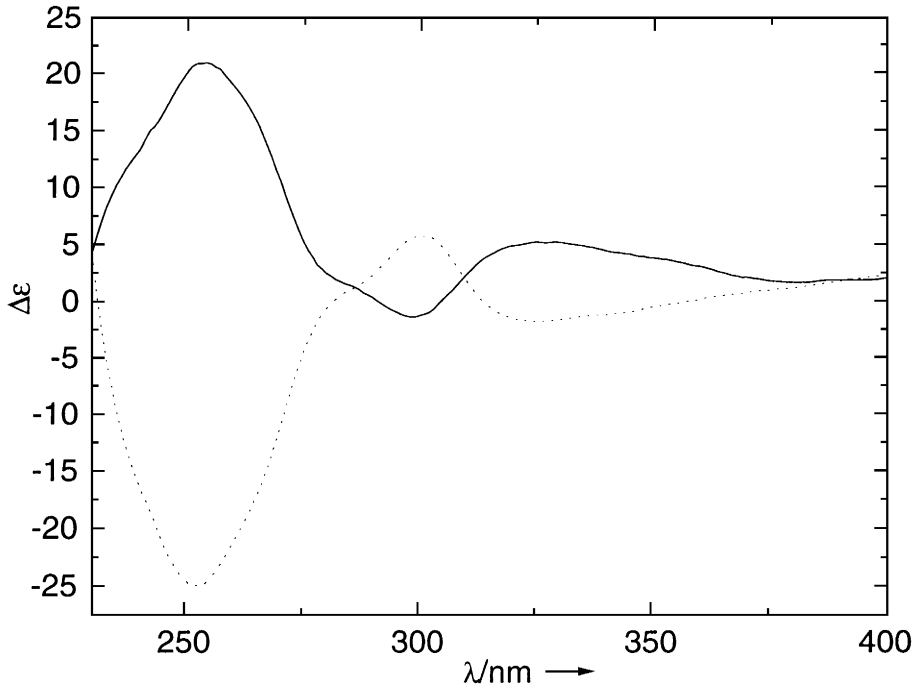


Fig. 1. CD spectra of HPLC-separated diastereomers of the optically active spiropyran **1** in hexane:2-propanol, 9:1, at 5°C; (—): (2*R*,3*R*)-**1**, $c=3.07\times10^{-5}$ M; (- - -): (2*S*,3*R*)-**1**, $c=3.3\times10^{-5}$ M

With the CD spectra of the diastereomers with 100% de known, the composition of any diastereomeric mixture resulting from photochemical interconversion can be calculated if the ee is 100%, and contamination by the open form does not affect the CD spectra too much.

2.3. Photochemical equilibration

Irradiation of both fractions with UV produces the open merocyanine form in which the stereogenic spirocenter is lost (Scheme 1). Upon irradiation with visible light the merocyanine is closed back to the spiro form, and the stereogenic center at C(3) is formed again. In contrast to **1**[10] the open merocyanine form of **2** cannot be detected at room temperature even after prolonged irradiation with UV light. The

