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Structure Determination of Photoproducts of Anthracenes with (Arylmethoxymethyl) Sidechains

Silvia Dobis,[a] Dieter Schollmeyer,[a] Chunmei Gao,[b] Derong Cao,[b,c] and
Herbert Meier*[a,c]

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Irradiation of 9-(arylmethoxymethyl)anthracenes **3** leads either to a cyclomer and cyclodimer mixture (**3a**→**4a**,**5a**), to selectively formed dimers (**3b**→**5b**), or a selectively formed cyclomer (**3c**→**4c**). The [4π+4π]cyclodimerization is under the conditions used a regioselective head-to-tail process. In the crystals of the dimers **5a**,**b**, the sidechains are attached in an antiperiplanar position related to the CC bonds generated in the dimerization. In solutions, however, the structures consist of three rotamers the equilibration of which was studied by temperature-dependent NMR spectra.

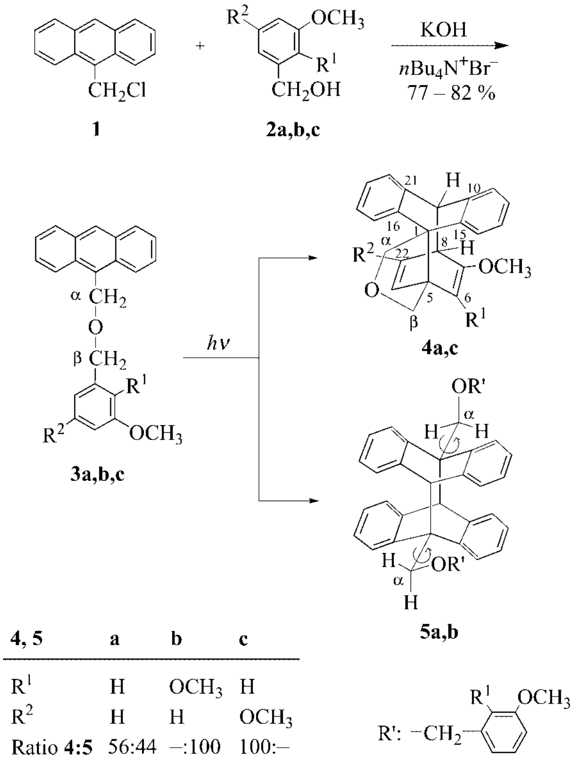
Introduction

Molecular switches and memories attract a lot of attention in organic chemistry and materials science.[1–15] Some time ago we found a seco-cyclo isomerism which is based on the reversible intramolecular [4π+4π]photocycloaddition of benzene rings to anthracene.[16] The utility of such a system depends strongly on clean switching processes in both directions. The photochemistry of anthracenes, however, contains several reaction types. The [4π+4π]photodimerization of two anthracene molecules was already discovered – without structural interpretation – by Fritzsche in the 19th century.[17] Bulky sidechains in 9-position lead to a remarkable valence isomerization (disrotatory [4π] electrocyclic reaction) to "Dewar anthracenes".[18–20] Apart from the intramolecular [4π+4π]cycloaddition of anthracene and benzene moieties mentioned above, we found in concentrated solutions of 9,10-disubstituted anthracenes the corresponding intermolecular process.[21] Moreover, anthracenes with special substituents exhibit several further photoreactions.[22–27]

The switching process discussed here, is typical for anthracenes which have in 9-position a phenylmethoxymethyl sidechain with an electron-rich benzene ring.[16] We describe in this paper such compounds which bear methoxyphenyl and dimethoxyphenyl groups.

Results and Discussion

9-(Chloromethyl)anthracene (**1**) reacts with the benzyl alcohols **2a–c** and KOH under phase-transfer conditions to give the anthracene derivatives **3a–c** (Scheme 1). These compounds contain two independent chromophores separated by a CH_2–O–CH_2 chain. The anthracene moiety has



4, 5	a	b	c
R^1	H	OCH_3	H
R^2	H	H	OCH_3
Ratio **4**:**5**	56:44	–:100	100:–

Scheme 1. Preparation and photoreactivity of 9-[(arylmethoxy)-methyl]anthracenes (**3**).

