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Synthesis, structural characterization and photoisomerization of cyclic stilbenes

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ABSTRACT

Six cyclic stilbene derivatives with hindered free rotation around the C(vinyl)-C(phenyl) single bond were synthesized by McMurry coupling. The torsion angles around the double and the single bond, and the C=C bond length were obtained for many of the compounds from their solid-state structures. The photochemical isomerization was subsequently investigated for all derivatives under various conditions. The parent 1-(1-tetralinylidene)tetralin underwent efficient oxidative electrocyclization. The 2,2,2',2'-tetramethylated analogue was resistant towards photooxidation, however, its *cis*-isomer thermally re-isomerized to the more stable *trans*-isomer.

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1. Introduction

The photochemistry of stilbene and its derivatives has been intensively studied over the last decades.^{1,2} In a number of reports, four- and five-membered cyclic stilbene derivatives have been employed as sterically restricted substrates since the torsion around the single bond is hindered in these systems.³ However, despite recent applications as light-driven molecular rotors,⁴ molecular force probes⁵ or model compounds for enantiodifferentiphotoisomerizations with chiral sensitizers,⁶ ating no comprehensive study on the photoinduced isomerization of cyclic stilbenes has been reported so far. Isolated examples have been described in the literature but no experimental details were given. This study aims to fill this gap by describing the synthesis and structural characterization of several cyclic stilbene derivatives as well as the results of photoisomerization experiments.

2. Results and discussions

2.1. Synthesis of cyclic stilbenes

Six cyclic compounds were chosen for the present study (Fig. 1) varying in the size of the attached ring (1-3 and 6) and/or the substitution pattern (3-5).

All derivatives were prepared in moderate to good combined yields of 22–73% by reductive coupling of the corresponding ketones with low valent titanium (Scheme 1; Table 1).^{7,8} In almost all cases, mixtures of both geometric isomers were obtained. Analysis of the crude reaction product of **1** by ¹H NMR spectroscopy revealed that, besides the desired stilbene **1**, the corresponding 1,2-diol (not shown) was formed. Subsequent column chromatography gave a 1:1 mixture of both isomers of **1**. Schroeder and co-workers have recently described the separation of these isomers via their picric acid complexes,⁹ but since these authors did not obtain pure *cis*-**1**, preparative HPLC was applied for their separation instead. The cis-



Fig. 1. Selected cyclic stilbene derivatives (only trans-isomers shown).



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isomer of **2** was clearly detected in an amount of ca. 5% by TLC and GC–MS analysis of the crude mixture but is known to be unstable towards ambient light.¹⁰ Consequently, solely the trans-isomer of **2** could be isolated in pure form. GC–MS analysis also revealed the presence of dimeric products and higher oligomers. Repeated crystallization of **3** gave two crops of pure *trans*-**3** and a third fraction of both isomers (ca. 2:1 in favour of *cis*-**3**). The cis-isomer of **3** was subsequently isolated from this mixture by preparative HPLC. Due to the known thermal instability of its cis-isomer,¹¹ the 2,2,2',2'-tetramethyl substituted substrate **5** gave exclusively its trans-isomer. The conversion of the McMurry coupling was low with approximately 50% in this case.



Scheme 1. Synthesis of 1–6 via McMurry coupling.

Table 1Product yields and selectivity for 1–6

| Compound | п | R | Yield (%) | Trans/cis ratio ^a |
|----------|---|-----------------------------|-----------|------------------------------|
| 1 | 1 | Н | 22 | 50:50 |
| 2 | 2 | Н | 70 | 100:0 ^b |
| 3 | 3 | Н | 52 | 80:20 |
| 4 | 3 | CH ₃ (5,7,5′,7′) | 73 | 52:48 |
| 5 | 3 | CH ₃ (2,2,2',2') | 30 | 100:0 ^b |
| 6 | 4 | Н | 51 | 70:30 |

^a Determined by ¹H NMR spectroscopic analysis of the crude product.

^b No cis-isomer detected.

2.2. Experimental ground-state geometries

For almost all derivatives, recrystallization from *n*-hexane or *n*-pentane gave suitable crystals for X-ray structure analysis. Solely *cis*-**4** gave a micro-crystalline, cotton like material. The structures of *cis*-**1**, *cis*- and *trans*-**3**, *trans*-**4** and *cis*-**6** are shown in Fig. 2. The structures of *trans*-**1** and *trans*-**6** were reported by us earlier.¹²

Stilbene derivatives are commonly characterized using three important structural parameters (Scheme 2): the torsion angles



Fig. 2. Molecular structures of cis-1, cis-3, trans-3, trans-4 and cis-6.

around the double (Θ) and the single bond (φ), and the C=C bond length (r), respectively.¹³ The values obtained experimentally from X-ray crystallographic analyses are summarized in Table 2 and are compared to those of parent stilbene. Noteworthy, different crystal modifications have been reported for *trans*-**2** and *trans*-**3**.



Scheme 2. Structural parameters (shown for trans-isomers).

| lable 2 | | | | | | | | | | |
|--------------|---------|--------|--------------|-----|------|--------|------|----------|-----|-----|
| Experimental | torsion | angles | Θ and | łφ, | bond | length | r of | stilbene | and | 1–6 |

| Compound | Θ (°) | φ(°) | <i>r</i> (Å) | Ref. |
|-----------------------------------|--------------|--------|----------------------|---------------|
| trans-Stilbene ^a | 1 | 5 | 1.324 (3) | 14a |
| <i>cis-</i> Stilbene ^b | _ | ~43 | 1.33 (2) | 15 |
| trans-1 | 1 | 0 | 1.327 (2) | 12 |
| cis- 1 | 3 | 4 | 1.330 (2) | This work |
| trans- 2^{c,d} | 1, 1 | 1, 0 | 1.335 (4), 1.349 (4) | 16 |
| trans- 2 ^d | 2 | 1 | 1.351 (1) | 17 |
| trans- 2 ^d | 0 | 2 | 1.351 (2) | 3e |
| cis- 2 ^c | 4, 9 | 21, 20 | 1.343 (2), 1.340 (2) | 18 |
| trans- 3 ^d | 6 | 46 | 1.348 (3) | This work, 19 |
| cis- 3 | 12 | 41 | 1.345 (3) | This work |
| trans- 4 ^e | 22 | 40 | 1.359 (4) | This work |
| trans- 5 ^f | 37 | 45 | 1.364 (3) | 11 |
| trans- 6 | 0 | 70 | 1.347 (2) | 12 |
| cis- 6 | 0 | 65 | 1.339 (2) | This work |

^a At 300 K for the non-disordered molecule.

