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In control of the speed of rotation in molecular motors. Unexpected retardation of rotary motion

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General Procedure. Melting points (uncorrected) were determined on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. ^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz), a Varian VXR-300 (300 MHz) or a Varian Unity Plus Varian-500 (500 MHz). ^{13}C NMR spectra were recorded on a Varian Gemini 200 (50 MHz), a Varian VXR-300 (75 MHz) or a Varian Unity Plus Varian-500 (125 MHz). Chemical shifts are denoted in δ -unit (ppm) relative to CDCl_3 . MS spectra were obtained with a JEOL JMS-600 spectrometer by the electron ionization (EI) procedure.

Crystal data for 5a. C₂₆H₂₂, monoclinic, space group P2₁/c, a = 7.4391(4), b = 26.165(2), c = 9.2788(6) Å, V = 1804.8(2) Å³, Z = 4, D_x = 1.231 g cm⁻³. A colorless colored block shaped crystal obtained by recrystallization from *n*-hexane, with the dimensions of 0.480 × 0.300 × 0.210 mm mounted on a glass filter was aligned on a Bruker SMART APEX CCD diffractometer (Platform with full three circle goniometer). The crystal was cooled to 90 K using the *Bruker* KRYOFLEX low-temperature device. Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (SIEMENS). Generator settings were 50 KV/ 40 mA. wR(*F*²) = 0.1098 for 3910 reflections and 323 parameters and *R*(*F*) = 0.0411 for 3449 reflections with F_o ≥ 4.0 σ(*F*_o) criterion of observability.

Synthetic Scheme

2-methyl-3,4-dihydro-1(2*H*)-naphthalenone hydrazone (8) The ketone 2-methyl-3,4-dihydro-1(2*H*)-naphthalenone (2.00 g, 12.49 mmol) was refluxed overnight in a mixture of ethanol (15 mL) and hydrazine monohydrate (15 mL). After cooling, the ethanol was evaporated *in vacuo* and the slightly yellow residue was dissolved in diethyl ether. The organic layer was washed twice with water, dried (Na₂SO₄), and concentrated *in vacuo* to yield pure **8** (1.90 g, 10.92 mmol, 87%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 7.95 – 8.00 (m, 1H), 7.14 – 7.20 (m, 2H), 7.07 – 7.11 (m, 1H),

5.38 (br, 2H), 3.10 – 3.20 (m, 1H), 2.92 – 3.04 (m, 1H), 2.65 (m, 1H), 1.94 – 2.06 (m, 1H), 1.75 – 1.84 (m, 1H), 1.17 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (200 MHz, CDCl_3 , 25°C): δ 150.18 (s), 137.22 (s), 132.52 (s), 128.39 (d), 127.64 (d), 126.10 (d), 124.16 (d), 28.46 (t), 25.96 (d), 25.20 (t), 13.65 (q); HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2$: 174.1157; found: 174.1162.

General procedure for the synthesis of thiiranes (episulfides). Under a nitrogen atmosphere a solution of hydrazone **8** (200 mg, 1.15 mmol) in CH_2Cl_2 (15 mL) was cooled to -10°C . MgSO_4 (450 mg), Ag_2O (450 mg) and a saturated solution of KOH in methanol (1 mL) were added successively. After stirring the mixture for 30 min at -10°C a purple solution of the diazo compound was obtained. When only an orange or red color was observed more Ag_2O and KOH in methanol were added and/or the temperature was allowed to raise to 0°C . The purple solution was filtered into another ice-cooled flash and the appropriate thioketone was added. Nitrogen evolution was observed and thioketone was added until the nitrogen formation stopped and the purple color had disappeared. Stirring was continued overnight and the reaction temperature was allowed to raise to room temperature. The reaction mixture was concentrated *in vacuo* to give a residue ready for further purification.

