

# Synthesis and Characterization of Novel Bifunctional Hemithioindigo Chromophores

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## Supporting material

*General Methods.* Solvents were used in p.a. quality and dried as follows: diethylether over lithium aluminum hydride, methanol over magnesium, benzene over sodium/benzophenone, piperidine and pyridine over calcium hydride.

Compounds **1**<sup>1</sup>, **2a**<sup>2</sup>, **2c**<sup>2</sup> and **5**<sup>3</sup> were prepared essentially by following the literature procedures.

Compound **2b** was bought from Acros Organics in p.a. quality.

All reactions were monitored by analytical thin-layer chromatography (TLC, silica gel, Merck 60 F<sub>254</sub> plates) and visualized by UV light, basic potassium permanganate or acidic phosphomolybdic acid/cerium(IV)sulfate. For the purification of products by column chromatography on Florisil (140-200 mesh; supplied by Aldrich or Fluka) the technique developed by Helquist et al. (but without inert gas atmosphere)<sup>4</sup> was used.

Melting Points were measured with a *Leica* Galen heating microscope with a control unit of the *Wagner-Munz* company or with a *Büchi* melting point determination apparatus and remain uncorrected. IR-spectra were measured on a *Perkin-Elmer* spectrometer 881 as ATR (Attenuated

Total Reflectance). The peaks are listed as wavenumbers ( $\text{cm}^{-1}$ ). The peak intensities were abbreviated as follows: vs = very strong, s = strong, m = medium strong, w = weak, br = broad.

**$^1\text{H}$  NMR** spectra were recorded on *Bruker* spectrometers AC 200 and DRX 500 at 200 MHz or 500 MHz. Solvents are mentioned for the particular substances. The chemical shifts are quoted as dimensionless  $\delta$ -values in ppm; residual solvent protons were used as internal standard. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and coupling constants are in Hz. The number of protons was determined by integration of the signals. Multiplicity of the signals were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

**$^{13}\text{C}$  NMR** spectra were recorded on *Bruker* spectrometers AC 200 and DRX 500 at 50 MHz or 125 MHz. Solvents are mentioned for the particular substances. The chemical shifts are quoted as dimensionless  $\delta$ -values in ppm.

**MS- and HR-MS**-spectra were recorded on a *Finnigan* MAT 95 SQ or *Varian* MAT 711. The samples were ionized at an ionization potential of 70 eV.

Compound **3a**: Thioindoxyl **1** (2.00 g, 9.4 mmol, 1.0 eq) was dissolved in 15 ml of benzene. To this solution 2.20 g **2a** (11.3 mmol, 1.2 eq) in 10 ml benzene were added by means of a cannula, followed by 2 ml methanol (1.58 g, 49.0 mmol, 5.0 eq) and 0.15 ml of piperidine (0.13 g, 1.5 mmol, 0.2 eq). The solution was stirred under nitrogen at room temperature for 1 h and then refluxed for 1 h. Stirring at room temperature was continued over night. The solution was diluted with 50 ml dichloromethane, washed with 1 N HCl and then with saturated sodium bicarbonate solution. The organic layer was dried ( $\text{MgSO}_4$ ) and the solvent was evaporated in vacuo. The solid residue was recrystallized from toluene/methanol 1:1 to give 1.80 g (50%) of **3a**. m.p. 200-

202°C; R<sub>f</sub> 0.5 (pentane/ethyl acetate 1:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, δ): 8.29-8.25 (m, 1H, Ar-H), 8.14-8.10 (m, 1H, Ar-H), 7.93 (s, 1H, C=CH); 7.77 (d, J = 8.81, 2H, Ar-H), 7.42-7.34 (m, 1H, Ar-H), 6.99 (d, J = 8.81, 2H, Ar-H), 4.70 (s, 2H, CH<sub>2</sub>), 4.02 (s, 3H, CH<sub>3</sub>), 3.82 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz, δ): 188.30, 168.91, 165.93, 159.56, 148.64, 136.47, 134.62, 133.56, 132.62, 131.06, 129.52, 128.15, 125.40, 124.78, 115.38, 65.29, 52.75, 52.60; HR-MS: calcd for C<sub>20</sub>H<sub>16</sub>O<sub>6</sub>S, *m/e* 384.0667; found, *m/e* 384.0667.