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[a] Institut für Organische Chemie der Johannes Gutenberg-Universität,
Duesbergweg 10–14, 55099 Mainz, Germany
Fax: +49-6131-39-25396
E-mail: hmeier@mail.uni-mainz.de
[b] LCLC, Guangzhou Institute of Chemistry, Chinese Academy of Sciences,
Guangzhou 510650, China
[c] South China University of Technology,
Guangzhou 510640, China

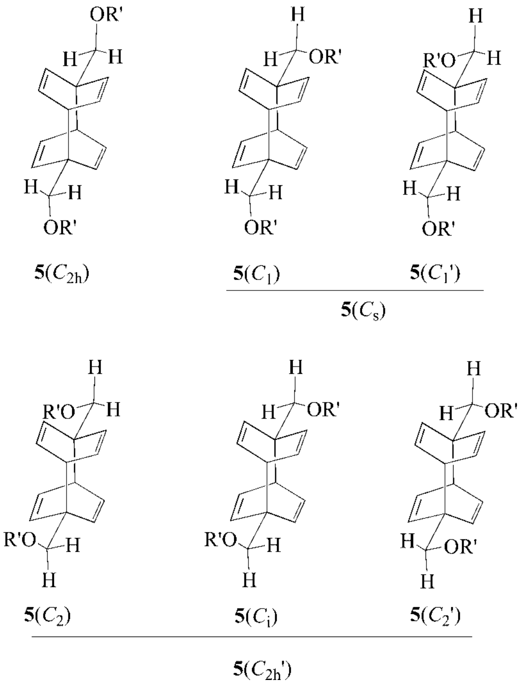
a typical absorption between 300 and 410 nm. Irradiation into this absorption of **3a** in diluted solution in oxygen-free benzene yields a mixture of cyclomer **4a** and cyclodimer **5a**. The same procedure selectively transforms **3b** into **5b** and **3c** into **4c**.[28] Obviously, small differences of the electronic effects in the benzene ring control the competition between the intramolecular and the intermolecular [4π+4π]cycloaddition. The ratio **4a/5a** of about 1:1 is typical of 0.5–1.0 mM solutions of **3a** in benzene. Enhanced concentrations (2.85 mM) of **3a** yield 82% dimer **5a** and only traces of **4a**. The selective dimerization **3b**→**5b** can not effectively be influenced by changing the concentration. Due to the high aggregation tendency of **3b**, cyclomer **4b** is found only in traces, when the concentration is lowered to about 0.1 mM. On the other hand, **3c** does not form a dimer of type **5** – even not in a saturated solution in benzene.

The structure determination of **4a**,**c** is based on one- and two-dimensional ^{1}H and ^{13}C NMR measurements. The products **5a**,**b** pose much more problems. Their ^{1}H-NMR spectroscopic data show at room temperature (25 °C) a double set of signals. Our original idea, that a mixture of head-to-head and head-to-tail cyclodimers[24–27] was generated, had to be dismissed, since the two signal sets coalesce reversibly to one set at high temperatures (≥ 90 °C). Consequently, stereoisomers must be present in the product mixture. Since the heptacyclic scaffold of **5a**,**b** is completely rigid, different rotamers of the sidechains have to be considered. Table 1 summarizes the staggered conformers consisting of two pairs of enantiomers having C_1 and C_2 symmetry, respectively, and two further diastereomers with C_{2h} and C_i symmetry, respectively.

Table 1. ^{1}H-NMR signals expected for different conformers of **5b**.

Conformation	Bridgehead CH	α-CH$_2$	β-CH$_2$	OCH$_3$
5b (C_{2h})	1s	1s	1s	2s
5b (C_1)/(C_1')	2s	2AB	2AB	4s
5b (C_2)/(C_2')	1s	1AB	1AB	2s
5b (C_i)	1s	1AB	1AB	1s

In principle, the rotamers of **5b**, shown in Scheme 2, should give the NMR signals listed in Table 1, when the rotations depicted in Scheme 1 are slow in terms of the NMR time scale.



Scheme 2. Rotamers of **5** (formula without condensed benzene rings).