Dispiro[2-methyl-3,4-dihydro-2H-naphthalene-1, 2'-thiirane-3', 9''-(9''H)-thioxanthene] (14)

See general procedure for synthesis of thiiranes. Starting from hydrazone **8** (200 mg, 1.15 mmol) and thioketone **10** (182 mg, 0.80 mmol), thiirane **14** was obtained as a white solid (204 mg, 0.55 mmol, 48% yield based on hydrazone) after recrystallization from ethanol. ^1H NMR (300 MHz, CDCl_3 , 25°C): δ 7.81 (dd, $J = 7.3, 1.5$ Hz, 1H), 7.73 (dd, $J = 7.3, 1.1$ Hz, 1H), 7.44 (dd, $J = 7.3, 1.5$ Hz, 1H), 7.20 – 7.31 (m, 2H), 7.10 – 7.15 (m, 3H), 6.98, (t, $J = 7.3$ Hz, 1H), 6.83 – 6.91 (m, 2H), 6.66 (t, $J = 7.3$ Hz, 1H), 2.76 – 2.85 (m, 2H), 2.00 – 2.15 (m, 1H), 1.43 – 1.52 (m, 1H), 1.24 – 1.38 (m, 1H), 0.98 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3 , 25°C): δ 136.98 (s), 135.23 (s), 134.99 (s), 133.96 (s), 133.17 (s), 130.05 (s), 129.97 (d), 128.90 (d), 128.49 (d), 126.55 (d), 125.58 (d), 125.54 (d), 125.24 (d), 125.24 (d), 125.17 (d), 124.81 (d), 124.01 (d), 122.28 (d), 65.05 (s), 64.88 (s), 33.58 (d), 25.32 (t), 22.91 (t), 17.06 (q); HRMS calcd for $\text{C}_{24}\text{H}_{20}\text{S}_2$: 372.1006; found: 372.0991.

9-(2-Methyl_{axial}-3,4-dihydro-2H-naphthalen-1-ylidene)-9H-thioxanthene (2a) To a solution of thiirane **14** (80 mg, 0.22 mmol) in *p*-xylene (10 mL), Cu-bronze (55 mg, 0.88 mmol) was added. The resulting suspension was refluxed overnight. The mixture was carefully filtered while hot and the residue was washed with *p*-xylene. The filtrate was concentrated *in vacuo* to yield pure **2a** (70 mg, 0.21 mmol, 94%) as a white solid. ^1H NMR (500 MHz, benzene- d_6 , 25°C): δ 7.46 (d, $J = 7.0$ Hz, 1H), 7.45 (d, $J = 7.7$ Hz, 1H), 7.40 (d, $J = 7.7$ Hz, 1H), 7.04 – 6.93 (m, 4H), 6.89 (dt, $J = 7.3, 1.1$ Hz, 1H), 6.81 – 6.77 (m, 2H), 6.71 – 6.67 (m, 2H), 3.78 (ddq, $J = 7.0, 6.6, 6.6$ Hz, 1H), 2.78 (ddd, $J = 15.4, 7.5, 7.2$ Hz, 1H), 2.60 (ddd, $J = 15.4, 6.4, 6.0$ Hz, 1H), 2.16 (dddd, $J = 7.2, 6.6, 6.6, 6.4$ Hz, 1H), 1.35 (dddd, $J = 7.5, 6.6, 6.6, 6.0$ Hz, 1H), 0.63 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3 , 25°C): δ 139.05 (s), 138.58 (s), 138.58 (s), 137.11 (s), 135.64 (s), 134.75 (s), 134.07 (s), 133.80 (s), 129.20 (d), 128.16 (d), 126.31 (d), 126.23 (d), 125.74 (d), 125.55 (d), 125.55 (d), 124.62 (d), 124.54 (d), 124.54 (d), 124.42 (d), 123.00 (d), 28.72 (t), 28.58 (d), 25.83 (t), 18.51 (q); HRMS calcd for $\text{C}_{24}\text{H}_{20}\text{S}$: 340.1286; found: 340.1283.