Compound **3b**: Thioindoxyl **1** (1.50 g, 7.1 mmol, 1.0 eq) was dissolved in 15 ml of benzene. To this solution **2b** (1.40 g, 8.5 mmol, 1.2 eq) dissolved in 10 ml benzene was added by means of a cannula followed by 1.50 ml methanol (1.2 g, 36.8 mmol, 5 eq) and by 0.15 ml of piperidine (0.13 g, 1.5 mmol, 0.2 eq). The solution was stirred under nitrogen at room temperature for 1 h and then refluxed for 1 h. Stirring at room temperature was continued over night. The solution was diluted with 50 ml dichloromethane, washed with 1N HCl and then with saturated sodium bicarbonate solution. The organic layer was dried (MgSO<sub>4</sub>) and the solvent was evaporated in vacuo. The solid residue was recrystallized from toluene/methanol 1:1 to give 1.25 g (50%) **3b**. m.p. 250°C; R<sub>f</sub> 0.48 (pentane/ethyl acetate 2:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, δ): 8.31-8.27 (m, 1H, Ar-H), 8.15-8.10 (m, 3H, Ar-H), 7.95 (s, 1H, C=CH); 7.83 (d, J = 8.81, 2H, Ar-H), 7.40 (m, 1H, Ar-H), 4.02 (s, 3H, CH<sub>3</sub>), 3.94 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz, δ): 188.27, 166.47, 165.75, 148.59, 138.44, 136.88, 133.52, 133.12, 132.03, 131.21, 131.15, 130.30, 125.77, 124.95, 52.81, 52.51; HR-MS: calcd for C<sub>19</sub>H<sub>14</sub>O<sub>5</sub>S, *m/e* 354.0561; found, *m/e* 354.0561.

Compound **3c**: Thioindoxyl **1** (1.00 g, 4.6 mmol, 1.0 eq) was dissolved in 10 ml of benzene. To this solution 1.5 ml methanol (1.2 g, 36.8 mmol, 5 eq) and 0.41 ml of pyridine (0.40 g, 5.1 mmol, 1.1 eq) were added followed by **3c** (1.25 g, 5.4 mmol, 1.2 eq) dissolved in 10 ml of benzene.

After the addition of 0.07 ml of piperidine (0.06 g, 0.8 mmol, 0.1 eq) the solution was stirred under nitrogen at room temperature for 1 h and then refluxed for 1 h. Stirring at room temperature was continued for 10 h. The solution was diluted with 50 ml of dichloromethane and washed with saturated sodium bicarbonate solution. The organic layer was dried ( $\text{MgSO}_4$ ) and the solvent was evaporated in vacuo. The solid residue was recrystallized from diethylether/pentane (1:1) to give 1.25 g (52%) of **3c**. m.p.  $157^\circ\text{C}$ ;  $R_f$  0.62 (pentane/ethyl acetate 1:1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz,  $\delta$ ): 8.29-8.25 (m, 1H, Ar-H), 8.14-8.10 (m, 1H, Ar-H), 7.93 (s, 1H, C=CH), 7.77 (d,  $J = 8.79$ , 2H, Ar-H), 7.42-7.34 (m, 1H, Ar-H), 6.98 (d,  $J = 8.79$ , 2H, Ar-H), 4.57 (s, 2H,  $\text{CH}_2$ ), 4.02 (s, 3H,  $\text{CH}_3$ ), 1.49 (s, 9H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz,  $\delta$ ): 187.92, 167.22, 165.58, 159.55, 148.31, 136.10, 134.41, 133.22, 132.34, 130.68, 128.99, 127.58, 125.03, 124.45, 115.08, 82.63, 65.45, 52.39, 27.91; IR (ATR,  $\nu[\text{cm}^{-1}]$ ): 2978 (w), 1751 (m), 1713 (m), 1678 (s), 1588 (m), 1509 (s), 1264 (m), 1155 (s), 1071 (m), 749 (s); HR-MS: calcd for  $\text{C}_{23}\text{H}_{22}\text{O}_6\text{S}$ ,  $m/e$  426.1137; found,  $m/e$  426.1133.

Compound **4**: Thioindoxyl **1** (2.00 g, 9.2 mmol, 1.0 eq) was dissolved in 15 ml of benzene. To this solution **2c** (2.60 g, 11.0 mmol, 1.2 eq) and 2.1 ml of piperidine (21.2 mmol 2.3 eq) in 15 ml of benzene were added by means of a cannula followed by 2 ml methanol (1.58 g, 49.0 mmol, 5.0 eq). The solution was stirred under nitrogen at room temperature for 1 h and then refluxed for 1 h. After stirring at room temperature over night the solution was diluted with 50 ml dichloromethane, washed with 1 N HCl and after that with saturated sodium bicarbonate solution. The organic layer was dried ( $\text{MgSO}_4$ ) and the solvent was evaporated in vacuo. The solid residue was recrystallized from methanol to give 2.10 g (54%) of **4**. m.p.  $167^\circ\text{C}$ ;  $R_f$  0.33 (pentane/ethyl acetate 1:1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz,  $\delta$ ): 7.98-7.93 (m, 2H, Ar-H), 7.68 (d,  $J = 8.79$ , 2H, Ar-H), 7.54-7.50 (m, 1H, Ar-H), 7.35-7.28 (m, 1H, Ar-H), 6.97 (d,  $J = 8.79$ , 2H, Ar-H), 4.56 (s, 2H,  $\text{CH}_2$ ), 3.57 (br. s, 4H,