Many temperature-dependent ^{1}H and ^{13}C NMR spectra of **5b** were recorded. Signals of methylene groups having diastereotopic geminal protons (AB spin patterns) could not be found in the temperature range between –40 and +90 °C. Therefore we assume that a fast AB exchange process in the α- and β-CH$_2$ groups takes place. The number of singlet signals depends strongly on the temperature of the ^{1}H-NMR measurement (Figure 1 and Table 2). At 90 °C, sharp singlets exist for the α- and β-CH$_2$ groups and for the two different methoxy groups, and a broad coal-

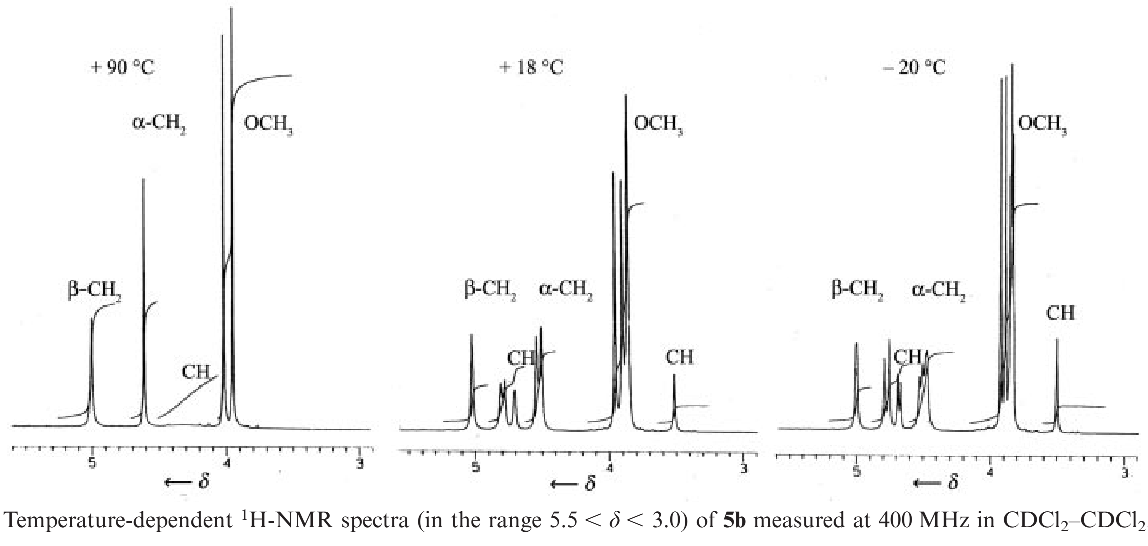


Figure 1. Temperature-dependent ^{1}H-NMR spectra (in the range $5.5 < \delta < 3.0$) of **5b** measured at 400 MHz in CDCl$_2$–CDCl$_2$.

escence signal can be found for the bridgehead protons. Cooling to 25 °C causes doubling of all signals (Table 2). At 18 °C a further splitting of the signals starts and at –20 °C all signals are doubled again – except for the high-field resonance at $\delta = 3.544$.[29] Six singlets for the methoxy groups can be seen at –20 °C. Consequently three conformers exist in the range of slow exchange (Scheme 2), namely **5b**(C_{2h}) and the equilibrated species **5b**(C_s) and **5b**(C_{2h}'). The sidechains having antiperiplanar position of the OR′ groups (present twice in **5b**(C_{2h}) and a single time in the equilibrated **5b**(C_s) conformer) are restricted in their rotation.[30] This interpretation is based on the proximity of OR′ to two benzene ring hydrogen atoms. Although a complete assignment of the signals, shown in Figure 1 and Table 2, to the three conformers was not possible, a conformer ratio **5b**(C_{2h}):**5b**(C_s):**5b**(C_{2h}') = 1:2:1 can be evaluated.

Table 2. Selected ^{1}H-NMR signals of **5b** (δ values measured at different temperatures in $C_2D_2Cl_4$, related to δ ($CHCl_2$–$CDCl_2$) = 5.995 ppm).