UV (*n*-hexane, λ ϵ): 273 nm (25600), 321 nm (10900)

Dispiro[2-methyl-3,4-dihydro-2H-naphthalene-1, 2'-thiirane-3', 10''-(9'',9''-dimethyl-9'',10''-dihydro-anthracene)] (15) See general procedure for synthesis of thiiranes. Starting from hydrazone **8** (100 mg, 0.57 mmol) and thioketone **11** (70 mg, 0.29 mmol), thiirane **15** (94 mg, 0.25 mmol, 43% yield based on hydrazone) was obtained as a white solid after recrystallization from ethanol. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 8.08 – 8.05 (m, 1H), 7.81 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.19 (m, 3H), 7.11 – 7.05 (m, 2H), 6.96 – 6.90 (m, 1H), 6.84 (t, *J* = 7.3 Hz, 2H), 2.84 – 2.71 (m, 1H), 2.53 (m, 1H), 2.03 (m, 1H), 1.77 (s, 3H), 1.59 – 1.46 (m, 1H), 1.26 (s, 3H), 1.26 – 1.17 (m, 1H), 1.01 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃, 25°C): δ 147.33 (s), 147.03 (s), 137.99 (s), 137.99 (s), 134.98 (s), 133.85 (s), 132.03 (d), 131.02 (d), 128.34 (d), 127.93 (d), 127.25 (d), 127.17 (d), 126.89 (d), 125.09 (d), 124.58 (d), 124.50 (d), 124.10 (d), 123.07 (d), 66.18 (s), 65.48 (s), 39.39 (s), 35.28 (d), 34.32 (q), 27.91 (q), 24.74 (t), 24.30 (t), 19.09 (q); HRMS calcd for C₂₇H₂₆S: 382.1755; found: 382.1744.

9,9-dimethyl-10-(2-methyl_{axial}-3,4-dihydro-2H-naphthalen-1-ylidene)-9,10-dihydro-anthracene (3a) To a solution of thiirane **15** (80 mg, 0.21 mmol) in *p*-xylene (10 mL), Cu-bronze (40 mg, 0.63 mmol) was added. This suspension was refluxed overnight. The mixture was carefully filtered while hot and the residue was washed with *p*-xylene. The filtrate was concentrated *in vacuo* to yield pure **3a** (70 mg, 0.20 mmol, 95%) as a light yellow solid. ¹H NMR (500 MHz, CDCl₃, 25°C): δ 7.56 – 7.54 (m, 1H), 7.51 – 7.50 (m, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.21 – 7.20 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.10 – 6.98 (m, 2H), 6.87 – 6.79 (m, 3H), 6.69 (d, *J* = 7.7 Hz, 1H), 3.97 (ddq, *J* = 7.0, 6.6, 4.0 Hz, 1H), 2.96 (ddd, *J* = 15.7, 7.7, 7.5 Hz, 1H), 2.85 (ddd, *J* = 15.7, 6.2, 6.2 Hz, 1H), 2.44 (dddd, *J* = 13.2, 7.5, 6.6, 6.2 Hz, 1H), 1.88 (s, 3H), 1.64 (dddd, *J* = 13.2, 7.7, 6.2, 4.0 Hz, 1H), 1.61 (s, 3H), 0.65 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃, 25°C): δ 147.17 (s), 146.51 (s), 140.10 (s), 139.06 (s), 138.41 (s), 136.47 (s), 136.30 (s), 130.74 (s), 130.17 (d), 128.95 (d), 127.37 (d), 126.94 (d), 126.70 (d), 126.13 (d), 125.90 (d), 124.93 (d), 124.67 (d), 124.40 (d), 123.13 (d), 122.70 (d), 40.31 (s), 30.04 (t), 29.90 (d), 29.62 (q), 27.26 (t), 24.47 (q), 19.44 (q); HRMS calcd for C₂₇H₂₆: 350.2035; found: 350.2039.