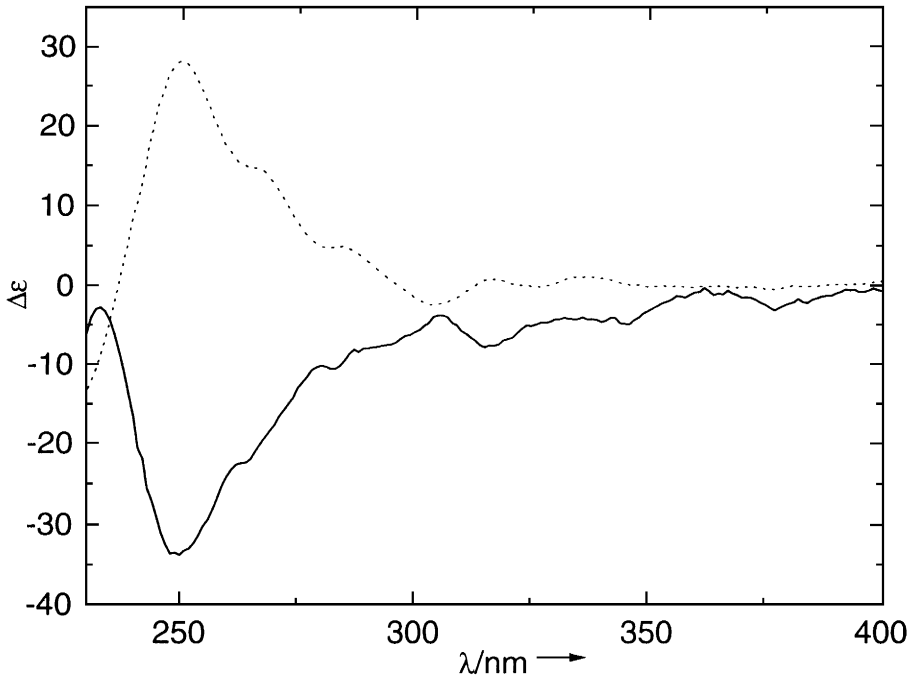


Fig. 2. CD spectra of HPLC-separated diastereomers of the optically active spiropyran **2** in hexane:2-propanol, 9:1, at 20°C; (—): (2*S*,3*S*)-**2**, c=3.04×10^{-5} M; (- - -): (2*R*,3*S*)-**2**, c=2.92×10^{-5} M

spiro form is favored under these conditions which is well known from similar compounds without a nitro group,[4] and equilibration occurs too fast for us to detect (Fig. 3, solid line). The CD spectrum reflects the diastereomeric composition of **2** after photochemical equilibration at this temperature (Fig. 4, solid line). The small Cotton effects observed are a measure of the small diastereomeric excess remaining under these conditions. However, the positive peak at 250 nm followed by a smaller negative one at 255 nm is proof that the (2*R*,3*S*) diastereomer is the preferred one (in contrast, a negative peak was followed by a smaller positive one in the case of **1**, indicating that for that compound the (2*S*,3*R)* diastereomer is prevalent). According to high-quality ab initio calculations at the RHF/6-31-G** level with complete geometry optimization and second derivatives for the energy minima[11] the energy difference between (2*S*,3*R*)-**1** and the (2*R*,3*R*) epimer is 0.494 kcal/mol in favor of the former, which agrees with our configurational assignment, at least at this temperature.

We have recently described the temperature dependent UV/vis and CD spectra of **1**.[10] The existence of an isosbestic point and theoretical calculations lead us to conclude that the change, which is observed in the temperature dependent CD spectrum after irradiation with UV or visible light, is due to a change in the diastereomeric composition of **1**.

Fig. 3 shows what happens when the sample is irradiated at −30°C. Only a small amount of the merocyanine is formed after UV irradiation for 45 min (dotted line). The long wavelength maximum occurs around 590 nm, which is a bathochromic shift of 60 nm compared with **1**: a consequence of the more extended π-system. The spiro form is not completely restored by visible light at this temperature (dashed line). The CD spectra taken under identical conditions are shown in Fig. 4. The increase of the negative band at 255 nm at the expense of the positive one at 250 nm (dotted line) indicates that UV light at −30°C effects an inversion of the diastereomeric excess from (2*R*,3*S*) to (2*S*,3*S*). After irradiation with visible light (dashed line) the CD amplitudes decrease indicating that the equilibrium between the diastereomers is now closer to 1. Repeating the irradiation with UV restores the dotted spectrum with