Temperature [°C]	Bridgehead CH (s)	α-CH_2 (s)	β-CH_2 (s)	OCH_3 (s)
–10	3.512	4.766	4.481	3.838
	4.680	4.802	4.493	3.850
	4.700	5.011	4.515	3.851
		5.019	4.538	3.861
				3.897
				3.931
+25	3.544	4.823	4.538	3.894
	4.735	5.051	4.569	3.894
				3.930
				3.990
+90	4.30 (br.)	5.002	4.613	3.952
				4.019

Head-to-head regioisomers could not be detected under the reaction conditions used – even not in the ^{1}H-NMR spectra of the crude reaction mixtures. The substituents in 9-position of **3a**,**b** are probably too bulky to permit the formation of head-to-head dimers.

The arrangement of the sidechains of **5a**,**b** in the crystalline state is shown in Figures 2 and 3. The OR′ groups are in both cases in an antiperiplanar arrangement related to the CC single bonds formed in the photocyclodimerization. The important structural features of the attachment of the sidechains in **5a**,**b** are listed in Table 3. Crystal structure **5b** contains two independent molecules (A) and (B) which are located at different special positions (A: 0.5, 0.5, 0; B: 0, 0, 0.5) of the unit cell. The molecular geometry of the two molecules is identical.

Both molecules **5a**,**b** have a center of inversion, so that the arrangement of the two sidechains is equivalent. The antiperiplanar conformation is characterized by torsion angles between 178.5 and 179.9°. The relatively small non-bonding distances between O16 and the hydrogen atoms H3, H13 and H9, respectively, indicate the difficulty of the rotation of the sidechains (see Table 1, Scheme 1, Figures 2 and 3). The two graphics also demonstrate the steric interaction of the hydrogen atoms on C15 (α-CH_2) and C17 (β-CH_2) with those on C3 and C13. Interestingly, the splitting of the ^{1}H-NMR signals is larger for the β-CH_2 group than for the α-CH_2 group.

The photodimerization of 9-substituted anthracenes normally leads to head-to-tail regioisomers; however, some head-to-head dimers were reported as well.[23–27] Certainly head-to-head regioselectivity is due to the reaction in constrained media or due to the topochemical control in the solid state, but the structures of those head-to-head dimers, which were postulated in solution, should be scrutinized in the light of the results obtained here for the existence of different rotamers. We suspect that particularly many dimers with long and/or bulky sidechains may give at room temperature a double set of NMR signals for pure head-to-tail structures.

To the best of our knowledge, only one discussion of rotamers in the structure elucidation of anthracene dimers has been published.[31] Crystal structure analyses reveal two different rotamers as separable photodimers of 9-(2-hydroxy-2-propyl)anthracene. Since an antiperiplanar arrangement of the OH group can be excluded, both stereoisomers give almost identical ^{1}H-NMR spectra with the same singlet for the bridgehead protons. On the contrary we observe for the rotamers of our compounds **5a**,**b** fairly different ^{1}H-NMR signals, but only one crystal structure.

Both reaction types, **3**→**4** and **3**→**5**, are thermally as well as photochemically reversible. The system **3c** ⇄ **4c** is

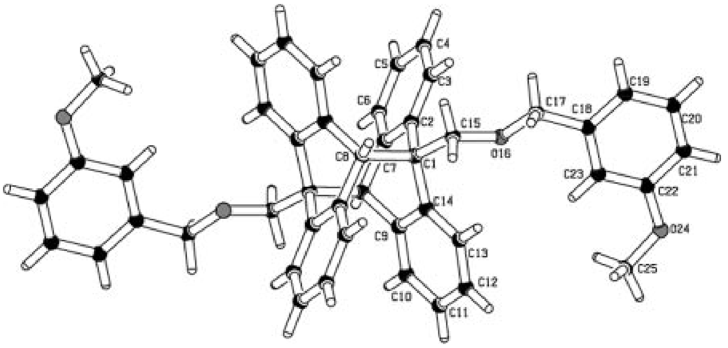


Figure 2. Crystal structure of dimer **5a** (atom numbering not in accord with nomenclature rules).