UV (*n*-hexane, χ ε): 297 nm (16100)

10,11-Dihydro-dibenzo[*a,d*]cycloheptene-5-thione (12)

10,11-Dihydro-dibenzo[*a,d*]cycloheptene-5-one (2.00 g, 9.62 mmol) was dissolved in toluene (45 mL). P₂S₅ (8.60 g, 38.69 mmol, ~ 4 eq.) was added and this mixture was refluxed overnight. After cooling, the mixture was filtered and the residue was washed three times with hot toluene. The combined toluene layers were concentrated *in vacuo* to yield a blue oil. The oil was purified by column chromatography (silica gel, *n*-hexane/CH₂Cl₂ 1/1, R_f = 0.40 for starting ketone, R_f = 0.80 for product) to yield pure **12** (1.25 g, 55.80 mmol, 58%) as a blue solid. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 7.74 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.34 (dt, *J* = 7.7, 1.1 Hz, 2H), 7.18 (dt, *J* = 7.7, 1.1 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 3.16 (s, 4H); ¹³C NMR (125 MHz, CDCl₃, 25°C): δ 246.53 (s), 149.27 (s), 136.37 (s), 130.88 (d), 129.44 (d), 128.87 (d), 126.18 (d), 33.73 (t); HRMS calcd for C₁₅H₁₂S: 224.0660; found: 224.0669.

Dispiro[2-methyl-3,4-dihydro-2H-naphthalene-1, 2'-thiirane-3', 5''-(10'',11''-dihydro-5''H-dibenzo[*a,d*]cycloheptene)] (16) See general procedure for synthesis of thiiranes. Starting from hydrazone **8** (400 mg, 2.30 mmol) and thioketone **12** (412 mg, 1.84 mmol), thiirane **16** (380 mg, 1.03 mmol, 45% yield based on hydrazone) was obtained as yellow crystals after recrystallization from ethanol. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 7.81 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.22 – 6.95 (m, 7H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.60 (t, *J* = 7.7 Hz, 1H), 3.41 – 3.34 (m, 1H), 3.19 – 2.90 (m, 4H), 2.32 – 2.14 (m, 2H), 1.70 – 1.59 (m, 2H), 1.14 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃, 25°C): δ 141.26 (s), 138.15 (s), 137.86 (s), 137.27(s), 135.68 (s), 132.43 (s), 131.26 (s), 131.19 (s), 131.15 (s), 129.85 (d), 127.98 (d), 127.71 (d), 127.46 (d), 126.94 (d), 126.77 (d), 125.92 (d), 125.26 (d), 124.03 (d), 70.73 (s), 65.71 (s), 34.91 (d), 33.36 (t), 29.75 (t), 26.59 (t), 24.48 (t), 19.04 (q); HRMS calcd for C₂₆H₂₄S: 368.1599; found: 368.1591.