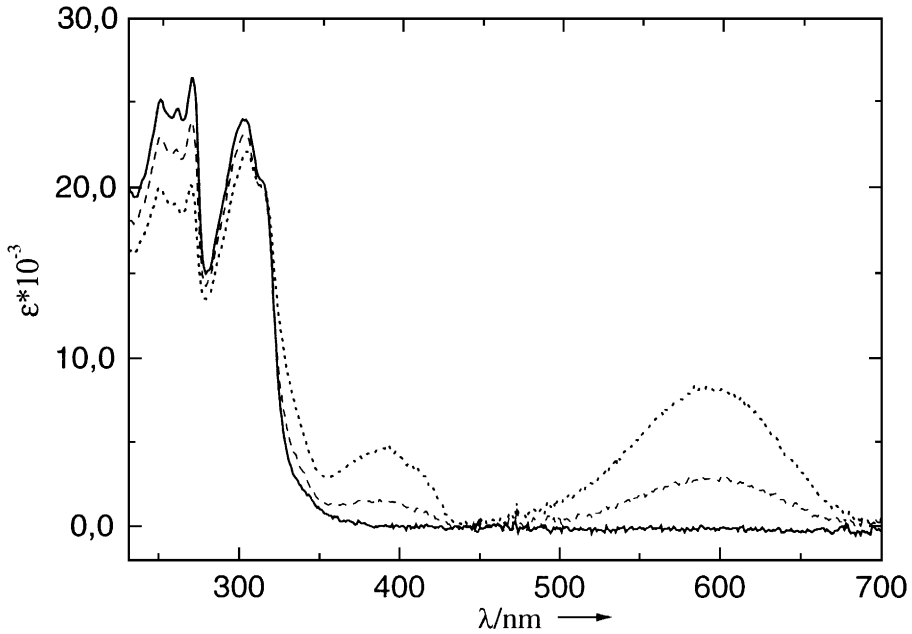


Fig. 3. UV/vis spectra of **2** in methanol:ethanol, 1:4, c=3.3.10^{-5} M, cooled in the dark from room temperature to −30°C (—); after UV irradiation for 45 min (···) and after vis irradiation for 20 min (- - -)

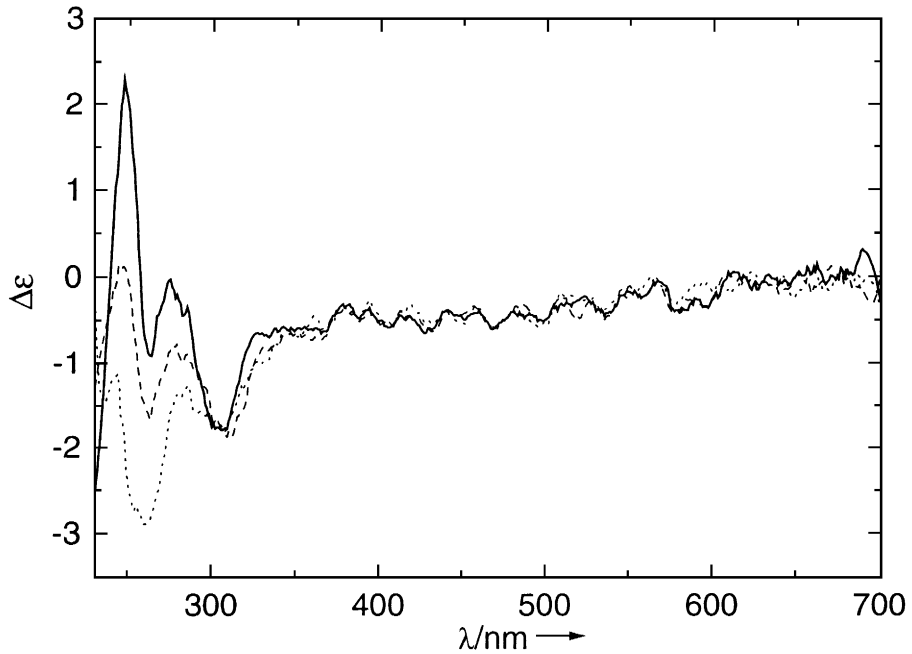


Fig. 4. CD spectra of **2** in methanol:ethanol, 1:4, c=3.3×10^{-5} M, cooled in the dark from room temperature to −30°C (—); after UV irradiation for 45 min (···) and after vis irradiation for 20 min (- - -)

the strong negative amplitude; the effect of visible light on this spectrum is now almost nil and is only a manifestation of the equilibrium between the closed and the open forms.

For an explanation we assume the existence of two different processes: photochemical interconversion between the closed and the open spiropyran and thermal isomerization of the open merocyanine, a view which is supported by the recent ab initio calculations by Robb et al.[12] According to these calculations the photochemically generated *cis*-configured open spiropyran relaxes via a conical intersection into the ground state from where it can either return to the closed form or undergo bond isomerization to the *trans*-merocyanine. This latter step is the necessary prerequisite for inversion of the configuration at C(2). For the −30°C equilibrium to be established every molecule must have had a chance to react via this latter path. The initial observation of an intermediate spectrum at −30°C is thus a direct indication of these two competing processes. Once the equilibrium between the open *cis*-configured merocyanines has been established changes of the diastereomeric composition upon excitation with UV or visible light are no longer observed.

In a preliminary investigation, no liquid crystalline properties were detected for the chiral spiropyran **2**. The introduction of the phenylacetylene group did not improve the suitability of spiropyrans for optical data storage, although it was possible to raise the temperature necessary for the diastereomeric switch of 2, somewhat, to −30°C.