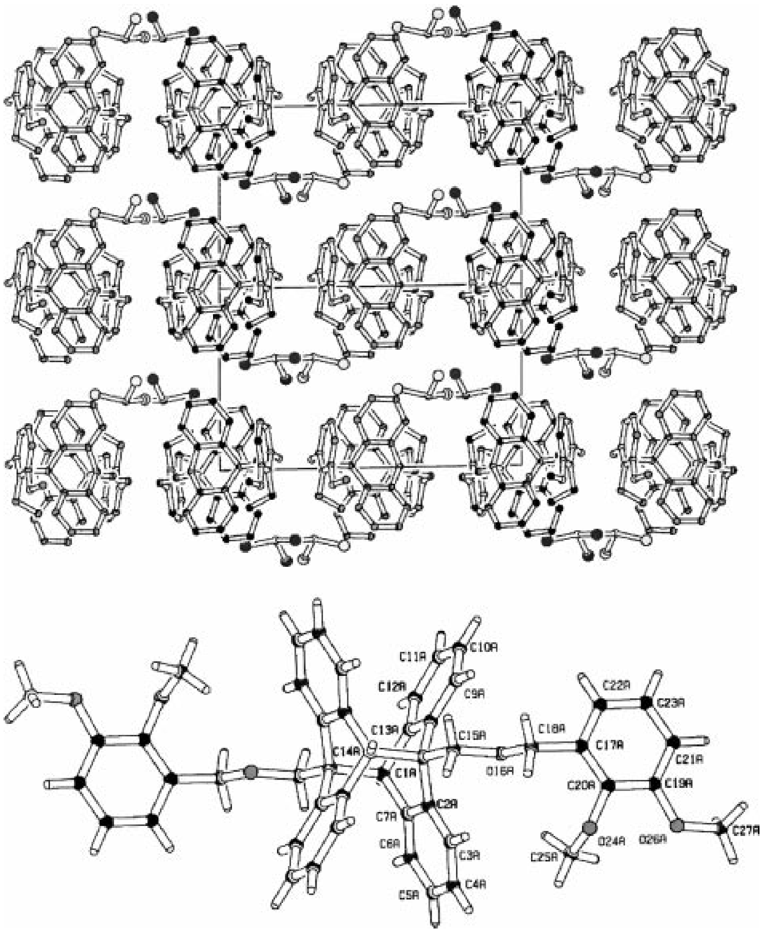


Figure 3. Crystal structure of dimer **5b**. Upper part: Unit cell which contains two molecules **5b** (A,B) in slightly different positions which are separated by two molecules $CHCl_3$. Lower part: Platon plot of **5b** (A). (atom numbering not in accord with nomenclature rules).

Table 3. Selected data of the crystal structures of the dimers **5a** and **5b** (The numbering corresponds to Figure 2 and Figure 3 and not to the nomenclature).

5a		**5b**	Molecule A	Molecule B
Bond lengths [Å]				
C1–C8	1.632(2)	C1–C14	1.636(7)	1.617(9)
C1–C15	1.526(2)	C1–C15	1.514(8)	1.527(8)
C15–O16	1.420(2)	C15–O16	1.433(7)	1.433(8)
Bond angles [°]				
C8–C1–C15	104.6(1)	C14–C1–C15	104.7(4)	105.2(5)
C1–C15–O16	109.7(1)	C1–C15–O16	109.4(4)	109.2(5)
Torsion angles [°]				
C8–C1–C15–O16	178.5(2)	C14–C1–C15–O16	–179.2(5)	–179.9(5)
Distances [Å]				
O16–H3	2.65	O16–H3	2.62	2.65
O16–H13	2.58	O16–H9	2.60	2.60

best suited for a clean and fast switching process.[32] The change of the absorption as well as the change of the fluorescence can be used to control the switching. In contrast to **3c**, cyclomer **4c** does not emit fluorescence light.

Conclusions

Depending on the substitution pattern on the benzene ring, anthracenes **3** bearing 9-(benzyloxy)methyl chains, react under the irradiation conditions used ($\lambda \geq 300$ nm) to give cyclomers **4** and/or cyclodimers **5**. The selectivity of the mono- or bimolecular process is determined by the electron density in *p*-position of the benzene ring; high electron density favors the intramolecular reaction.