5-(2-Methyl-3,4-dihydro-2H-naphthalen-1-ylidene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (4a) To a solution of thiirane **16** (167 mg, 0.45 mmol) in toluene (5 mL), PPh₃ (238 mg, 0.91 mmol) was added. This mixture was refluxed overnight. After cooling, the solvent was evaporated *in vacuo* to yield a yellow residue. Column chromatography (silica gel, *n*-hexane/CH₂Cl₂ 15/2, *R_f* = 0.41 for **4a**) gave pure **4a** (107 mg, 0.32 mmol, 71%) as a colorless oil which solidified upon standing. ¹H NMR (125 MHz, CDCl₃, 25°C): δ 7.26 – 7.14 (m, 4H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.98 (m, 3H), 6.78 (dt, *J* = 7.7, 0.7 Hz, 1H), 6.75 – 6.73 (m, 2H), 6.68 (dd, *J* = 7.7, 1.1 Hz, 1H), 3.61 (ddd, *J* = 14.1, 12.1, 5.1 Hz, 1H), 3.49 (ddd, *J* = 16.5, 5.1, 5.1 Hz, 1H), 3.27 (ddq, *J* = 7.0, 6.6, 6.2 Hz, 1H), 2.97 (ddd, *J* = 16.5, 12.1, 5.1 Hz, 1H), 2.84 (ddd, *J* = 14.1, 5.1, 5.1 Hz, 1H), 2.83 – 2.76 (m, 2H), 2.24 (dddd, *J* = 13.2, 6.6, 6.6, 6.6 Hz, 1H), 1.47 (dddd, *J* = 13.2, 6.6, 6.6, 6.6 Hz, 1H), 0.70 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (200 MHz, CDCl₃, 25°C): δ 143.01 (s), 140.73 (s), 139.76 (s), 138.62 (s), 138.18 (s), 137.29 (s), 135.94 (s), 135.16 (s), 130.82 (d), 130.08 (d), 129.85 (d), 128.28 (d), 127.30 (d), 127.00 (d), 126.90 (d), 126.50 (d), 126.36 (d), 125.86 (d), 125.53 (d), 124.46 (d), 33.18 (t), 31.51 (t), 31.04 (d), 30.53 (t), 27.44 (t), 18.59 (q); HRMS calcd for C₂₆H₂₄: 336.1878; found: 336.1872.

UV (*n*-hexane, λ_c ε): 274 nm (14300)

Dispiro[2-methyl-3,4-dihydro-2H-naphthalene-1, 2'-thiirane-3', 5''(5''H-dibenzo[*a,d*]cycloheptene)] (17) See general procedure for synthesis of thiiranes. Starting from hydrazone **8** (200 mg, 1.15 mmol) and thioketone **13** (150 mg, 0.67 mmol), thiirane **17** (126 mg, 0.34 mmol, 30% yield based on hydrazone) was obtained as a white solid after recrystallization from ethanol. ¹H NMR (300 MHz, CDCl₃, 25°C): δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.24 (m, 4H), 7.08 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.96 (d, *J* = 11.7 Hz, 1H), 6.88 – 6.84 (m, 3H), 6.68 – 6.44 (m, 3H), 2.97 – 2.71 (m, 2H), 2.30 – 2.18 (m, 1H), 1.44 – 1.36 (m, 1H), 1.27 – 1.18 (m, 1H), 1.02 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃, 25°C): δ 138.48 (s), 137.83 (s), 136.57 (s), 134.90 (s), 134.12 (s), 132.21 (s), 131.91 (d), 131.33 (d), 130.19 (d), 129.98 (d), 129.54 (d), 128.38 (d), 127.88 (d), 127.82 (d), 127.74 (d), 126.87 (d), 126.76 (d), 126.42 (d), 126.13 (d), 123.54 (d), 69.92 (s), 65.18 (s), 34.54 (d), 26.75 (t), 24.29 (t), 19.62 (q); HRMS calcd for C₂₆H₂₂S: 366.1442; found: 366.1431.

5-(2-Methyl_{axial}-3,4-dihydro-2H-naphthalen-1-ylidene)-5H-dibenzo[*a,d*]cycloheptene (5a) To a solution of thiirane **17** (100 mg, 0.27 mmol) in toluene (5 mL), PPh₃ (143 mg, 0.54 mmol) was added. This mixture was refluxed overnight. After cooling the solvent was evaporated *in vacuo* to yield an