^b Gas electron diffraction.

^c Two crystallographically independent molecules.

^d Different modifications.

^e Cis-isomer not obtained in crystalline form.

^f Cis-isomer thermally unstable and reisomerizes to trans-isomer.

Only the trans-isomers incorporating the four- and fivemembered rings (trans-1 and 2) are planar or almost planar with respect to their torsion angles Θ and φ . While the cis-isomer of **1** is fairly planar, the corresponding cis-2 shows considerable torsion around the double ($\Theta = 4^{\circ}$ and 9°) and the single bond ($\varphi = 21^{\circ}$ and 20°), respectively. All derivatives carrying six- and sevenmembered aliphatic rings (3-6) exhibit a pronounced torsion around the single bond, whereas the double bond twist is, however, significant only for the six-membered cyclic compounds **3–5**. The increased flexibility of the aliphatic rings in compounds 3-6 allows for the population of different conformations.²⁰ This conformational flexibility is particularly noticeable in the solid-state structures of both isomers of 3. While one of the aliphatic six-membered rings in cis-3 adopts a twist-boat-like conformation, the second one accepts a boat-like geometry. Both aliphatic rings additionally show large degrees of disorder in the crystal. Notably, both of the known solid-state structures of the trans-isomer of 3 are similarly distorted due to packing differences in the crystal.¹⁹ The conformational flexibility in solution is largest for the seven-membered ring containing stilbenes 7 as noticeable by their broad and unresolved ¹H NMR spectra.

2.3. Photochemical isomerizations

2.3.1. UV/vis spectra of **1–6**. The UV/vis spectra of **1–6** in *n*-hexane are shown in Fig. 3. With increasing ring size of the stilbenes, the absorption bands of both cis- and trans-isomers of **2**, **3** and **6** steadily shifted to shorter wavelengths due to the decrease in conjugation between the π -electronic systems of the phenyl rings and that of the double bond. Interestingly, the incorporation of a four-membered ring drove the main bands of *cis-* and *trans-***1** to



Fig. 3. (a-c) UV/vis spectra of 1-6 (in *n*-hexane).

shorter wavelengths relative to the higher homologue **2**, probably due to the deformation of the central double bond and/or the hindered conjugation with the phenyl rings. In line with literature reports, solely the four- and five-membered stilbene analogues **1** and **2** demonstrate vibrational fine structures, which are broadened for *cis*-**2**.³ Remarkably, both cis-isomers of **1** and **2** underwent rapid photoisomerization during UV/vis measurement. For example, virtually pure *cis*-**2** was converted to over 90% (by GC) to *trans*-**2** after one scan. Due to their structural freedom and large torsion around the single bond (φ), the larger derivatives **3**-**6** gave broad absorption bands without any vibrational structure.¹²

2.3.2. Synthesis of cis-**2** through preparative photoisomerization. Since the cis-isomer of **2** could not be obtained via McMurry coupling, it was synthesized by preparative photoisomerization instead. Optimization studies were initially conducted on a small scale in a Rayonet chamber reactor to find the most suitable reaction

conditions (Table 3). Solutions of *trans*-**2** in *n*-hexane were irradiated at 300 or 350 nm (\pm 20 nm) in either Quartz or Duran vessels. Irradiations were monitored by GC until photostationary states were apparently reached. The highest amount of *cis*-**2** of 46.5% was achieved with UVB light in a Quartz vessel. Subsequent irradiation on a large preparative scale for 8 h furnished a *cis*-**2** content of 45.6% (by GC). Careful isolation and purification under exclusion of light gave two batches of *cis*-**2** in high purities of >98% (by GC).

 Table 3

 Experimental irradiation conditions

| Glass | Wavelength (nm) | Time (h) | <i>cis</i> - 2 (%) ^a |
|--------|-----------------|----------|--|
| Quartz | 350 ± 20 | 1 | 3.8 |
| Quartz | 350 ± 20 | 2 | 4.0 |
| Quartz | 300 ± 20 | 1 | 46.0 |
| Quartz | 300 ± 20 | 2 | 46.5 |
| Duran | 300 ± 20 | 1 | 41.3 |

^a Determined by GC analysis.

2.3.3. Photoisomerizations of **1–6**. Photoinduced isomerizations were studied for all trans-isomers in *n*-hexane (Scheme 3). With the exception of compound **6**, irradiations were performed using 254 and 300 nm light. Selected irradiations were additionally conducted with the corresponding *cis*-isomers. The experiments were monitored by UV/vis or HPLC analysis, respectively. Selected reactions were furthermore performed in cyclohexane- d_{12} in a quartz NMR-tube to allow for monitoring by ¹H NMR spectroscopy.



On irradiation with 254 nm light from a 60 W low-pressure mercury lamp under nitrogen, the four-membered ring analogue *trans*-1 underwent efficient trans/cis isomerization. The major peaks of *trans*-1 between 260 and 330 nm steadily decreased and isosbestic points were observed near 250 and 330 nm (Fig. 4), respectively. Similar results were achieved using a high-pressure mercury lamp equipped with a 300 nm filter (not shown).