Both processes are thermally as well as photochemically ($\lambda = 254$ nm) reversible. The quantitative process **3c** ⇄ **4c** is best suited as molecular switch.

The structure elucidations of the dimers **5a** and **5b** reveal a new aspect. According to crystal structure analyses, both dimers are [4π+4π] head-to-tail adducts. In solution, they show temperature-dependent (+90 °C to –40 °C) NMR spectra indicating the existence of three different rotamers. Head-to-head dimers could not be found.

Experimental Section

General: The FT-IR spectra were obtained with the Perkin–Elmer spectrometer GX. The ^{1}H and ^{13}C NMR spectra were recorded with the Bruker spectrometer AMX 400. If not otherwise indicated, $CDCl_3$ served as solvent, and TMS was used as internal standard. The field desorption (FD) mass spectra were obtained with a Finnigan MAT 95. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry of the University of Mainz. The melting points were measured with a Stuart Scientific SMP/3 apparatus and are uncorrected.

The preparation of the 9-[(benzyloxy)methyl]anthracenes **3a**–**c** was accomplished according to a procedure given in the literature.[33]

9-{[(3-Methoxybenzyl)oxy]methyl}anthracene (3a): Yellowish solid, yield 1310 mg (80%) from 1130 mg (5.0 mmol) **1** and 760 mg (5.5 mmol) **2a**; m.p. 101 °C. ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 3 H, OCH_3), 4.69 (s, 2 H, β-CH_2), 5.48 (s, 2 H, α-CH_2), 6.86 (m, 1 H, phenyl H), 6.97 (m, 2 H, phenyl H), 7.28 (m, 1 H, phenyl H), 7.39–7.54 (m, 4 H, anthracene H), 7.99 (m, 2 H, anthracene H), 8.31 (m, 2 H, anthracene H), 8.45 (s, 1 H, 10-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.2 (OCH_3), 64.0 (α-CH_2), 72.3 (β-CH_2), 113.0, 113.8, 120.3, 124.4, 124.4, 124.9, 126.1, 128.4, 129.0 (aromat. CH), 129.4, 131.1, 131.5 (C_q, anthracene), 140.1, 159.8 (C_q, benzene) ppm. FD MS: *m*/*z* (%) = 328 (100) [$M^{+\cdot}$]. $C_{23}H_{20}O_2$ (328.4): calcd. C 84.12, H 6.14; found C 83.97, H 6.08.

9-{[(2,3-Dimethoxylbenzyl)oxy]methyl}anthracene (3b): Yellowish solid, yield 1380 mg (77%) from 1130 mg (5.0 mmol) **1** and 925 mg (5.5 mmol) **2b**; m.p. 111 °C. ^{1}H NMR ($CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 4.83 (s, 2 H, β-CH_2), 5.53 (s, 2 H, α-CH_2), 6.88 (m, 1 H, phenyl H), 7.06 (m, 2 H, phenyl H), 7.43–7.54 (m, 4 H, anthracene H), 8.00 (m, 2 H, anthracene H), 8.35 (m, 2 H, anthracene H), 8.45 (s, 1 H, 10-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.8, 61.1 (OCH_3), 64.5 (α-CH_2), 67.4 (β-CH_2), 112.1, 121.7, 124.0, 124.5, 124.9, 126.1, 128.3, 128.9 (aromat. CH), 128.8, 131.1, 131.5, 132.2 (aromat. C_q), 147.4, 152.7 (aromat. C_qO) ppm. FD MS: *m*/*z* (%) = 358 (100) [$M^{+\cdot}$]. $C_{24}H_{22}O_3$ (358.4): calcd. C 80.42, H 6.19; found C 80.39, H 6.27.