oily residue. Column chromatography (silica gel, *n*-hexane/CH₂Cl₂ 5/1, *R_f* = 0.45 for **5a**) gave pure **5a** (63 mg, 0.19 mmol, 70%) as a white solid. ¹H NMR (500 MHz, CDCl₃, 25°C): δ 7.44 – 7.33 (m, 4H), 7.25 (dt, *J* = 8.1, 1.8 Hz, 1H), 7.16 (dt, *J* = 7.3, 1.1 Hz, 1H), 7.07 – 7.04 (m, 4H), 6.96 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.83 (dd, *J* = 7.7, 0.7 Hz, 1H), 6.64 (t, *J* = 7.7 Hz, 1H), 6.21 (dd, *J* = 7.1, 1.1 Hz, 1H), 3.23 (ddq, *J* = 6.6, 6.6, 5.9 Hz, 1H), 2.82 (ddd, *J* = 15.8, 7.3, 7.0 Hz, 1H), 2.76 (ddd, *J* = 15.8, 6.6, 6.6 Hz, 1H), 2.24 (dddd, *J* = 13.2, 7.0, 6.6, 6.6 Hz, 1H), 1.44 (dddd, *J* = 13.2, 7.3, 6.6, 5.9 Hz, 1H), 0.57 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃, 25°C): δ 140.76 (s), 139.76 (s), 139.55 (s), 138.76 (s), 135.27 (s), 135.22 (s), 135.04 (s), 134.42 (s), 131.22 (d), 131.14 (d), 130.19 (d), 128.43 (d), 128.18 (d), 128.03 (d), 127.97 (d), 127.94 (d), 127.55 (d), 127.05 (d), 126.27 (d), 126.15 (d), 126.15 (d), 124.37 (d), 30.45 (t), 30.21 (d), 27.55 (t), 19.38 (q); HRMS calcd for C₂₆H₂₂: 334.1722; found: 334.1722.

UV (*n*-hexane, λ ε): 224 nm (41200), 227 nm (41300), 264 nm (21800), 277 nm (23700)

Photochemical and thermal conversions of compounds 2a – 5a at –40°C monitored by UV-spectroscopy. A solution of compound **2a** – **5a** in *n*-hexane (UV-concentration) was transferred into a UV-fluorescence-cuvet. The sample was cooled to –40°C (Peltier element controller) inside the UV-spectrometer. Subsequently, the sample was irradiated with a Hg-lamp applying a 313 nm filter. At regular time intervals UV-spectra were recorded in order to monitor conversion of starting material into product(s). Irradiation was ceased when UV-spectra did not change anymore. Subsequently, the sample was allowed to raise to room temperature and a UV-spectrum was recorded. The sample was left overnight at room temperature and a UV-spectrum was recorded. Finally the sample was transferred to a flask equipped with a cooler and refluxed for 24 h. After cooling the sample, another UV-spectrum was recorded. The concentration of the sample changed to a little extent during this sequence of events. However, shapes of the spectra could be compared conveniently to draw reliable conclusions.

Irradiation of compound 2a. See general procedure. A solution of compound **2a** (1.360×10^{-5} M) was irradiated for 2 h after which no more changes were observed. In the UV-spectrum at the photostationary state maxima were observed at 253, 263, 300 and 378 nm, respectively. After heating the sample no significant changes in the UV-spectrum were observed anymore.

Irradiation of compound 3a. See general procedure. A solution of compound **3a** (2.528×10^{-5} M) was irradiated for 6 min after which no more changes were observed. In the UV-spectrum at the photostationary state maxima were observed at 263, 298, 333 and 348 nm, respectively. After heating the sample no significant changes in the UV-spectrum were observed anymore. See irradiation experiments monitored by ¹H NMR-spectroscopy for further characterization.

Irradiation of compound 4a. See general procedure. A solution of compound **4a** (2.745×10^{-5} M) was irradiated for 2 h after which no more changes were observed. In the UV-spectrum at the photostationary state one maximum was observed at 248 nm. After heating the sample no significant changes in the UV-spectrum were observed anymore.