An additional irradiation experiment at 254 nm was performed with a more concentrated and degassed solution of *trans*-**1** in cyclohexane- d_{12} in a quartz NMR-tube. The progress of the reaction was subsequently monitored by ¹H NMR spectroscopy every 30 min. The amount of *trans*-**1** dropped gradually until a photostationary state of 55:45 (*trans/cis*) was reached after 2.5 h of irradiation. The final reaction mixture showed a strong yellow fluorescence and ¹H NMR spectroscopic analysis revealed the presence of several degradation products (Fig. 5). No attempt was made to isolate or characterize these products. Since neither isomer of **1** can undergo oxidative electrocyclization,²¹ the degradation products most likely arose from intermolecular cycloaddition reactions at this high concentration. Intramolecular H-shifts have alternatively been reported for the related five-membered analogue **2**.²²

The photoisomerization of *trans*-**2** was likewise investigated in *n*-hexane. Using 254 nm light (not shown), the main peaks in the UV-spectra dropped marginally until a photostationary state was apparently reached after approximately 5 min. An isosbestic point was observed at 342 nm and HPLC analysis confirming that clean photoisomerization had occurred.^{3a} To prevent undesirable cis-to-trans reisomerization, an additional reaction was monitored by HPLC. To



Fig. 4. UV/vis spectral changes of *trans*-**1** on irradiation with 254 nm light in *n*-hexane (10 min intervals).



Fig. 5. ¹H NMR (400 MHz; cyclohexane- d_{12}) of *trans*-**1** prior to (bottom) and after (top) irradiation at 254 nm.

allow for sufficient amounts of samples for the monitoring process, the experiment was conducted on preparative scale. After approximately 25 min of irradiation, a constant trans/cis ratio of 77:23 was achieved. The same ratio was determined by ¹H NMR spectroscopy when a degassed solution of *trans*-**2** was irradiated in cyclohexane- d_{12} in a quartz NMR-tube. No other products could be detected by HPLC or ¹H NMR analysis. The cis-isomer of **2** behaved similarly when irradiated at 254 nm in *n*-hexane (Fig. 6a). Upon irradiation at 300 nm, the UV-spectral changes of *trans*-**2** were more pronounced (Fig. 6b). The photostationary state was reached after 6 min and the *trans/cis* ratio was determined by HPLC to be 37:63. An isosbestic point was again observed at 342 nm indicating clean photoisomerization. No degradation products could be detected by HPLC analysis.

The parent six-membered stilbene analogue **3** showed a more complex photoreactivity. Upon irradiation, the corresponding hexahydroperylene derivative **7** was obtained under all conditions examined. The cis-isomer of **3** obviously has a favourable geometry for electrocyclic ring-closure to the octahydroperylene intermediate **8**.²¹ The formation of **8** was noticeable from its distinct yellow colour, which gradually faded on standing. Electrocyclic



Fig. 6. UV/vis spectral changes of (a) *cis*-**2** on irradiation with 254 nm light (1 min intervals) and (b) *trans*-**2** on irradiation with 300 nm light (10 s intervals) in *n*-hexane.

ring-opening regenerated *cis*-**3** whereas oxidation furnished **7** (Scheme 4). Even under degassed conditions, the formation of **7** could not be suppressed. A similar behaviour has been reported, for example, for 3,3',5,5'-tetramethoxystilbene.²³

Upon irradiation at 254 nm under degassed conditions, the main absorption band of *trans*-**3** at 286 nm decreased steadily and a bathochromic shift was noticeable (Fig. 7a). The characteristically structured absorption of the cyclization product **7** emerged during the course of the reaction. Irradiation of *trans*-**3** was additionally conducted on a preparative scale and the progress was monitored by HPLC. After approximately 2 h, a *trans/cis* ratio of 56:44 was reached. Despite exhaustive purging with argon prior to exposure to light, the



Scheme 4. Photoisomerization and oxidative electrocyclization of trans-3.



Fig. 7. UV/vis spectral changes of (a) *trans***-3** on irradiation with 254 nm light (degassed) and (b) *trans***-3** on irradiation with 300 nm light (aerated) in *n*-hexane (1 min intervals).

cyclization product **7** was still formed. ¹H NMR spectroscopic analysis of the crude reaction mixture revealed a composition of **5**:41:4 (*trans*-**3**/*cis*-**3**/**7**). As would be expected, the formation of **7** was more pronounced when *cis*-**3** was used as starting material (not shown). When *trans*-**3** was irradiated at 300 nm under aerated conditions, the absorption bands of **7** readily appeared and dominated the UV/ vis spectra (Fig. 7b). The sample was kept in the dark for 15 min prior to recording to allow for a disappearance of the octahydroperylene intermediate **8**. The hexahydroperylene derivative **7** was subsequently isolated from this reaction mixture by preparative HPLC²⁴ When the UV/vis was recorded immediately after irradiation, the characteristic absorption band of **8** could be observed at 454 nm. Its disappearance was followed by repeated UV/vis scans over a period of 15 min (shown as inset in Fig. 7b). Oxidative electrocyclization was again more prominent for the cis-isomer of **3** (not shown).

A non-degassed solution of *trans*-**3** in cyclohexane- d_{12} was furthermore irradiated at 254 nm in a quartz NMR-tube and the reaction was monitored in 30 min intervals by ¹H NMR spectroscopic analysis (Fig. 8). The signals corresponding to *trans*-**3** dropped gradually whereas those of *cis*-**3** increased initially before reaching a plateau after approximately 5 h. The amount of the oxidation product **7** increased almost linearly. After 11 h of irradiation, a mixture of *trans*-**3**/**7** in a ratio of 63:23:14 was obtained.