(CH<sub>2</sub>)<sub>2</sub>N), 1.67-1.58 (m, 6H, CH<sub>2</sub>), 1.49 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz, δ): 188.67, 167.90, 167.53, 160.14, 145.33, 134.56, 133.65, 133.33, 132.20, 131.86, 128.66, 128.07, 125.81, 115.72, 83.26, 66.04, 48.77, 44.43, 28.54, 26.80, 24.98; HR-MS: calcd for C<sub>27</sub>H<sub>29</sub>O<sub>5</sub>NS, *m/e* 479.1766; found, *m/e* 479.1767.

Compound **6**: Thioindoxyl **1** (0.75 g, 3.5 mmol, 1.5 eq) was suspended in 10 ml of benzene in the presence of molecular sieve (4Å). After addition of 1.15 ml of methanol (0.57 g, 17.7 mmol, 7.5 eq) and 3.75 ml of pyridine (3.66 g, 46.5 mmol, 19.5 eq) at 0°C the mixture was stirred at room temperature for 30 min. The solution was refluxed for 3 h and then allowed to cool to room temperature. Compound **5** (0.48 g, 2.4 mmol, 1.0 eq) dissolved in 10 ml of benzene was added dropwise to the mixture at 0°C. After the addition of 0.05 ml of piperidine (0.04 g, 0.5 mmol, 0.3 eq) the solution was stirred under nitrogen at room temperature over night and then refluxed for 1 h. The solution was diluted with 50 ml of diethyl ether and washed with ice water. The organic layer was dried (MgSO<sub>4</sub>) and the solvent was evaporated in vacuo to yield 0.92 g (98%) of crude **6** (98% purity; <sup>1</sup>H NMR). m.p. 173°C; R<sub>f</sub> 0.50 (pentane/diethyl ether 1:2); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, δ): 8.29-8.25 (m, 1H, Ar-H), 8.13-8.10 (m, 1H, Ar-H), 7.93 (s, 1H, C=CH), 7.77 (d, *J* = 7.81, 2H, Ar-H), 7.42-7.29 (m, 3H, Ar-H), 4.37-4.34 (m, 2H, CH<sub>2</sub>), 4.01 (s, 3H, CH<sub>3</sub>), 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz, δ): 188.02, 165.49, 155.79, 148.41, 141.65, 136.29, 134.25, 132.94, 132.03, 131.49, 130.73, 128.67, 127.74, 125.17, 124.47, 79.59, 52.44, 44.18, 28.26; HR-MS: calcd for C<sub>23</sub>H<sub>22</sub>O<sub>6</sub>S, *m/e* 425.1297; found, *m/e* 425.1293.

Compound **7**: Hemithioindigo **4** (0.20 g, 0.3 mmol, 1.0 eq) was dissolved in 6 ml of reagent K (10 ml reagent K contain 8.25 ml trifluoroacetic acid, 0.5 ml water, 0.5 ml thioanisol, 0.5 g phenol, 0.25 ml ethanedithiol) and stirred under nitrogen for 30 min. The solution was

concentrated *in vacuo* and ether was added dropwise to the remaining oil. The precipitate was separated and recrystallized from diethyl ether to give 0.14 g (80%) of **7** as an orange powder. m.p. 223°C;  $R_f$  0.33 (ethyl acetate/acetic acid 80:1);  $^1\text{H NMR}$  ([D<sub>6</sub>]DMSO, 200 MHz,  $\delta$ ): 13.18 (s, 1H, COOH), 7.98-7.96 (m, 2H, Ar-H, C=CH), 7.83-7.75 (m, 3H, Ar-H), 7.55-7.48 (m, 1H, Ar-H), 7.17 (d,  $J = 8.79$ , 2H, Ar-H), 4.84 (s, 2H, CH<sub>2</sub>), 3.40 (br. s, 4H, (CH<sub>2</sub>)<sub>2</sub>N), 1.77-1.43 (m, 6H, CH<sub>2</sub>); HR-MS: calcd for C<sub>23</sub>H<sub>21</sub>NO<sub>5</sub>S,  $m/e$  423.1140; found,  $m/e$  423.1144.