9-{[(3,5-Dimethoxybenzyl)oxy]methyl}anthracene (3c): Yellowish solid, yield 1470 mg (82%) from 1130 mg (5.0 mmol) **1** and 925 mg (5.5 mmol) **2c**; m.p. 100 °C, spectroscopic characterization.[14]

Irradiation of 9-{[(3-Methoxybenzyl)oxy]methyl}anthracene (3a): A solution of 40.0 mg (0.12 mmol) **3a** in 160 mL of dry, degassed benzene was irradiated with a Hanovia 450-W medium-pressure mercury lamp equipped with a Duran glas filter. A slow Ar stream was purged through the solution. After 1 h the solvent was reduced, so that dimer **5a**, which has a low solubility, precipitated. Recrystallization from CH_2Cl_2/C_2H_5OH (1:2) yielded 21.0 mg (53%) of colorless, crystalline **5a** which melted at 213 °C. The remaining benzene solution contained the better soluble cyclomer **4a**. Further concentration gave 16.5 mg (41%) yellowish **4a** which melted at 206 °C. (The melting processes of **4a** and **5a** show clean decompositions to **3a**.) When 150 mg (0.46 mmol) **3a** were dissolved in 160 mL benzene, the photoreaction yielded under the same conditions 123 mg (82%) of dimer **5a** and only traces of **4a**.

Irradiation of 3b, 3c: The irradiation of **3b** (87 mg, 0.24 mmol) was performed as described above for **3a**. Yield after recrystallization from CH_2Cl_2/C_2H_5OH (1:2): 62 mg **5b** (71%), colorless crystals, which melted at 222 °C (decomp.). The irradiation of **3c** (60 mg, 0.17 mmol) afforded 60 mg (≈100%) of pure **4c**, which melted at 98 °C (decomp.).[31]

7-Methoxy-3-oxahexacyclo[7.6.6.2^{5,8}.0^{1,5}.0^{10,15}.0^{16,21}]tricosa-6,10,12,14,16,18,20,22-octaene (4a): IR (KBr): $\tilde{\nu}$ = 1597, 1490, 1467, 1454, 1268, 1165, 1135, 1108, 1037, 780, 694 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.75 (s, 3 H, OCH_3), 3.18 (m, 1 H, 8-H), 3.69/3.83 (AB, ^2J = –8.9 Hz, 2 H, 4-H), 4.03 (d, ^3J = 10.7 Hz, 1 H, 9-H), 4.11 (d, ^4J = 2.2 Hz, 1 H, 6-H), 4.49 ("s", 2 H, 2-H), 5.70 (m, 2 H, 22-H, 23-H), 6.78–7.36 (m, 8 H, aromat. H) ppm. ^{13}C NMR (C_6D_6): δ = 47.0 (C-8), 54.1, 54.8, 54.9 (C-5, C-9, OCH_3), 64.4 (C-1), 72.1 (C-2), 80.5 (C-4), 103.9 (C-6), 122.7, 123.1, 124.2, 124.7, 124.8, 125.4, 127.4 (aromat. CH, signals partly superimposed), 132.9, 141.3 (C-22, C-23), 143.8, 144.6, 146.0, 146.2 (aromat. C_q), 160.6 (C_qO) ppm. FD MS: *m*/*z* (%) = 329 (100) [M + H^+]. $C_{23}H_{20}O_2$ (328.4): calcd. C 84.12, H 6.14; found C 84.52, H 6.04.

To the spectroscopic characterization of **4c** see reference.[33] The quantitative process **3c**→**4c** can be quantitatively reversed (**4c**→**3c**) by heating to 110 °C or by irradiation with λ = 254 nm.

5,11-Bis{[(3-methoxybenzyl)oxy]methyl}-5,6,11,12-tetrahydro-5,12-[1′,2′]:6,11[1′′,2′′]dibenzenodibenzo[*a*,*e*]cyclooctene (5a): IR (KBr): $\tilde{\nu}$ = 1597, 1454, 1268, 1164, 1108, 1036, 780, 694 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 3.53, 4.72 (2 br. s, 2 H, bridgehead H), 3.79, 3.84 (2 s, 6 H, OCH_3), 4.46 (br. s, 4 H, α-CH_2), 4.73 (br. s, 2 H, β-CH_2), 4.97 (br. s, 2 H, β-CH_2), 6.75–7.40 (m, 24 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 55.2 (OCH_3), 71.1 (br.), 73.6, 73.9, 75.0 (CH_2), 112.9, 113.4, 113.7, 120.0, 120.5, 123.6, 124.0, 124.9, 125.3, 125.5, 127.4, 128.0, 129.5, 129.6 (aromat. CH, signals partly superimposed), 139.8, 142.9, 144.9, 159.8 (br., aromat. C_q, partly superimposed) ppm. Due to the exchange mechanism of rotamers, some signals are very broad; the signals of the bridgehead carbon atoms can not be found at all. FD MS: *m*/*z* (%) = 657 (1) [M + H^+], 329 (100) [M + 2 H^+]. $C_{46}H_{40}O_4$ (656.8): calcd. C 84.12, H 6.14; found C 84.15, H 6.11.