Introduction of methyl substituents as sterical blockers, either at the aromatic rings as in **4** or the aliphatic rings as in **5**, completely suppressed electrocyclization. For example, irradiation of the 5,5',7,7'-tetramethyl substituted *cis*-**4** at 254 nm gave selective photoisomerization. The absorption band at 293 nm dropped continuously and shifted to longer wavelengths until a photostationary state was reached after 10 min (Fig. 9a). Isosbestic points



Fig. 8. ¹H NMR (400 MHz; cyclohexane- d_{12}) of *trans*-**3** prior to (bottom) and after (top) irradiation at 254 nm.

were found at 262 and 327 nm, respectively. When a preparativescale reaction was monitored by HPLC, a constant *trans/cis* ratio of 64:36 was reached after 2 h. The same ratio was determined by ¹H NMR spectroscopic analysis of the reaction mixture. Upon irradiation at 300 nm, *cis*-**4** showed a similar behaviour. The



Fig. 9. UV/vis spectral changes of (a) *trans*-**4** on irradiation with 254 nm light and (b) *cis*-**4** on irradiation with 300 nm light in *n*-hexane (1 min intervals).

photostationary state was readily reached after just 3 min of irradiation (Fig. 9b). An attempt was made to detect the corresponding octahydroperylene analogue; however, its characteristic absorption between 350 and 550 nm could not be detected.

When irradiated at 254 nm in cyclohexane- d_{12} in a quartz NMRtube, *trans*-**4** was efficiently converted into its cis-isomer. After 7.5 h, the trans/cis ratio remained constant at 68:32 (Fig. 10). Careful inspection of the ¹H NMR spectrum revealed the presence of a minor secondary photoproduct. Its structure remained unknown; however, it may have been formed via H-shift or cycloaddition reaction.

The photoisomerization of the 2,2,2',2'-tetramethylated stilbene analogue *trans*-**5** with 254 nm light in THF and at -78 °C has been described earlier.¹¹ The corresponding *cis*-**5** was found unstable at room temperature but could be detected by low temperature NMR analysis (Scheme 5).



Fig. 10. ¹H NMR (400 MHz; cyclohexane- d_{12}) of *trans*-**4** prior to (bottom) and after (top) irradiation at 254 nm.



Scheme 5. Photochemical and thermal isomerization of *trans*-**5**.

When irradiated at 254 nm in *n*-hexane, the absorption maximum at 308 nm decreased in intensity and shifted to shorter wavelengths. Isosbestic points were detected at 247 and 352 nm, respectively, suggesting clean isomerization. After approximately 6 min, a seemingly constant absorption was obtained (Fig. 11a). The thermal reisomerization was subsequently monitored and was found completed after 1 h (shown as inset in Fig. 11a). An analogous irradiation experiment at 300 nm gave similar results. The photo–thermal isomerization cycle was repeated seven times with only marginal changes in the absorption of the UV/vis (Fig. 11b). Compound *trans*-**5** thus functions as a photo-thermalchemical switch.²⁵ Subsequent HPLC analysis suggested the formation of a secondary side-product in a small amount (<5%).



Fig. 11. (a) UV/vis spectral changes of *trans*-**5** on irradiation with 254 nm light (degassed; 1 min intervals) and (b) photochemical—thermal switching of *trans*-**5** on irradiation with 300 nm light (degassed) followed by standing for 1 h in *n*-hexane.

Due to its weak absorption around 300 nm, the photoisomerization of the seven-membered cyclic stilbene **6** was investigated solely with 254 nm light. When *trans*-**6** was used, the UV/vis spectra showed only marginal changes (not shown). An additional, preparative-scale experiment was subsequently monitored by HPLC. After approximately 1 h, a constant trans/cis ratio of 77:23 was reached. ¹H NMR spectroscopic analysis of the reaction mixture confirmed this ratio. Likewise, *cis*-**6** was irradiated at 254 nm in *n*-hexane. The absorption maximum at 247 nm gradually increased and shifted to shorter wavelengths (Fig. 12). Isosbestic points were found at 250 and 303 nm, respectively. After 10 min, the photostationary state was reached.



Fig. 12. UV/vis spectral changes of *trans*-**6** on irradiation with 254 nm light in *n*-hexane (1 min intervals).

3. Conclusion

The syntheses and photoisomerizations of six cyclic stilbene analogues have been realized. The four-, five- and seven-membered derivatives underwent efficient photoisomerization reactions. The photochemistry of the six-membered ring compounds with and without methyl substituents was more diverse. While the parent 1-(1-tetralinylidene)tetralin underwent rapid oxidative electrocyclization under all conditions examined, substitution at the aromatic or aliphatic ring prevented electrocyclization and restored clean photoisomerization. The *cis*-2,2,2',2'-tetramethylated analogue showed rapid thermal reisomerization.

4. Experimental section

4.1. General

Column chromatography was carried out by using Merck or Wako Silica gel 60 (0.015-0.040 mm). Analytical HPLC analysis was performed on a Hitachi LaChrom or JASCO Gulliver instrument and preparative HPLC on a JAI LC-908, respectively. Melting points were determined on a Büchi SMP-20 melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC 400 or a JEOL EX 400 (400 and 100 MHz), respectively, using the solvent residual peak as internal standard. The chemical shifts (δ) are given in parts per million; coupling constants (J) in hertz. MS spectra were recorded on a Hewlett Packard HP 5889 A MS Engine (EI, 70 eV) and UV/vis spectra on a Shimadzu UV-3101PC spectrophotometer using *n*-hexane (Kanto Chemical) as solvent. IR spectra were measured on a IASCO FT/ IR-230 or Perkin Elmer 1600 Series FT/IR spectrometer. Elemental analysis was performed by Fa. Pascher, Andernach, Germany. X-ray crystallographic analyses were performed on a Rigaku AFC7R or a Nonius-Kappa-CCD diffractometer. Solvents and reagents were commercially available and were used without further purification.