3. Experimental

3.1. General

Mp: Thermovar (Reichert, Wien). MS*:* AMD 604 (AMD Intectra, Harpstedt/Germany) at 70 eV (EI). Elemental analysis: Carlo Erba 1106. IR spectra*:* Perkin–Elmer 1320. ^{1}H and ^{13}C NMR: Bruker DRX 500 or AM 300 spectrometer, TMS, chemical shifts (δ) in ppm, coupling constants J in hertz, carbon substitution by DEPT-135° and DEPT-90°. For the non-IUPAC numbering of the spiropyrans — to make comparison with the parent indole base easier — see the formulas above. UV/vis spectra: Perkin–Elmer Lambda 5. CD spectra: 62 A DS (Aviv, USA), equipped with a liquid nitrogen Cryostat DN 1714, static (Oxford Instruments, UK). Solvents: spectrograde (Uvasole, Merck, Darmstadt). Column chromatography: silica gel 60 (70–230 mesh; Merck, art. 7734).

3.2. 5-Bromo-2-(p-toluenesulfonyloxy)benzaldehyde **4**

A mixture of 5 g (24.8 mmol) 2-hydroxy-5-bromobenzaldehyde **3** and 5.72 g (30 mmol) *p*-toluenesulfonyl chloride in 60 mL anhydr. pyridine was heated to 100°C for 2 h. The solution was stirred overnight at room temperature and then poured into ice/water (200 mL). The aqueous phase was extracted with $CHCl_3$ (2×50 mL). The organic layer was washed with dilute aq. HCl, $NaHCO_3$ solution, and brine, dried over $CaCl_2$, and evaporated. The residue was purified on silica gel by column chromatography (cyclohexane:EtOAc, 3:1; R_f=0.38) to give a yellow oil of **4**; yield: 5.85 g (66.5%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.47 (s, 3H, CH_3), 7.09 (d, ^{3}J=8.7 Hz, 1H), 7.34–7.37 (m, 2H), 7.66–7.72 (m, 3H), 7.97 (d, ^{4}J=2.5 Hz, 1H), 9.90 (s, 1H, CHO); MS (relative intensity, %): *m/z*=356 (8.7, M^{+} ^{81}Br), 354 (8.5, M^{+} ^{79}Br), 201 (9.3), 155 (76.5), 139 (6.6), 91 (100), 65 (19.6), 39 (7.1).

3.3. 2-(p-Toluenesulfonyloxy)-5-(phenylethynyl)benzaldehyde **5**

Aldehyde **4** (1.6 g, 2.2 mmol) and 0.88 mL phenylethyne (816 mg, 4 mmol) were dissolved in 100 mL anhyd. triethylamine and 40 mL anhydr. THF. To this mixture 20 mg CuI, 20 mg $PdCl_2(PPh_3)_2$ and 40 mg PPh_3 were added, stirred and heated under reflux for 3 h and at 20°C for 16 h. A precipitate was filtered off and the solution evaporated under reduced pressure. Chromatography on silica gel (cyclohexane/EtOAC 3:1; R_f=0.49) gave a yellowish viscous oil: yield: 1.42 g (86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.46 (s, 3H, H-22), 7.20 (dd, ^3J=8.5, ^5J=0.3 Hz, 1H, 3-H), 7.33–7.37 (m, 5H, H-12, 13, 14, 18, 20), 7.50–7.53 (m, 2H, H-11, 15), 7.68–7.72 (m, 3H, H-4, 17, 21), 7.99 (dd, ^4J=2.2, ^5J=0.3 Hz, 1H, 6-H), 9.96 (s, 1H, H-7); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=21.8 ppm (-CH_3), 86.9 (C≡C), 91.7 (C≡ C), 122.3 (q), 123.3 (q), 124.0, 128.5, 128.6 (q), 128.9, 130.2, 131.5 (q), 131.70, 131.73, 137.8, 146.5 (q), 150.4 (q), 186.6 (-CHO); MS (%): *m/z*=376 (61, M^+), 221 (100), 193 (22), 165 (35), 155 (29), 91 (53); anal. calcd for $C_{22}H_{16}O_4S$: C, 70.20; H, 4.28; found: C, 70.21; H, 4.34.

