A donor–acceptor substituted molecular motor

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General Remarks

^{1}H NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Varian Unity Plus Varian-500 (500 MHz). ^{13}C NMR spectra were recorded on a Varian VXR-300 (75 MHz) or a Varian Unity Plus Varian-500 (125 MHz). Unless stated otherwise, ^{1}H NMR data are obtained at 300 MHz and ^{13}C NMR data are obtained at 75 MHz measurement, both in $CDCl_3$. Chemical shifts are denoted in δ-unit (ppm) relative to $CDCl_3$, and the NMR data of C_2-symmetrical compounds are listed for half a molecule. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and b (broad) for ^{1}H NMR. For ^{13}C NMR the carbon atoms are assigned as t (primary carbon), d (secondary carbon), s (tertiary carbon) and q (quaternary carbon). CD spectra were recorded on a JASCO J-715 spectropolarimeter and UV measurements were performed on a Hewlett-Packard HP 8453 FT Spectrophotometer using UVASOL grade solvents (Merck). MS spectra were obtained with a Jeol JMS-600 spectrometer by Mr. A. Kieviet. Column chromatography was performed on silica gel (Aldrich 60, 230-400 mesh). HPLC analyses were performed on a Waters HPLC system

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equipped of a 600E solvent delivery system and a 996 Photodiode Array Detector. Preparative HPLC was performed by Mr. M. van Gelder on a preparative Gilson HPLC system consisting of a 231XL sampling injector, a 306 (10SC) pump, an 811C dynamic mixer, a 805 manometric module, with a 119 UV-VIS detector and a 202 fraction collector, using the (chiral) columns as mentioned. Elution speed was 1 ml min^{-1}, unless stated otherwise. Elemental analyses were performed in our microanalytical department by Mr. J. Hommes. X-ray diffraction measurements were performed by Drs. A. Meetsma in our laboratory employing a Bruker SMART APEX CCD diffractometer. If necessary, solvents were distilled and dried before use by standard methods. Reagents and starting materials were used as obtained from Aldrich, Acros Chimica, Fluka or Merck.

Irradiation experiments.

Irradiations were performed with an 150 W Oriel Xe-lamp attached to an Oriel monochromator or a 180 W Oriel Hg-lamp adapted with a suitable Mercury line filter for 313, 365, 405 and 435 nm irradiations (typical bandwidth 10 nm). Photostationary states are ensured by monitoring composition changes in time

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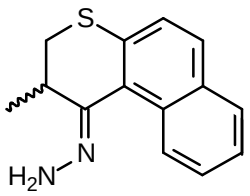
by taking UV spectra at distinct intervals until no changes were observed. Ratios of the different forms of the molecular switches were determined by HPLC by monitoring at the isosbestic point or by NMR analysis. HPLC elution times and NMR details are denoted throughout the synthetic procedures.



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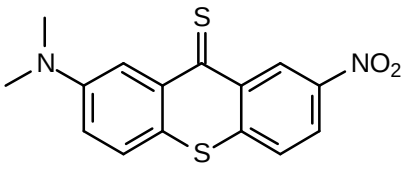

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***N*,*N*-dimethyl-9-(2-methyl-2,3-dihydro-1*H*-benzo[*f*]thiochromen-1-ylidene)-7-nitro-9*H*-thioxanthen-2-amine 1**.

Under a nitrogen atmosphere a solution of 2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1-one hydrazone **2** (242 mg, 1 mmol) in dry dichloromethane (40 mL) was cooled to -10°C, whereupon $MgSO_4$ (approximately 350 mg), Ag_2O (350 mg, 2.02 mmol) and a saturated solution of KOH in methanol (0.8 mL) were added subsequently. The mixture was stirred while allowing to warm to 0°C whereupon the color of the mixture

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turned red. After stirring for 10 min at 0°C, the deep red suspension was filtered into another ice-cooled bulb and the remaining residue was washed with cold dichloromethane. To the deep red solution was added a solution of 1 mmol (316 mg) of thioketone **3** in dichloromethane. Nitrogen evolution was observed and the red color of the solution slowly disappeared. The reaction mixture was stirred overnight and the reaction temperature was allowed to raise to room temperature. The solvents were evaporated under reduced pressure to give the episulfide as a solid residue (170 mg, 0.33 mmol, 33%) that was used without further purification.