Compound **8**: Hemithioindigo **6** (50 mg, 0.13 mmol, 1.0 eq) was dissolved in 10 ml of HCl in dioxane (4.0 M) at 0°C. The solution was warmed to room temperature and stirred under nitrogen for 3 h. After complete consumption of the starting material (tlc monitoring) the solvent was removed *in vacuo* and the solid residue was washed with EtOAc and dried *in vacuo* to give 47 mg (quant.) of **8** as a yellow powder.  $^1\text{H NMR}$  (CD<sub>3</sub>OD, 200 MHz,  $\delta$ ): 8.42-8.38 (m, 2H, Ar-H), 8.19-8.15 (m, 1H, Ar-H), 7.99 (s, 1H, C=CH), 7.95 (d,  $J = 8.30$ , 2H, Ar-H), 7.68 (d,  $J = 8.30$ , 2H, Ar-H), 7.56 (m, , 1H, Ar-H), 4.25 (s, 2H, CH<sub>2</sub>), 4.06 (s, 3H, CH<sub>3</sub>); IR (ATR,  $\nu[\text{cm}^{-1}]$ ): 3344 (w), 2957 (s), 1712 (s), 1666 (m), 1588 (m), 1559 (m), 1468 (m), 1412 (m), 1271 (s), 1146 (m), 1049 (m), 748 (s); (C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>SxHCl: 361.84 g/mol) HR-MS: calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>S,  $m/e$  325.0772; found,  $m/e$  325.0772.

Compound **9**: Hemithioindigo **3a** (50 mg, 0.13 mmol, 1.0 eq), thiophenol (217 mg, 2.0 mmol, 15.0 eq) and potassium carbonate (30 mg, 0.22 mmol, 1.7 eq) were dissolved in 5 ml of *N*-methylpyrrolidone and stirred under nitrogen at 190°C for 10 min. The solution was cooled to room temperature and diluted with saturated sodium bicarbonate solution (25 ml). After extraction with diethyl ether, the aqueous layer was acidified with 6 N HCl and again extracted with diethyl ether. The combined organic layers were dried (MgSO<sub>4</sub>) and the solvent was

evaporated to give 41 mg (89%) of **9**. m.p. >280°C (decomp.); R<sub>f</sub> 0.11 (ethyl acetate/acetic acid 80:1); <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 200 MHz, δ): 13.93 (s, 1H, COOH), 13.19 (s, 1H, COOH), 8.36-8.33 (m, 1H, Ar-H), 8.17-8.13 (m, 1H, Ar-H), 7.97 (s, 1H, C=CH); 7.86 (d, *J* = 8.81, 2H, Ar-H), 7.62-7.55 (m, 1H, Ar-H), 7.20 (d, *J* = 8.81, 2H, Ar-H), 4.86 (s, 2H, CH<sub>2</sub>); HR-MS: calcd for C<sub>20</sub>H<sub>16</sub>O<sub>6</sub>S, *m/e* 356.0354; found, *m/e* 356.0354.

Compound **10**: Thioindoxyl **1** (0.78 mg, 3.7 mmol, 1.5 eq) was dissolved in a mixture of 30 ml 1% NaOH and 5 ml *t*BuOH at 0°C. To this solution **5** (0.50 g, 2.4 mmol, 1.0 eq) dissolved in 5 ml *t*BuOH was added at 0°C. The mixture was stirred for 1 h at room temperature and then refluxed for 1 h. The solution was cooled to room temperature and acidified with acetic acid (pH 5-6). The precipitate was filtered off and dried in vacuo. Purification by chromatography on Florisil using ethyl acetate/pentane (2:1) → ethyl acetate/acetic acid (500:1) gave 0.40 g (80%) of **10**. m.p. >290°C (decom.); R<sub>f</sub> 0.21 (ethyl acetate/pentane 2:1); <sup>1</sup>H NMR (CD<sub>3</sub>OD, 200 MHz, δ): 8.34 – 8.31 (m, 1H, Ar-H), 8.08-8.04 (m, 1H, Ar-H), 7.89 (s, 1H, C=CH), 7.77 (d, *J* = 8.30, 2H, Ar-H), 7.49-7.42 (m, 3H, Ar-H), 4.30 (s, 2H, CH<sub>2</sub>), 1.47 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); IR (ATR, ν[cm<sup>-1</sup>]): 3344 (m), 2976 (m), 1683 (s), 1589 (m), 1559 (m), 1511 (m), 1418 (m), 1253 (s), 1168 (s), 1049 (m), 747 (s); HR-MS: calcd for C<sub>22</sub>H<sub>21</sub>O<sub>5</sub>SN, *m/e* 411.1140; found, *m/e* 411.1149.