4.2. Synthesis of stiff stilbenes via McMurry coupling

General procedure: TiCl₄ (0.77 ml, 7 mmol) was added carefully to anhydrous THF (75 ml) at 0 °C under nitrogen. The yellow reaction mixture was stirred for 10 min before zinc powder (1.33 g, 4 mmol) was added in one portion. To the stirred mixture was added dropwise a solution of the corresponding ketone (6 mmol) in THF (25 ml) and the resulting black slurry was refluxed for 20 h. After cooling down to room temperature, the reaction mixture was treated with 75 ml of 10% aqueous K₂CO₃ solution. The black mixture was filtered and the filtrate was extracted with diethylether (2×50 ml) and *n*hexane (2×50 ml). The combined organic layers were washed with water and brine, dried over MgSO₄, and the solvent was evaporated in vacuo. The crude products were purified in small portions by column chromatography or recrystallization, respectively.

4.2.1. 1 - (1 - Benzocyclobutenylidene) benzocyclobutene (1).⁹ McMurry coupling (using 6 mmol benzocyclobuten-1-one²⁶) and subsequent column chromatography (eluent:*n*-hexane/10% acetone) gave a ca. 1:1 mixture of*trans*-1 and*cis* $-1 (0.45 g, 22%) as a colourless solid. This isomeric mixture was separated by preparative HPLC (Chiralcel OD-R column; <math>20 \times 250$ mm; particle size 10 µm; eluent: acetonitrile/water 2:1; flow: 9.5 ml/min; 25 °C). *trans*-1: colourless solid. Mp 148–150 °C. ¹H NMR (400 MHz; CDCl₃): δ =3.80 (s, 4H, CH₂), 7.11–7.33 (2m, 8H, H_{arom}). ¹³C NMR (100 MHz; CDCl₃): δ =37.6 (2t, CH₂), 118.8 (2d, CH), 122.7 (2d, CH), 127.4 (2s, Cq), 127.5 (2d, CH), 128.1 (2d, CH), 144.9 (2s, Cq), 145.0 (2s, Cq). MS (EI, 70 eV): *m/z* (%)=204 (M⁺, 74), 203 (100), 202 (97), 201 (16), 101 (11). IR (gas, 200 °C): *v*_{max} (cm⁻¹)=3080, 2937, 1598, 1453, 751. Calcd for C₁₆H₁₂: C 94.07, H 5.92; found: C 93.69, H 6.30%. *cis*-1: colourless solid. Mp 123–125 °C. ¹H NMR (400 MHz; CDCl₃):

 δ =3.71 (s, 4H, CH₂), 7.17–7.34 (2m, 8H, H_{arom}). ¹³C NMR (100 MHz; CDCl₃): δ =36.6 (2t, CH₂), 119.2 (2d, CH), 122.7 (2d, CH), 127.4 (2s, Cq), 127.5 (2d, CH), 127.9 (2d, CH), 144.6 (2s, Cq), 144.8 (2s, Cq). MS (EI, 70 eV): m/z (%)=204 (M⁺, 71), 203 (100), 202 (90), 201 (18), 101 (10). IR (gas, 200 °C): v_{max} (cm⁻¹)=3081, 2937, 1599, 1452, 743. Calcd for C₁₆H₁₂: C 94.07, H 5.92; found: C 93.75, H 6.23%. Crystal data (from *n*-hexane): monoclinic, space group *P*2₁/*c*, *a*=5.320(1), *b*=9.566(1), *c*=20.937(1) Å, β=90.48(1)°, *V*=1065.5(2) Å³; *Z*=4; Mo Kα radiation, 2317 reflections measured, 2018 reflections with *I*>2*σ*(*I*), *R*₁=0.036, *wR*₂=0.089. The crystallographic data have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-852805.

4.2.2. 1-(1-Indanylidene)indane (2).^{7a} McMurry coupling (using 17.5 mmol 1-indanone) and subsequent recrystallization from methanol gave 1.44 g (70%) of *trans*-2 as yellowish plates. Although *cis*-2 could be clearly detected by TLC and GC–MS analysis in amounts of ca. 5%, all attempts to isolate it in pure form failed. *trans*-2: yellowish plates. Mp 138–140 °C. ¹H NMR (400 MHz; CDCl₃): δ =3.09 (m, 8H, CH₂), 7.10–7.27 (br m, 6H, H_{arom.}), 7.55 (d, 2H, H_{arom.}). ¹³C NMR (100 MHz; DMSO-*d*₆): δ =30.0 (2t, CH₂), 30.8 (2t, CH₂), 123.6 (2d, CH), 124.2 (2d, CH), 125.7 (2d, CH), 126.2 (2d, CH), 134.3 (2s, Cq), 142.0 (2s, Cq), 146.0 (2s, CH). MS (EI, 70 eV): *m*/*z* (%)=232 (M⁺, 100), 217 (68), 202 (23), 117 (56). IR (KBr): *v*_{max} (cm⁻¹)=3100, 3060, 3020, 2920, 1600, 1475, 770, 760, 720. Calcd for C₁₈H₁₆: C 93.06, H 6.94: found: C 92.83, H 7.09%.