3.4. 2-Hydroxy-5-(phenylethynyl)benzaldehyde **6**

A solution of potassium hydroxide (6 g) in water (100 mL) and ethanol (100 mL) was prepared. The alkaline solution was added in three 50 mL portions at 15 min intervals to the tosylated tolan **5** and stirred at 20°C. After refluxing for 1 h, the solution was cooled, neutralized with acetic acid and concentrated to half the original volume at 50°C under reduced pressure. A yellow precipitate was sucked off and washed with diethylether. The filtrate was extracted three times with diethylether. The combined organic extracts were washed with aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and the solvent removed. The residue was recrystallized from ethanol/water and filtered hot to separate insoluble particles. The resulting yellow precipitate was washed with methanol and dried in vacuo in a desiccator; mp=79–80°C ; yield: 0.52 g (32%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.87 (s [br], 1H, OH), 7.04 (d, ^3J=8.6 Hz, 1H, H-3), 7.40–7.44 (m, 3H, H-12, 13, 14), 7.53–7.56 (m, 2H, H-11, 15), 7.74 (dd, ^3J=8.6, ^4J=2.2 Hz, 1H, H-4), 7.98 (dd, ^4J=2.2, ^4J=0.4 Hz, 1H, H-6), 10.08 (d, ^4J=0.4 Hz, 1H, CHO); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=88.6 ppm (C-8), 89.3 (C-9), 115.8 (C-5), 118.8 (C-3), 122.1 (C-1), 124.0 (C-10), 129.5 (C-13), 129.6 (C-12/14), 132.3 (C-11/15), 137.7 (C-6), 140.3 (C-4), 162.2 (C-2), 197.5 (C-7); MS (%): *m/z*=222 (100, M^+), 221 (29), 178 (10), 165 (26), 163 (11), 88 (9); anal. calcd for $C_{15}H_{10}O_2$: C, 81.07; H, 4.54; found: C, 81.07; H, 4.54.

3.5. 1,3,3-Trimethyl-6′-(phenylethynyl)-spiro-(2H-1′-benzopyran-2,2′-indoline) **9**

To a solution of 200 mg (0.9 mmol) of the salicylaldehyde **6** and 0.4 mL triethylamine in 15 mL anhyd. methanol, 210 mL (1.2 mmol) Fischer base **7** were added with stirring under N_2. The mixture was heated to reflux for 5 h. After cooling a yellow-green precipitate was filtered off and recrystallized from methanol and a few mL $CHCl_3$ to yield 180 mg. [The ^{1}H NMR spectrum revealed that this was not compound **9** but the bicondensation product **8**; mp 192–194°C dec.; MS (FD): *m/z*=505.4 (100).] A Kugelrohr distillation at 150–200°C under reduced pressure was performed with this product; the Fischer base was distilled off and **2** remained as a tarry blue residue. Yield: 100 mg (29%); UV (EtOH:MeOH, 4:1): 298 nm (ε=29010), 268 (32060), 259.5 (30300), 248.5 (31600), 222 (29042); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.16 (s, 3H, -CH_3), 1.30 (s, 3H, -CH_3), 2.72 (s, 3H, N-CH_3), 5.71 (d, ^3J=10.2 Hz, 1H, H-3′), 6.52 (d, ^3J=7.7 Hz, 1H, H-7), 6.67 (d, ^3J=8.1 Hz, 1H, H-8′), 6.80–6.87 (m, 2H, H-5, H-4′), 7.07 (dd, ^3J=7.2, ^4J=0.7 Hz, 1H, H-4), 7.16 (‘dd’, ^3J=7.7, ^4J=1.2 Hz, 1H, H-6), 7.20–7.45 (m, 5H, H-5′, 7′, 13′, 14′, 15′), 7.47–7.51 (m, 2H, H-12′, H-16′); ^{13}C NMR (125 MHz, $CDCl_3$): δ=20.1 ppm (C-9),

25.9 (C-10), 28.9 (C-8), 51.8 (C-3), 87.8 (C-9′), 89.3 (C-10′), 104.7 (C-2), 106.8 (C-7), 114.7 (C-6′), 115.3 (C-8′), 118.9 (C-4a′), 119.2 (C-5), 120.2 (C-3′), 121.5 (C-6), 123.6 (C-11′), 127.6 (C-4), 127.9 (C-14′), 128.3 (C-12′/16′), 128.9 (C-4′), 130.0 (C-5′), 131.4 (C-13′/15′), 133.2 (C-7′), 136.6 (C-3a), 148.1 (C-7a), 154.7 (C-8a′); MS (%): *m/z*=377 (64, M^+), 362 (11), 173 (33, $C_{12}H_{15}N$), 159 (100), 144 (13), 163 (11), 88 (9).