Compound **11**: Hemithioindigo **9** (50 mg, 0.12 mmol, 1.0 eq), HOBt (22 mg, 0.14 mmol, 1.2 eq) and EDC (28 mg, 0.14 mmol, 1.2 eq) were dissolved in 3 ml of DMF at -30°C under nitrogen. After the solution had warmed to 5°C over a period of 90 min, (*S*)-H-Lys(Cbz)-OMexHCl (54 mg, 0.18 mmol, 1.5 eq) and DIEA (31 mg, 0.05 ml, 0.24 mmol, 2 eq) were added and the mixture was stirred for 29 h at room temperature (tlc monitoring). The solvent was removed in vacuo and the solid residue was distributed between EtOAc/*i*PrOH (75:25) and 1 N HCl. The organic layer

was washed with saturated NaHCO<sub>3</sub> solution and dried (MgSO<sub>4</sub>). The crude material was purified by chromatography on Florisil to yield 69 mg (88%) of **11** as a yellow solid. R<sub>f</sub> 0.78 (ethyl acetate/acetic acid 80:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, δ): 7.95 (d, *J* = 7.32, 2H, Ar-*H*), 7.83 (s, 1H, Ar-*H*), 7.68 (d, *J* = 8.30, 2H, C=CH), 7.38-7.20 (m, 7H, Ar-*H*), 5.07-4.92 (m, 5H), 4.82-4.72 (m, 1H), 4.33-4.23 (m, 2H), 3.76 (s, 3H, CH<sub>3</sub>), 3.16 (m, 3H), 1.96-1.76 (m, 3H), 1.44 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.34-0.83 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz, δ): 188.29, 172.83, 165.46, 156.67, 155.87, 147.33, 141.52, 136.51, 136.23, 134.02, 133.00, 132.38, 132.25, 131.53, 131.31, 129.47, 128.68, 128.35, 128.29, 127.96, 127.86, 127.73, 127.67, 127.18, 126.89, 125.03, 79.58, 77.14, 66.48, 52.64, 52.53, 44.13, 39.98, 31.23, 29.47, 28.27, 22.33; IR (ATR, ν[cm<sup>-1</sup>]): 3340 (m), 2932 (m), 1696 (s), 1652 (s), 1529 (s), 1365 (m), 1250 (s), 1167 (s), 1050 (m), 747(s); HR-MS: calcd for C<sub>37</sub>H<sub>41</sub>N<sub>3</sub>O<sub>8</sub>S, *m/e* 687.2614; found, *m/e* 687.2625.

**UV-spectra** were measured on a Zeiss MCS 320/340 diode array spectrometer and a Shimadzu UV-1601 UV-Visible spectrometer in methanol, dichloromethane and acetonitrile from Acros (spectroscopic or HPLC-grade) using 1x1x4 cm quartz cuvettes at 25°C. For **3a** the chromophore concentration was  $c = 4.83 \times 10^{-5}$  mol/l in methanol and dichloromethane, for **3b** the chromophore concentration was  $c = 4.02 \times 10^{-5}$  mol/l in dichloromethane, for **9** the chromophore concentration was  $c = 1.24 \times 10^{-4}$  mol/l in methanol, for **10** the chromophore concentration was  $c = 1.02 \times 10^{-4}$  mol/l in methanol and  $c = 1.07 \times 10^{-4}$  mol/l in dichloromethane. The UV spectra of the pure *Z*-isomers (> 97%, see Table 3 publication) were recorded upon storage in the dark at room temperature for several hours. The UV spectra of the *E*-isomers in the photostationary state (pss) were recorded after illumination at 406 nm until the pss was reached (see, NMR spectroscopy, photoisomerization).



## Photoisomerization

A 1000 W Xe-lamp (Hanovia 976C1010) in a lamp-casing L 1000 from Müller Elektronik was used for the irradiation experiments at 406 and 480 nm (interference filters; Ø 25 mm; ± 0.5 nm; Amko). Between the lamp and the interference filters an IR-Filter (Müller Elektronik-Optik; MHO 60) and a lense were placed.

The ratio of isomers was determined by  $^1\text{H}$  NMR spectroscopy at the photostationary state on a *Bruker* spectrometers AC 200 at 200 MHz using either  $\text{CD}_2\text{Cl}_2$  (**3a**, **10**) or  $\text{CD}_3\text{OD}$  as solvent (**9**).