Irradiation of compound 5a. See general procedure. A solution of compound **5a** (2.406×10^{-5} M) was irradiated for 20 min after which the photostationary state was reached. In the UV-spectrum at the

photostationary state maxima were observed at 228 and 278 nm, respectively. After heating the sample reversal to the initial UV-spectrum was observed. See irradiation experiments monitored by ^1H NMR-spectroscopy for further characterization.

Irradiation experiments with compounds 2a – 5a at room temperature monitored by NMR-spectroscopy.

Irradiation of compound 2a. In an NMR-tube olefin **2a** (2.5 mg, 7.35×10^{-3} mmol) was dissolved in toluene- d_8 (0.75 mL). This solution (9.8×10^{-3} M) was irradiated at room temperature for 21 h with a Hg-lamp with a Pyrex filter. An undefined black precipitate was observed while a ^1H NMR-spectrum of the reaction mixture revealed some unreacted starting material.

7,7,12-trimethyl-7,12,13,14-tetrahydrobenzo[a]perylene (7) In an NMR-tube olefin **3a** (2.5 mg, 7.14×10^{-3} mmol) was dissolved in benzene- d_6 (0.75 mL). This solution (9.5×10^{-3} M) was irradiated at room temperature for 21 h with a Hg-lamp with a Pyrex filter. ^1H NMR revealed a 47:53 ratio of **3a**:**7**. No separation of **3a** and **7** was achieved but from the ^1H NMR spectrum the signals of **3a** and **7** were observed separately. ^1H NMR (300 MHz, benzene- d_6 , 25°C) (**7**): δ 8.47 (d, $J = 8.1$ Hz, 1H), 8.42 (d, $J = 8.1$ Hz, 1H), 7.66 – 7.60 (m, 3H), 7.55 – 7.45 (m, 3H), 7.30 – 7.24 (m, 2H), 4.61 – 4.58 (m, 1H), 3.43 – 3.31 (m, 1H), 3.15 – 3.12 (m, 1H), 2.35 – 2.26 (m, 1H), 2.09 – 2.04 (m, 1H), 1.87 (s, 3H), 1.38 (s, 3H), 1.10 (d, $J = 7.0$ Hz, 3H); HRMS calcd for $\text{C}_{27}\text{H}_{24}$: 348.1878; found: 348.1891. ^1H NMR (300 MHz, benzene- d_6 , 25°C) (**3a**): δ 7.39 – 7.37 (m, 3H), 7.18 – 7.15 (m, 2H), 7.12 (d, $J = 7.7$ Hz, 1H), 7.07 – 7.01 (m, 2H), 6.86 – 6.74 (m, 3H), 6.65 (d, $J = 7.3$ Hz, 1H), 4.00 – 3.90 (m, 1H), 3.08 – 2.76 (m, 2H), 2.46 – 2.37 (m, 1H), 1.85 (s, 3H), 1.62 – 1.57 (m, 1H), 1.57 (s, 3H), 0.61 (d, $J = 7.0$ Hz, 3H).

Irradiation of compound 4a In an NMR-tube olefin **4a** (2.3 mg, 6.84×10^{-3} mmol) was dissolved in benzene- d_6 (0.75 mL). This solution (9.1×10^{-3} M) was irradiated at room temperature for 21 h with a Hg-lamp with a Pyrex filter. A ^1H NMR-spectrum of the reaction mixture revealed unreacted starting material (95%) and an undefined product (5%) which was not examined further.