3.6. (3S)-1,3-Dimethyl-3-propyl-6′-(phenylethynyl)-spiro-(2H-1′-benzopyran-2,2′-indoline) **2**

Salicylaldehyde **6** (250 mg, 1.1 mmol) was dissolved in 10 mL of abs. methanol and 0.5 mL of triethylamine under nitrogen. A solution of (3*S*)-(−)-1,3-dimethyl-2-methylene-3-propylindoline **10** (180 mg, 0.8 mmol) in 5 mL of anhyd. methanol was prepared. This solution was added in one portion to the benzaldehyde and heated to reflux for 4 h. After cooling to room temperature the solvent was removed and the residue recrystallized from ethanol/water. The precipitate was dissolved in ca. 5 mL diethyl ether and allowed to stand at 4°C for 1 day. The precipitate (educt **6**) was filtered off, the filtrate evaporated and dried under reduced pressure at 65°C. The blue residue was recrystallized from ethanol to yield 250 mg (76%) **2**: mp 42–43°C ; UV (*n*-hexane:2-propanol, 9:1): 313.5 nm (ε=25700), 297.5 (30700), 267.5 (34500), 259 (33100), 248.5 (35200); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.75 (t, 3H, H-12*), 0.80 (t, 3H, H-12), 1.19–1.25 (m, 3H, H-10$_a$, 11), 1.21 (s, 3H, H-9*), 1.27 (s, 3H, H-9), 1.41–1.49 (m, 3H, H-10$_b$, H-11*), 1.73–1.79 (m, 1H, H-10$_a$*), 1.86–1.91 (m, 1H, H-10$_b$*), 2.64 (s, 3H, H-8*), 2.73 (s, 3H, H-8), 5.75 (d, ^3J=10.2 Hz, 1H, H-3′), 5.77 (d, ^3J=10.2 Hz, 1H, H-3′*), 6.49 (d, ^3J=7.6 Hz, 1H, H-7*), 6.53 (d, ^3J=7.6 Hz, 1H, H-7), 6.67 (d, ^3J=8.3 Hz, 1H, H-8′), 6.70 (d, ^3J=8.3 Hz, 1H, H-8′*), 6.78–6.85 (m, 4H, H-5, H-4′, H-5*, H-4′*), 7.02 (dd, ^3J=7.2, ^4J=1.2 Hz, 1H, H-4), 7.09 (dd, ^3J=7.3, ^4J=1.2 Hz, 1H, H-4*), 7.15–7.20 (m, 2H, H-6, H-6*), 7.23–7.36 (m, 10H, H-5′, 7′, 13′, 14′, 15′, H-5′*, 7′*, 13′*, 14′*, 15′*), 7.48–7.53 (m, 4H, H-12′, 16′, H-12′*, 16′*) [*, minor compound, integral=1; major compound, integral=1.7]; ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.61 ppm (CH_3), 15.13 ppm (CH_3), 17.56 (CH_2), 17.62 (CH_3), 17.71 (CH_2), 22.93 (CH_3), 28.18 (N-CH_3), 29.06 (N-CH_3), 36.97 (CH_2), 38.94 (CH_2), 53.63 (C-3*), 55.70 (C-3), 87.81 (C≡C), 87.86 (C≡C), 89.28 (C≡C), 89.29 (C≡C), 103.48 (C-2*), 105.58 (C-2), 106.81 (C-7*), 106.82 (C-7), 114.61 (C-6′), 114.62 (C-6′*), 115.22 (C-8′*), 115.28 (C-8′), 118.65 (C-4a′*), 118.71 (C-5), 118.94 (C-4a′), 119.15 (C-5*), 120.38, 120.77, 121.74, 123.19, 123.58 (C-11′*), 123.61 (C-11′), 127.57, 127.62, 127.90, 127.92, 128.30, 128.42, 128.86, 129.22, 130.05, 131.43, 131.52, 133.21, 134.36 (C-3a), 136.87, 137.06 (C-3a*), 139.83, 147.53 (C-7a*), 148.81 (C-7a), 154.25 (C-8a′*), 154.83 (C-8a′) [*, minor compound]; MS (EI): *m/z*=405 (100, M^+), 376 (15), 363 (33), 362 (32), 347 (16), 334 (8), 222 (22), 187 (78), 165 (7), 159 (18), 158 (63), 144 (7); HRMS: calcd for $C_{29}H_{27}NO$: 405.20927; found: 405.21093.

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