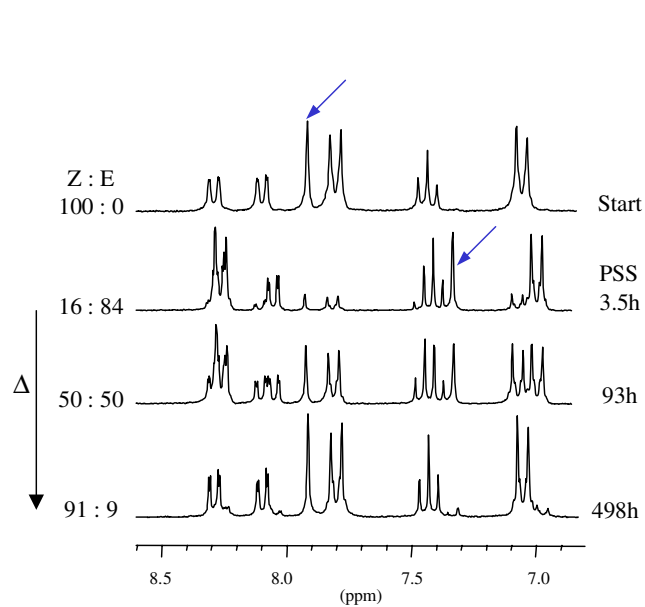
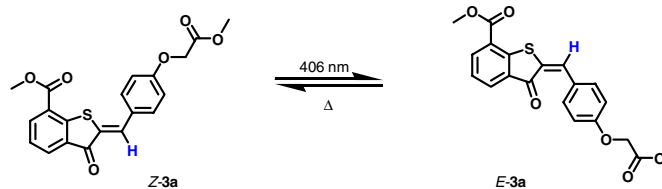
The thermal isomerization was measured on a *Bruker* spectrometer AC 200 at 200 MHz by keeping the sample at a constant temperature in the dark. For determination of the half-life at room temperature (25°C) about 8-10  $^1\text{H}$  NMR spectra were recorded.

Details are given in Table 1.

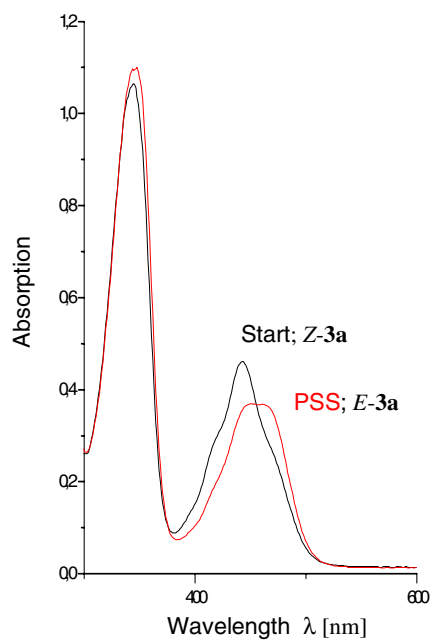
Table 1.  $^1\text{H}$  NMR Data of Photoisomerization Experiments

Entry	Compound	Solvent	c [mol/l]	$\delta$ [ppm]
1	<b>3a</b>	$\text{CD}_2\text{Cl}_2$	$1,99 \times 10^{-2}$	Z : 7.78 (C=CH) E : 7.17 (C=CH)
2	<b>9</b>	$\text{CD}_3\text{OD}$	$1,02 \times 10^{-2}$	Z : 7.90 (C=CH) 7.11 (d, Ar-H) E : 7.42 (C=CH) 7.00 (d, Ar-H)
3	<b>10</b>	$\text{CD}_3\text{OD}$	$2,55 \times 10^{-2}$	Z : 7.98 (s, C=CH) 7.77 (d, Ar-H) E : 7.50 (C=CH) 8.16 (d, Ar-H)