5,11-Bis{[(2,3-dimethoxybenzyl)oxy]methyl}-5,6,11,12-tetrahydro-5,12[1′,2′]:6,11[1′′,2′′]dibenzenodibenzo[*a*,*e*]cyclooctene (5b): IR (KBr): $\tilde{\nu}$ = 1588, 1477, 1454, 1431, 1351, 1276, 1233, 1135, 1099, 1077, 1059, 1023, 1009, 777, 751, 693 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 3.55, 4.73 (2 s, 2 H, bridgehead H), 3.88, 3.92, 3.99 (3 s, 12 H, OCH_3), 4.55 (br. s, 4 H, α-CH_2), 4.83 (br. s, 2 H, β-CH_2), 5.05 (s, 2 H, β-CH_2), 6.73–7.35 (m, 22 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 55.8, 61.1 (OCH_3), 57.1, 60.0 (CH, bridgehead), 67.7, 68.5 (β-CH_2), 71.3, 75.3 (α-CH_2), 111.9, 121.3, 121.9, 123.7, 124.2, 125.2, 125.5, 127.3, 128.0 (aromat. CH, some signals superimposed), 132.1, 143.0, 145.0, 147.1, 152.6 (aromat. C_q) ppm. Some signals are broad, some signals look like doublets. FD MS: *m*/*z* (%) = 717 (5) [M + H^+], 359 (100) [M + 2 H^+]. $C_{48}H_{44}O_6$ (716.9): calcd. C 80.42, H 6.19; found C 80.59, H 6.16.

Crystal Structure Analysis of 5a and 5b: The measurement was done on an Enraf–Nonius CAD-4-diffractometer with the software Collect V5 (Enraf–Nonius B. V., 1989, Delft, The Netherlands). The structures were solved with SIR 92[34] and refined by full-matrix least-squares technique on F^2 with SHELXL-97.[35] Details of the X-ray crystal structure analysis are listed in Table 4.

Table 4. Details of X-ray crystal structure analysis of the dimers **5a** and **5b**.

	5a	**5b**
Formula	$C_{46}H_{40}O_4$	$C_{48}H_{44}O_6$·2$CHCl_3$
M_r	656.78	955.57
Habit	block	block
Crystal size [mm]	0.04 × 0.35 × 0.55	0.1 × 0.1 × 0.2
Space group	$P2_1/c$	$P\bar{1}$
Cell constants:		
a [Å]	12.284(3)	10.589(2)
b [Å]	17.215(2)	14.276(3)
c [Å]	8.208(2)	16.416(5)
α [°]	90	92.93(2)
β [°]	92.64(1)	90.61(2)
γ [°]	90	111.54(2)
V (Å^3)	1733.8(5)	2304(1)
Z	2	2
D_x (Mg m^{-3})	1.258	1.377
Radiation	Cu-K_α	Cu-K_α
μ [mm^{-1}]	0.62	3.801
F (000)	696	992
T [K]	25	–80
θ_{max} [°]	70	71
Number of reflections		
Measured reflections	3506	9070
Indepependent reflections	3265	8700
Observed reflections		
$\lvert F\rvert/\sigma(F) > 4.0$	2500	5142
R_σ	0.048	0.0624
Parameters	226	559
wR (F^2, all reflections)	0.1557	0.3061
R, $F > 4\sigma(F)$	0.0560	0.0883
S	1.071	1.054
Max. $\Delta\rho$ (e Å^{-3})	0.19	0.65
Min. $\Delta\rho$ (e Å^{-3})	–0.24	–0.72

CCDC-634267 -634268 (for **5a** and **5b**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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