4.2.3. 1-(1-Tetralinylidene)tetralin (3).^{7b} McMurry coupling (using 24 mmol 1-tetralone) and subsequent column chromatography (eluent: *n*-hexane/1% ethyl acetate) gave 1.05 g (46%) of trans-**3** and 0.1 g (6%) of cis-3. The trans/cis ratio of the crude product was determined by ¹H NMR spectroscopic analysis as 80:20. *trans*-**3**: colourless solid. Mp (from *n*-hexane) 143–145 °C. ¹H NMR (400 MHz; acetone- d_6): δ=1.84 (q, J=6.8, 4H, CH₂), 2.77 (t, J=6.8, 4H, CH₂), 2.83 (t, J=6.8, 4H, CH₂), 7.28 (m, 6H, H_{arom}.), 7.47 (m, 2H, H_{arom}.). ¹³C NMR (100 MHz; CDCl₃): δ=24.3 (2t, CH₂), 29.4 (2t, CH₂), 29.7 (2t, CH₂), 124.7 (2d, CH), 126.6 (2d, CH), 127.7 (2d, CH), 130.0 (2d, CH), 132.9 (2s, Cq), 138.1 (2s, Cq), 139.7 (2s, Cq). MS (EI, 70 eV): m/z (%)=260 (M⁺, 100), 232 (20), 231 (23), 217 (21), 215 (19), 202 (13), 131 (15), 130 (41), 129 (33), 128 (25), 117 (11), 116 (13), 115 (25), 91 (14), 77 (6). Calcd for C₂₀H₂₀: C 92.26, H 7.74; found: C 92.05, H 7.85%. Crystal data (from *n*-pentane): monoclinic, space group P2₁/n, a=13.101(2), b=8.291(2), c=13.488(1) Å, $\beta = 96.233(8)^{\circ}$, V = 1456.3(3) Å³; Z = 4; Mo K α radiation, 3584 reflections measured, 2140 reflections with $I > 3\sigma(I)$, $R_1 = 0.055$, $wR_2 = 0.041$. The crystallographic data have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-168613. cis-3: colourless solid. Mp (from methanol) 113-115 °C. ¹H NMR (400 MHz; CDCl₃): δ=1.84 (q, J=6.8, 4H, CH₂), 2.55 (t, J=6.8, 4H, CH₂), 2.71 (t, J=6.8, 4H, CH₂), 6.77 (t, J=7.6, 2H, H_{arom}.), 6.89 (d, J=7.6, 2H, H_{arom.}), 7.02 (t, *J*=7.6, 2H, H_{arom.}), 7.10 (d, *J*=7.6, 2H, H_{arom.}). ¹³C NMR (100 MHz; CDCl₃): δ=23.2 (2t, CH₂), 28.3 (2t, CH₂), 30.2 (2t, CH₂), 124.6 (2d, Cq), 126.2 (2d, CH), 127.3 (2d, CH), 130.5 (2d, CH), 131.6 (2s, Cq), 137.7 (2s, Cq), 140.3 (2s, Cq). MS (EI, 70 eV): $m/z(\%)=260 (M^+, 100), 232$ (21), 231 (23), 217 (24), 215 (18), 202 (12), 131 (17), 130 (44), 129 (32), 128 (25), 117 (10), 116 (14), 115 (26), 91 (13), 77 (5). Calcd for C₂₀H₂₀: C 92.26, H, 7.74; found: C 92.01, H 7.70%. Crystal data (from *n*-hexane): monoclinic, space group $P2_1/c$, a=13.507(1), b=5.529(1), c=19.902(1) Å, $\beta=97.37(1)^{\circ}$, V=1474.0(3) Å³; Z=4; Mo K α radiation, 3192 reflections measured, 2141 reflections with $I > 2\sigma(I)$, $R_1 = 0.069$, wR_2 =0.208. The crystallographic data have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-852806.

4.2.4. 5,5',7,7'-Tetramethyl-1-(1-tetralinylidene)tetralin (**4**). McMurry coupling (using 17.5 mmol 5,7-dimethyl-1-tetralone) and subsequent column chromatography (eluent: *n*-hexane) gave 1.1 g (40%)

of trans-4 and 0.92 g (33%) of cis-4. The trans/cis ratio of the crude product was determined by ¹H NMR spectroscopic analysis as 55:45. trans-4: colourless solid. Mp (from n-hexane) 191–193 °C. ¹H NMR (400 MHz; CDCl₃): δ=1.73 (q, J=6.0, 4H, CH₂), 2.15 (s, 6H, CH₃), 2.23 (s, 6H, CH₃), 2.53 (t, J=6.0, 4H, CH₂), 2.65 (t, J=6.0, 4H, CH₂), 6.84 (s, 2H, H_{arom.}), 6.94 (s, 2H, H_{arom.}). ¹³C NMR (100 MHz; CDCl₃): δ=19.7 (2q, CH₃), 20.7 (2q, CH₃), 23.9 (2t, CH₂), 26.3 (2t, CH₂), 28.6 (2t, CH₂), 128.6 (2d, CH), 129.3 (2d, CH), 131.7 (2s, Cq), 132.8 (2s, Cq), 134.4 (2s, Cq), 134.5 (2s, Cq), 137.6 (2s, Cq). IR (NaCl): ν_{max} (cm⁻¹)=2982, 2922, 2858, 2820, 1470, 1439, 1190, 874, 852. Calcd for C24H28: C 91.08, H 8.92; found: C 90.91, H 9.02%. Crystal data (from *n*-hexane): monoclinic, space group C2/c, a=18.768(1), b=4.976(1), c=20.051(1)Å, $\beta = 91.91(1)^\circ$, V = 1871.5(4) Å³; Z=4; Mo K α radiation, 2033 reflections measured, 1095 reflections with $I > 2\sigma(I)$, $R_1 = 0.065$, $wR_2 = 0.121$. The crystallographic data have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-852808. cis-4: colourless solid. Mp (from n-hexane) 190-192 °C. ¹H NMR (400 MHz; CDCl₃): δ=1.89 (q, *J*=6.4, 4H, CH₂), 1.93 (s, 6H, CH₃), 2.23 (s, 6H, CH₃), 2.50 (t, J=6.4, 4H, CH₂), 2.66 (t, J=6.4, 4H, CH₂), 6.52 (s, 2H, H_{arom}), 6.73 (s, 2H, H_{arom}). ¹³C NMR (100 MHz; CDCl₃): δ=19.7 (2q, CH₃), 20.7 (2q, CH₃), 23.9 (2t, CH₂), 26.3 (2t, CH₂), 28.6 (2t, CH₂), 128.6 (2d, CH), 129.3 (2d, CH), 131.7 (2s, Cq), 132.8 (2s, Cq), 134.4 (2s, Cq), 134.5 (2s, Cq), 137.6 (2s, Cq). IR (NaCl): v_{max} (cm⁻¹)=2925, 2857, 1470, 1441, 850. Calcd for C₂₄H₂₈: C 91.08, H 8.92; found: C 90.92, H 9.04%.