Under a nitrogen atmosphere Cu-bronze (0.95 g) was added to a stirred solution of 170 mg of crude episulfide (0.33 mmol) in *p*-xylene. After heating at reflux overnight, the reaction mixture was allowed to cool to room temperature. The brown copper residue was removed by silica gel filtration and washed with dichloromethane, and the solvents were evaporated under reduced pressure. The crude product which was purified by rapid flash column chromatography (SiO_2, *n*-hexane : CH_2Cl_2 2 : 1, R_f = 0.17) to give 135 mg (0.28 mmol, 85%) of the desired alkene as a *cis / trans* mixture. Crystallization from absolute ethanol first yielded crystals of *cis*-**1** and further cooling of the mother liquid resulted in precipitation of *trans*-**1**. Solid material decomposes

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above 270°C, ^{1}H NMR cis-**1**: δ 0.86 (d, , *J* = 6.9 Hz, 3H), 3.05 (s, 6H), 3.13 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.57 (dt, *J* = 9.5, 3.9 Hz 1H), 4.31 (m, 1H), 6.85 (bd, J= 8.4 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.39-7.46 (m, 3H), 8.01 (bd, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 1H). *trans*-**1**: ^{1}H NMR δ 0.74 (d, *J* = 6.9 Hz, 3H), 2.20 (s, 6H), 3.03 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.76 (m, 1H), 3.92 (m, 1H), 5.73 (bs, 1H), 6.14 (bd, *J* = 7.5 Hz, 1H), 6.92-7.21 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.37-7.55 (m, 3H), 7.63 (d, *J* = 8.4 Hz, 1H), 8.05 (dd, *J* = 8.7, 2.1 Hz, 1H), 8.37 (d, *J* = 2.1 Hz, 1H). Due to solubility limitations for the stable *cis*-isomer and the small amounts of unstable forms that are only generated *in situ* ^{13}C NMR was only performed on the stable *trans*-isomer (*2'R*)-(*M*)-*trans*-**1**: ^{13}C NMR δ 19.78 (t), 33.18 (s), 37.29 (d), 40.61 (t), 112.48 (s), 114.33 (s), 119.07 (q), 121.71 (s), 122.94 (s), 124.52 (s), 124.86 (s), 125.87 (s), 126.37 (s), 127.09 (s), 127.37 (q), 127,89 (s), 127.97 (s), 128.28 (s), 131.04 (q), 131.82 (q), 135.51 (q), 137.06 (q), 137.86 (q), 138.52 (q), 141.72 (q), 146.31 (q), 146.77 (q), 149.75 (q).

Resolution was performed on a Chiralcel OD HPLC column for preparative separation using *n*-heptane : 2-propanol (90 : 10) for *trans*-**1** (elution times: 6.02 min for (2'*R*)-(*M*)-*trans*-**1** and 11.75 min for (2'*S*)-(*P*)-*trans*-**1** (not used in

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the experiments). For *cis*-**1** *n*-heptane : 2-propanol (99 : 1) was used on the same chiral column to give (2'*R*)-(*M*)-*cis*-**1** after 16.40 min and (2'*S*)-(*P*)-*cis*-**1** (again not used for the experiments) after 19.69 min. For analytical HPLC the same column was used with *n*-heptane : 2-propanol 90 : 10 as an eluent. Elution times were: (2'*R*)-(*M*)-*trans*-**1**: 6.02 min; (2'*R*)-(*M*)-*cis*-**1**: 6.73 min; (2'*R*)-(*P*)-*cis*-**1**: 6.80 min; (2'*R*)-(*P*)-*trans*-**1**: 8.97 min.