## Photochromic Properties of Compound 3a

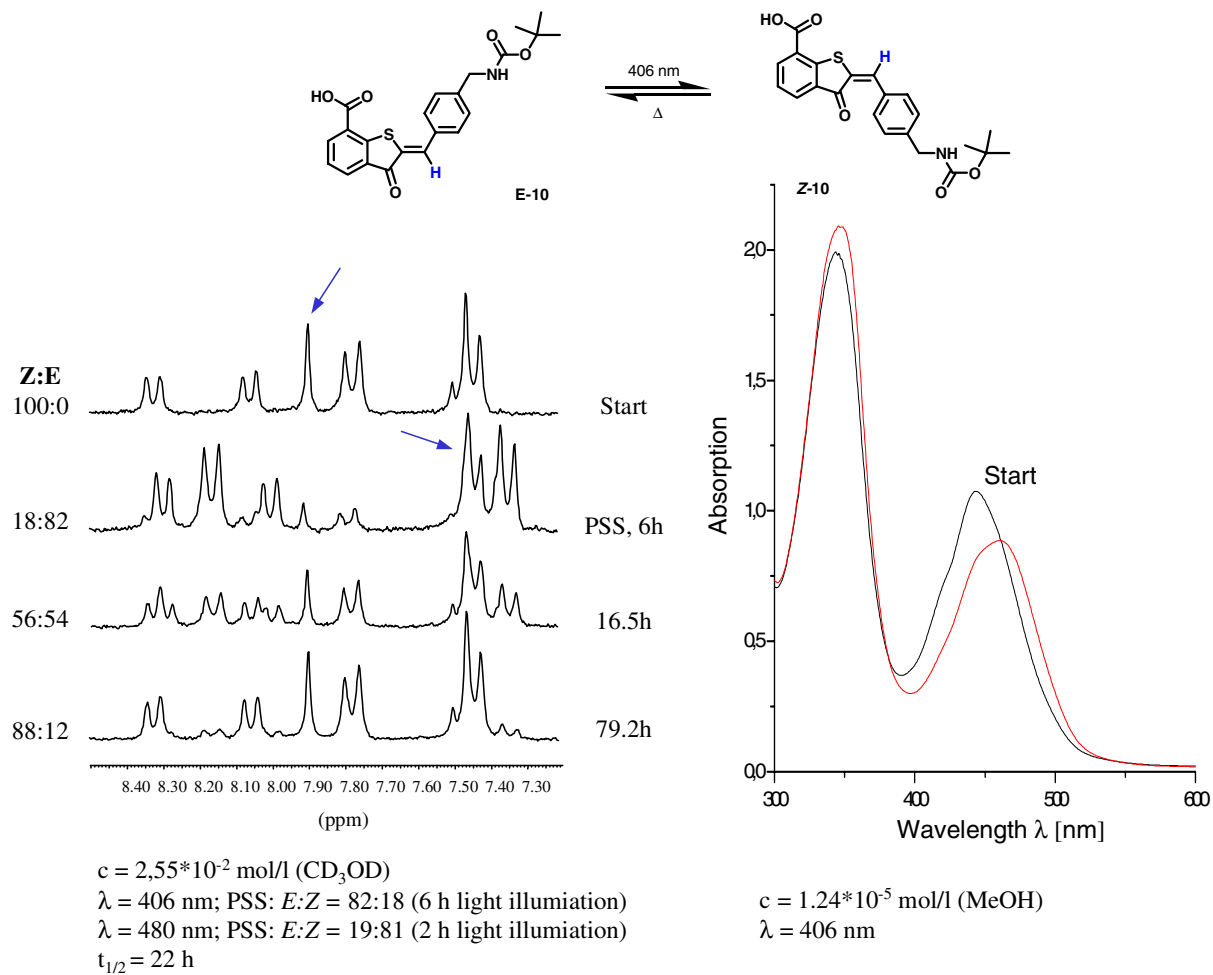


$c = 1,99 \cdot 10^{-2} \text{ mol/l (CD}_2\text{Cl}_2)$   
 $\lambda = 406 \text{ nm; PSS: } E:Z = 84:16 \text{ (3.5 h light illumination)}$   
 $\lambda = 480 \text{ nm; PSS: } E:Z = 5:95 \text{ (1.25 h light illumination)}$   
 $t_{1/2} = 138 \text{ h}$

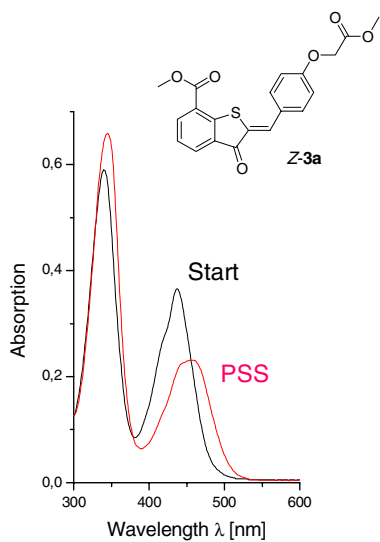


$c = 4,83 \cdot 10^{-5} \text{ mol/l (DCM)}$   
 $\lambda = 406 \text{ nm}$

# Photochromic Properties of Compound 10



## UV/VIS-Data



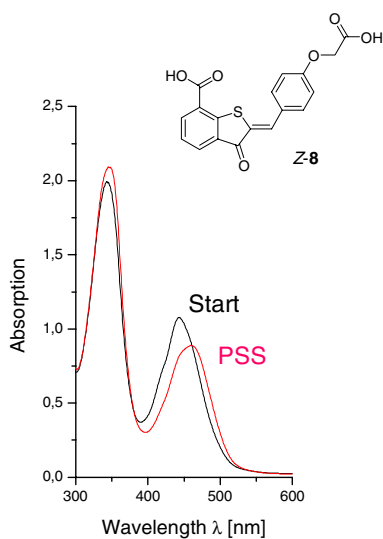
$c = 4.83 \times 10^{-5} \text{ mol/l (MeOH)}$

$\lambda = 406 \text{ nm}$

Z-isomer:  $\lambda_{\text{max}} = 438 \text{ nm}$

E-isomer:  $\lambda_{\text{max}} = 457 \text{ nm (pss)}$

Z-isomer:  $\epsilon = 7453 \text{ dm}^3 \times \text{M}^{-1} \times \text{cm}^{-1}$