4.2.5. 2,2,2',2'-Tetramethyl-1-(1-tetralinylidene)tetralin (**5**).¹¹ McMurry coupling (using 17.5 mmol 2,2-dimethyl-1-tetralone²⁷) and subsequent recrystallization from methanol gave 0.83 g (30%) of *trans*-**5** as a colourless solid. *cis*-**2** could not be detected by TLC or GC–MS analysis, respectively. *trans*-**5**: colourless solid. Mp 195 °C. ¹H NMR (400 MHz; CDCl₃): δ =0.68 (s, 6H, CH₃), 1.10 (s, 6H, CH₃), 1.53 (m, 2H, CH₂), 1.80 (m, 2H, CH₂), 2.86 (m, 4H, CH₂), 7.10–7.25 (br m, 8H, H_{arom}). ¹³C NMR (100 MHz; CDCl₃): δ =26.7 (2t, CH₂), 27.4 (2q, CH₃), 31.8 (2q, CH₃), 39.4 (2s, Cq), 41.8 (2t, CH₂), 124.2 (2d, CH), 126.9 (2d, CH), 127.2 (2d, CH), 133.0 (2d, CH), 137.4 (2s, Cq), 141.0 (2s, Cq), 143.8 (2s, Cq). MS (EI, 70 eV): *m/z* (%)=316 (M⁺, 100), 301 (21), 260 (24), 246 (13), 245 (54), 232 (21), 231 (16), 225 (42), 217 (21), 202 (30), 158 (42), 143 (75), 131 (42), 105 (32), 91 (22). IR (KBr): ν_{max} (cm⁻¹)=3060, 3000, 2840, 1595, 1570, 1490, 1430, 1390, 1370, 760. Calcd for C₂₄H₂₈: C 91.08, H 8.92; found: C 89.90, H 8.92%.

4.2.6. 1-(1-Benzocycloheptenylidene)benzocycloheptene (6).¹² McMurry coupling (using 24 mmol 1-benzosuberone) and subsequent column chromatography (eluent: n-hexane/5% acetone) gave 0.92 g (27%) of trans-6 and 0.83 g (24%) of cis-6. The trans/cis ratio of the crude product was determined by ¹H NMR spectroscopic analysis as 70:30. trans-6: colourless solid. Mp 179–180 °C. ¹H NMR (400 MHz; THF- d_8 ; 253 K): δ =1.35 (br quintet, 4H, CH₂), 1.60–1.78 (br m, 2H, CH₂), 1.85–1.95 (br m, 4H, CH₂), 2.65-2.69 (m, 4H, CH₂), 3.0 (br dt, 2H, CH₂), 7.10-7.25 (m, 6H, H_{arom.}), 7.38 (d, 2H, H_{arom.}). ¹³C NMR (100 MHz; D₃CNO₂; 363 K): δ=27.9 (2t, CH₂), 30.4 (2t, CH₂), 32.8 (2t, CH₂), 36.0 (2t, CH₂), 125.8 (2d, CH), 126.5 (2d, CH), 128.9 (2d, CH), 128.6 (2d, CH), 138.6 (2s, Cq), 141.1 (2s, Cq), 143.7 (2s, Cq). MS (EI, 70 eV): *m*/*z* (%)=288 (M⁺, 100), 245 (7), 231 (10), 217 (10), 216 (7), 215 (10), 202 (7), 145 (54), 144 (14), 143 (19), 142 (7), 141 (7), 129 (17), 128 (14), 117 (10), 115 (14), 91 (10). Calcd for C₂₂H₂₄: C 91.61, H 8.39; found: C 91.84, H 8.15%. cis-6: colourless solid. Mp 149-151 °C. ¹H NMR (400 MHz; THF-*d*₈; 268 K): δ=1.50 (br q, 2H, CH₂), 1.80 (br q, 2H, CH₂), 1.98 (br m, 6H, CH₂), 2.72 (br dd, 2H, CH₂), 3.00 (br t, 4H, CH₂), 6.40 (d, 2H, Harom.), 6.64 (d, 2H, Harom.), 6.85 (dt, 2H, Harom.), 6.99 (d, 2H, Harom.). ¹³C NMR (100 MHz; D₃CNO₂; 345 K): δ =28.0 (2t, CH₂), 29.7 (2t, CH₂), 31.5 (2t, CH₂), 36.0 (2t, CH₂), 125.4 (2d, CH), 125.8 (2d, CH), 128.1 (2d, CH), 128.6 (2d, CH), 137.9 (2s, Cq), 140.4 (2s, Cq), 144.4 (2s, Cq). MS (EI, 70 eV): m/z (%)=288 (M⁺, 100), 245 (8), 231 (12), 217 (12), 216 (7), 215 (9), 202 (8), 145 (52), 144 (13), 143 (19), 142 (7), 141 (6), 129 (18), 128 (14), 117 (11), 115 (14), 91 (10). Calcd for $C_{22}H_{24}$: C 91.61, H 8.39; found: C 91.83, H 8.17%. Crystal data (from *n*-hexane): monoclinic, space group P_{21}/c , a=8.429(1), b=19.465(1), c=10.900(1) Å, $\beta=112.27(1)^{\circ}$, V=1655.0(3) Å³; Z=4; Mo K α radiation, 3576 reflections measured, 3046 reflections with $I>2\sigma(I)$, $R_1=0.039$, $wR_2=0.093$. The crystallographic data have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-852807.