(2'R)-(M)-trans-**1**: UV (*n*-hexane): $\lambda_{max}(\varepsilon)$ 256.2 (40156), 273.6 (28547), 357.0 (5607); CD (*n*-hexane): $\lambda_{max}(\Delta\varepsilon)$ 255.6 (+ 102.7), 276.4 (-95.6), 326.8 (-15.6), 356.2 (+10.0). UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ 258 (43373), 273 (32167), 308 (15418), 360 (5633), 429 (2211); CD ($CHCl_3$): $\lambda_{max}(\Delta\varepsilon)$ 257 (+ 102.3), 279 (-102.1), 327 (-18.3), 357 (+10.1).

(2'R)-(M)-cis-**1**: UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ 257 (45067), 274 (35023), 366 (7136); 429 (2858). CD ($CHCl_3$): $\lambda_{max}(\Delta\varepsilon)$ 259.2 (+ 66.9), 281.0 (-121.9), 327.2 (-12.4), 363.4 (+17.4).

The crystal structure determination of (2'*R*)-(*M*)-cis-**1** was performed on a red platelet of dimensions 0.52 × 0.44 × 0.33 mm obtained after crystallization from ethanol. Data: Orthorhombic $P2_12_12_1$, a = 7.7426(3) Å, b = 12.4048(5) Å,

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c = 24.2867(1) Å; V = 2388.36(16) $Å^3$. Z = 4. T = 100 K. The structure was solved to a final R index of 0.0170 for 6379 unique reflections.

HRMS calcd for $C_{29}H_{24}N_2O_2S_2$: 496.12792, found: 496.12798, anal. calcd: C 70.13, H 4.87, N 5.64, S 12.91, found: C 69.70, H 4.76, N 5.59, S 12.86.

NMR details for the unstable isomers were obtained from photostationary states in deuterated chloroform solution: unstable-*trans*-**1**: ^{1}H NMR δ 1.06 (d, *J* = 6.9 Hz, 3H), 2.25 (s, 6H), 2.78-2.89 (m, 1H), 3.37 (t, *J* = 11.6 Hz, 1H), 3.59 (bt, *J* = 8.8 Hz, 1H), 5.80 (d, *J* = 2.1 Hz, 1H,), 6.19 (dd, J= 8.6, 2.1 Hz, 1H), 6.92-7.21 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.37-7.55 (m, 3H), 7.63 (d, *J* = 8.4 Hz, 1H), 8.12 (dd, *J* = 8.6, 2.1 Hz, 1H), 8.42 (d, *J* = 2.7 Hz, 1H); unstable-*cis*-**1**: ^{1}H NMR δ 1.25 (d, *J* = 6.9 Hz, 3H), 2.88 (m, 1H), 3.07 (s, 6H), 3.41 (m, 1H), 3.59 (dd, *J* = 7.2, 2.7 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 6.9 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.29-7.77 (m, 9H).

2,3-Dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1-one hydrazone 2.

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This compound was synthesized in via a known procedure.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (br d, *J* = 8.4 Hz, 1H), 7.75 (br d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.41 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.54 (ddq, *J* = 9.9, 6.2, 7.0 Hz, 1H), 3.20 (dd, *J* = 12.8, 6.2 Hz, 1H), 2.71 (dd, *J* = 12.8, 9.9 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.33, 135.72, 132.95, 132.09, 130.82, 127.98, 127.71, 126.69, 126.12, 125.90, 125.13, 36.41, 34.00, 14.72; HRMS calcd for $C_{14}H_{14}N_2S$ 242.0878; found 242.0881.

7-(*N*,*N*-dimethylamino)-2-nitro-*9H*-thioxanthene-9-thione 3.

This compound was synthesized via a known procedure.[2] ^{1}H NMR δ 3.05 (s, 6H), 7.36 (dd, *J* = 8.7, 2.9 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.94 (dd, *J* = 8.8, 2.9 Hz, 1H), 8.10 (d, *J* = 2.9 Hz, 1H), 8.30 (dd, *J* = 8.8, 2.6 Hz, 1H), 9.67 (d, *J* = 2.6 Hz, 1H). HRMS calcd for $C_{15}H_{12}N_2O_2S$ 316.034; found 316.035.

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