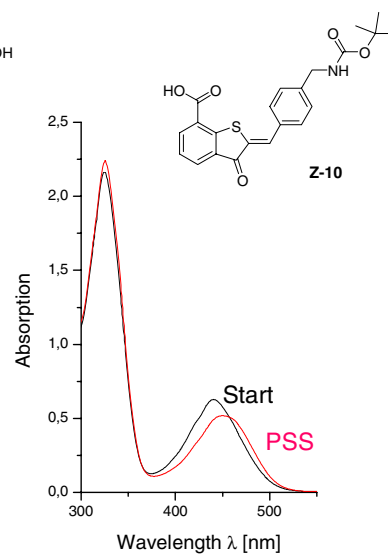
$c = 1.24 \times 10^{-4} \text{ mol/l (MeOH)}$

$\lambda = 406 \text{ nm}$

Z-isomer:  $\lambda_{\text{max}} = 444 \text{ nm}$

E-isomer:  $\lambda_{\text{max}} = 461 \text{ nm (pss)}$

Z-isomer:  $\epsilon = 8667 \text{ dm}^3 \times \text{M}^{-1} \times \text{cm}^{-1}$



$c = 1.02 \times 10^{-4} \text{ mol/l (MeOH)}$

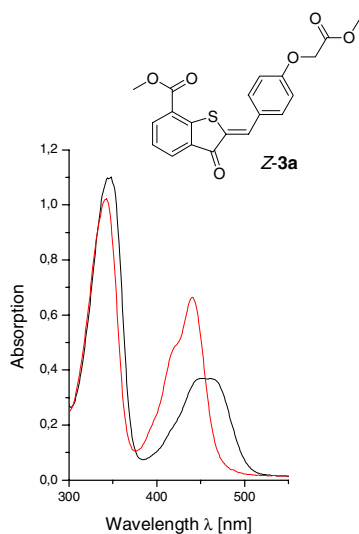
$\lambda = 406 \text{ nm}$

Z-isomer:  $\lambda_{\text{max}} = 442 \text{ nm}$

E-isomer:  $\lambda_{\text{max}} = 450 \text{ nm (pss)}$

Z-isomer:  $\epsilon = 6155 \text{ dm}^3 \times \text{M}^{-1} \times \text{cm}^{-1}$

## UV/VIS-Data



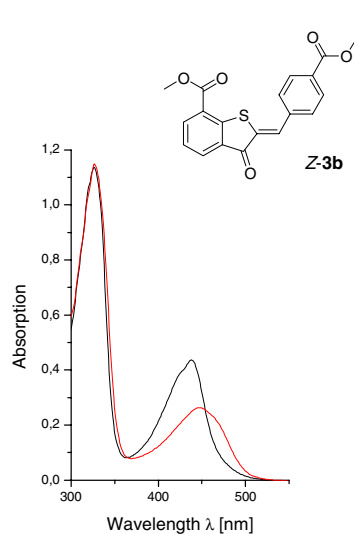
$c = 4.83 \times 10^{-5} \text{ mol/l (DCM)}$

$\lambda = 406 \text{ nm}$

Z-isomer:  $\lambda_{\text{max}} = 440 \text{ nm}$

E-isomer:  $\lambda_{\text{max}} = 450 \text{ nm (pss)}$

Z-isomer:  $\epsilon = 13830 \text{ dm}^3 \times \text{M}^{-1} \times \text{cm}^{-1}$



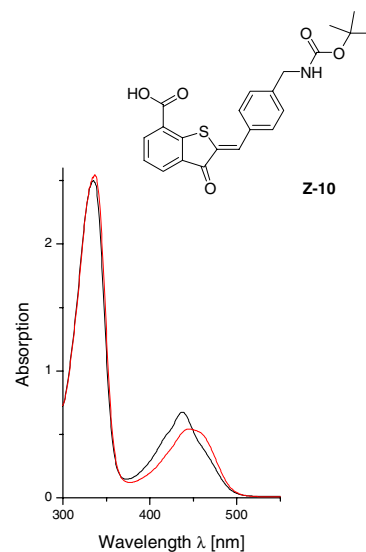
$c = 4.02 \times 10^{-5} \text{ mol/l (DCM)}$

$\lambda = 406 \text{ nm}$

Z-isomer:  $\lambda_{\text{max}} = 438 \text{ nm}$

E-isomer:  $\lambda_{\text{max}} = 447 \text{ nm (pss)}$

Z-isomer:  $\epsilon = 10846 \text{ dm}^3 \times \text{M}^{-1} \times \text{cm}^{-1}$



$c = 1.07 \times 10^{-5} \text{ mol/l (DCM)}$

$\lambda = 406 \text{ nm}$

Z-isomer:  $\lambda_{\text{max}} = 438 \text{ nm}$

E-isomer:  $\lambda_{\text{max}} = 450 \text{ nm (pss)}$

Z-isomer:  $\epsilon = 6290 \text{ dm}^3 \times \text{M}^{-1} \times \text{cm}^{-1}$

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