5-(2-Methyl_{equatorial}-3,4-dihydro-2H-naphthalen-1-ylidene)-5H-dibenzo[a,d]cycloheptene (5a) In an NMR-tube olefin **5a** (6.9 mg, 2.06×10^{-2} mmol) was dissolved in benzene- d_8 (0.75 mL). This solution was irradiated at room temperature for 11 h with a Hg-lamp with a Pyrex filter. ^1H NMR revealed a 38:62 ratio of **5a** (Me_{ax}):**5b** (Me_{eq}). No separation of **5a** and **5b** was achieved but from the ^1H NMR spectrum the signals of **5a** and **5b** were observed separately. ^1H NMR (500 MHz, benzene- d_6 , 25°C) (**5b**): δ 7.60 (dd, $J = 7.3, 1.5$ Hz, 1H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.45 (dd, $J = 7.7, 0.7$ Hz, 1H), 7.19 – 7.13 (m, 2H), 7.10 – 7.01 (m, 3H), 6.96 – 6.81 (m, 3H), 6.77 (d, $J = 7.0$ Hz, 1H), 6.72 (d, $J = 11.7$ Hz, 1H), 6.58 (d, $J = 11.7$ Hz, 1H), 2.68 (ddq, $J = 11.8, 7.0, 5.9$ Hz, 1H), 2.59 – 2.54 (m, 2H), 1.73 (dddd, $J = 13.1, 7.1, 5.9, 5.9$ Hz, 1H), 1.00 (d, $J = 7.0$ Hz, 3H), 0.95 (dddd, $J = 13.1, 11.8, 6.6, 5.9$ Hz, 1H).

Kinetics studies of thermal isomerization of less-stable isomer 5b into stable isomer 5a by ^1H NMR spectroscopy. The kinetic conversions of the irradiated samples in toluene- d_8 at a constant temperature in the range 40 – 70°C. (The irradiation experiments described above were performed in benzene- d_6 . However, these thermal kinetic studies were carried out with toluene- d_8 since a solvent

with a higher boiling point was required. Irradiation in toluene-*d*₈ under same conditions as described above resulted in ratio's close to 38:62 of **5a:5b** at photostationary states) The NMR tube containing the sample (~10 mg of compound in 0.75 mL of solvent) was heated in a water bath and immediately cooled to 0°C to stop the reaction, when measured. At each temperature ¹H NMR spectra were recorded at 9 or 10 regular time intervals. The ratios of less-stable form/stable form were determined by comparison of the integral values of chemical shifts of less-stable form and stable form. With these ratios, the conversions of the less-stable form into the stable form were calculated and analyzed applying equations for first-order reaction. The rate constants (k) of isomerization were determined, and the thermal parameters ($\Delta G^\ddagger$, E_a , $\Delta H^\ddagger$, $\Delta S^\ddagger$ etc) subsequently. Finally the Gibbs energy of activation at room temperature (20°C, $\Delta^\ddagger G^\theta$), rate constant at room temperature (20°C, k^θ) and half life time at room temperature (20°C, $t_{1/2}^\theta$) were calculated.

Thermal conversion of **5b** into **5a**. Solvent: toluene-*d*₈. Method: ¹H NMR

T/(°C)	T/(K)	K (s ⁻¹)	t _{1/2} (h)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
40.05	313.20	$7.25 \pm 0.37 \times 10^{-6}$	26.57	107.7 ± 0.3
50.00	323.15	$2.23 \pm 0.06 \times 10^{-5}$	8.63	108.1 ± 0.1
60.00	333.15	$6.35 \pm 0.02 \times 10^{-5}$	3.03	108.7 ± 0.1
70.00	343.15	$1.73 \pm 0.03 \times 10^{-4}$	1.11	109.2 ± 0.1

$$A = 3.9954 \times 10^{10}$$

$$E_a = 94.4 \pm 3.8 \text{ kJ mol}^{-1}$$

$$\Delta^\ddagger H = 91.7 \pm 3.7 \text{ kJ mol}^{-1}$$

$$\Delta^\ddagger S = 51 \pm 11 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta^\ddagger G^\theta (20^\circ\text{C}) = 106.6 \pm 0.4 \text{ kJ mol}^{-1}$$

$$k^\theta (20^\circ\text{C}) = 6.13 (\pm 0.97) \times 10^{-7} \text{ s}^{-1}$$

$$t_{1/2}^\theta (20^\circ\text{C}) = 314.2 \pm 49.5 \text{ h}$$