4.3. Synthesis of cis-2 by preparative irradiation

4.3.1. Small scale irradiation. Solutions of trans-**2** (10 mg in 10 ml *n*-hexane) were degassed with nitrogen, and irradiated in Pyrex or Quartz vessels using a Rayonet Photochemical Chamber Reactors (Model RPR-100) and various wavelengths. The progress of each isomerization was monitored by GC analysis.

4.3.2. Preparative irradiation. A solution of trans-2 (1.0 g, 4.3 mmol) in *n*-hexane (1000 ml) was carefully degassed with nitrogen and irradiated in a Rayonet Photochemical Chamber Reactor (Model RPR-100, 300 ± 20 nm) for 8 h. The content of *cis*-2 was determined by GC analysis as 45.6%. The solution was slowly concentrated in the dark, and crystalline fractions of pure trans-2 were repeatedly removed by decantation. After concentration to about 100 ml, the mother liquor contained 73% of cis-2 (determined by GC analysis). After further evaporation to dryness, the solid residue was purified by flash column chromatography (eluent: *n*-hexane) in the dark. *cis*- and *trans*-2 were eluted as overlapping zones. Fractions of 60 mg (99.6% *cis*-**2** by GC), 85 mg (97.6%), 60 mg (86.5%) and 40 mg (67.7%) were collected. Recrystallization of the first two fractions from methanol yielded colourless plates in GC-purities of 99.7% and 98.7%, respectively. cis-2: colourless plates. Mp 69.5 °C. ¹H NMR (500 MHz; CDCl₃): δ =2.81 (m, 4H, CH₂), 3.00 (m, 4H, CH₂), 7.15 (m, 4H, H_{arom.}), 7.29 (d, J=6.9, 2H, H_{arom.}), 8.07 (d, J=6.9, 2H, Harom.). ¹³C NMR (90 MHz; CDCl₃): 30.7 (2t, CH₂), 34.8 (2t, CH₂), 123.3 (2d, CH), 125.2 (2d, CH), 125.5 (2d, CH), 127.2 (2d, CH), 135.1 (2s, Cq), 140.6 (2s, Cq), 148.3 (2s, CH). MS (EI, 70 eV): m/z (%)=232 (M⁺, 100), 217 (68), 215 (42), 202 (33), 117 (80), 115 (66). Calcd for C₁₈H₁₆: C 93.06, H 6.94: found: C 92.95, H 7.01%.

4.4. Isolation of 7 by preparative irradiation

A solution of *trans*-**3** (42.8 mg, 0.16 mmol) in *n*-hexane (20 ml) was irradiated in a quartz vessel with a high-pressure mercury lamp EHB-300 (Eikosha) for 20 h while exposed to air. The solution was concentrated to dryness and the residue was purified by preparative HPLC (Sumichiral OA-3300 column; 20×250 mm; particle size 5 µm; eluent: *n*-hexane/*i*-PrOH 200:1; flow: $5.0 \rightarrow 9.0$ ml/min; 25 °C; detection: UV 254 nm). Drying in vacuo gave 2 mg (5%) of 1,2,3,10,11,12-hexahydroperylene **7** as a slightly yellowish solid. Compound **7**:²⁴ mp 190–192 °C. ¹H NMR (400 MHz; CDCl₃): δ =2.09 (m, 4H, CH₂), 3.09 (m, 8H, CH₂), 7.31 (d, *J*=8.4, 2H, H_{arom}), 7.44 (dd, *J*=8.4, 2H, H_{arom}), 8.51 (d, *J*=8.4, 2H, H_{arom}). UV/vis (*n*-hexane): λ_{max} =256, 264, 285, 297, 310 nm.

4.5. Photoisomerizations

Irradiations were conducted in *n*-hexane at ca. 25 °C using a ultra high-pressure mercury lamp HX-500 (Wacom) equipped with a bandpass filter 300 FS 10-50 (Andover) and a water filter (5 cm quartz cell), or a low-pressure mercury lamp EB-60 (Eikosha). Unless otherwise noted in the main text, the solutions were carefully deaerated with argon prior to irradiation. Quartz cuvettes (typically 0.05 mmol/l) or tubes (typically 1 mmol/l) were applied as reaction vessels. The course of the irradiation was followed by UV/vis spectroscopy, HPLC analysis or NMR spectroscopy, respectively. In the last case, quartz NMR-tubes and solutions in cyclohexane- d_{12} (typically 50 mmol/l) were used. Where necessary, UV/vis spectra were recorded after the absorption of the dihydrophenanthrene intermediate has disappeared (ca. 15 min after each irradiation step). For HPLC analysis, the conditions were as follows: compound **2**: Chiralcel OD column; (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane; flow: 2 ml/min; 30 °C; detection: UV 342 nm. Compound **3**: Chiralcel OJ (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane; flow: 1 ml/min; 25 °C; detection: UV 303 nm. Compound **4**: Chiralcel OD (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane; flow: 0.5 ml/min; 30 °C; detection: UV 263 nm. Compound **6**: Chiralcel OD (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane, flow: 0.5 ml/min; 30 °C; detection: UV 263 nm. Compound **6**: Chiralcel OD (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane, flow: 0.5 ml/min; 30 °C; detection: UV 263 nm. Compound **6**: Chiralcel OD (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane, flow: 0.5 ml/min; 30 °C; detection: UV 263 nm. Compound **6**: Chiralcel OD (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane, flow: 0.5 ml/min; 30 °C; detection: UV 263 nm. Compound **6**: Chiralcel OD (4.6×250 mm); particle size 10 µm; eluent: 100% *n*-hexane, flow: 0.5 ml/min; 30 °C; detection: UV 249 nm.

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