

Liquid Chromatography on Triacetylcellulose, 6¹⁾**Synthesis, Chromatographic Enrichment of Enantiomers, and Barriers to Enantiomerization of Helical Phenanthrenes***Herbert Scherübl, Ursula Fritzsche, and Albrecht Mannschreck**Institut für Organische Chemie, Universität Regensburg,
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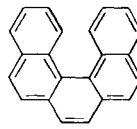
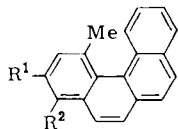
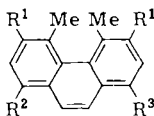
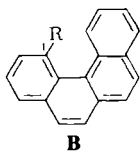
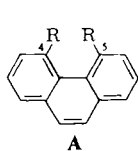
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Enantiomerization barriers (Table 1) for novel 4,5-disubstituted phenanthrenes of types **A** and **B** have been determined by coalescence of ¹H NMR signals or by thermal racemization of chromatographically enriched enantiomers. The barriers depend upon the size of the groups R = CMe₃, Br, Me, Cl, OBz in **A** and **B**, the behaviour of annelated benzo rings instead of R being particularly considered.

Flüssigkeits-Chromatographie an Triacetylcellulose, 6¹⁾**Synthese, chromatographische Anreicherung von Enantiomeren und Enantiomerisierungs-Schwellen helicaler Phenanthrene**

Die Enantiomerisierungs-Schwellen (Tab. 1) neuer 4,5-disubstituierter Phenanthrene der Typen **A** und **B** wurden durch Koaleszenz von ¹H-NMR-Signalen oder durch thermische Racemisierung chromatographisch angereicherter Enantiomere ermittelt. Die Schwellen hängen vom Raumbedarf der Gruppen R = CMe₃, Br, Me, Cl, OBz in **A** und **B** ab; das Verhalten anellierter Benzoringe anstelle von R wird diskutiert.

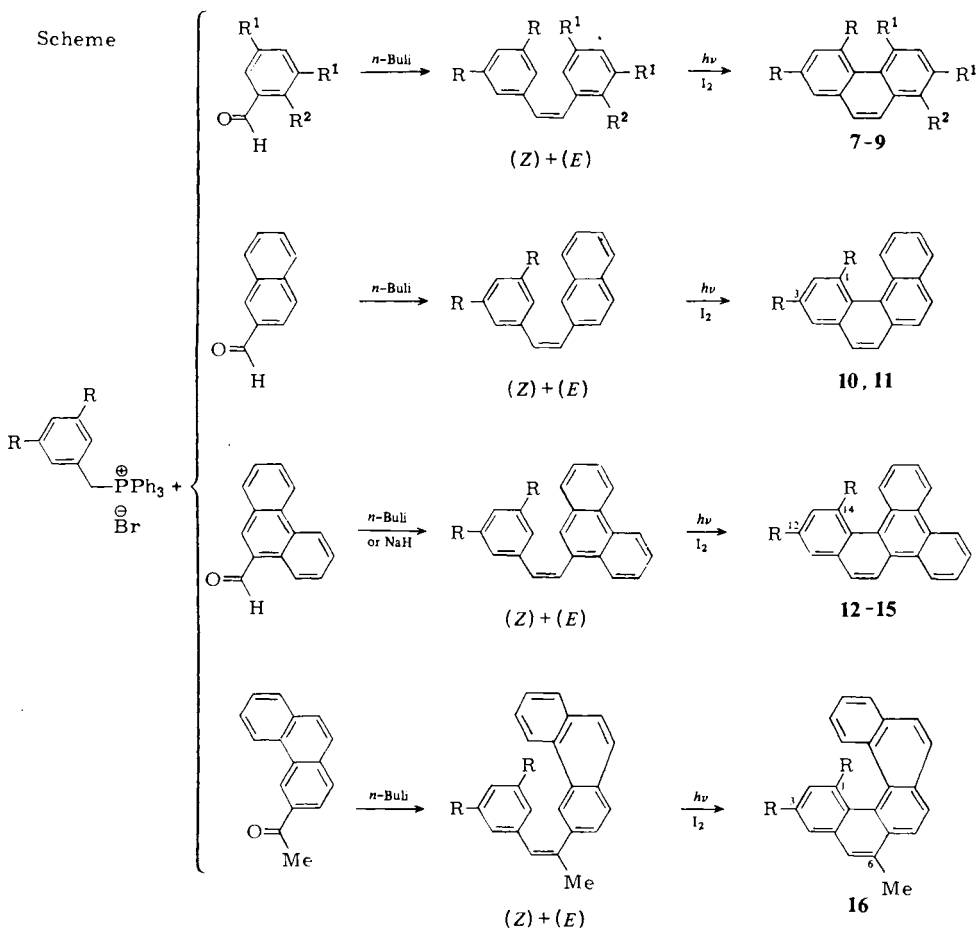
4,5-Disubstituted phenanthrenes of type **A**, R ≠ H, may be chiral, as shown by *Newman* and *Hussey's* finding²⁾ that enriched (+)-**1** racemizes rapidly at room tem-



	R ¹	R ²	R ³
1	H	CH ₂ CO ₂ H	Me
2	Me	H	H
3	H	H	H

	R ¹	R ²
4	H	CH ₂ CO ₂ H
5	Me	H

perature. Barriers to enantiomerization of $\Delta G^* = 60$ to 62 kJ/mol for some 4,5-phenanthrenedicarboxylic esters and of 75.8 kJ/mol for 4,5-bis(acetoxymethyl)phenanthrene were obtained from ^1H NMR line shapes³⁾. We are not aware of further facts^{4,5)} relevant to the chirality of phenanthrenes **A**. Since they represent the simplest known model for helicenes, we investigated further species **A** in order to compare their rates of enantio-merization. We included 1-substituted benzo[*c*]phenanthrenes (**B**, $R \neq \text{H}$), the only relevant³⁾ known information referring to the rapid racemization of enriched (+)-**4** at



	R	R ¹	R ²		R		R
7	OBz	Br	OBz	10	OBz	12	OBz
8	OBz	<i>t</i> Bu	H	11	<i>t</i> Bu	13	Cl
9	Me	<i>t</i> Bu	H			14	Me
						15	<i>t</i> Bu

room temperature⁶⁾. On the other hand, the barrier of dibenzo[*c,g*]phenanthrene (**6**), a reference molecule, is available ($\Delta G^\ddagger = 101 \text{ kJ/mol}$)⁷⁾.

Synthesis

The syntheses of phenanthrenes **7** through **16** were performed by photocyclization^{8,9)} of 1,2-diarylethenes obtained via Wittig reaction (Scheme). In the cases of **10** and **16**, a regioisomer had to be removed by repeated dry-column chromatography and recrystallizations. All products were checked by ¹H NMR; ¹³C NMR, UV, and MS spectra were included for some compounds bearing CMe₃ groups.

Coalescence of ¹H NMR Signals

NMR of diastereotopic methylene protons has been used^{3,5)} to prove helicene chirality. For this purpose, some of our phenanthrenes bear two OCH₂C₆H₅ groups. Indeed, the benzyloxy absorption in the hindered position (4-position in **A** and 1-position in **B**) splits into an AB system in the cases marked in Table 1. The coalescence of AB absorptions upon rising the temperature resulted in barriers to enantiomerization.

Thermal Racemization

Semipreparative enrichment and thermal racemization of enantiomers became necessary because the barriers of many of our phenanthrenes are too high to be determined by NMR. We chose liquid chromatography on triacetylcellulose which has been successful for racemates devoid of reactive groups^{1,10)}, including hydrocarbons¹¹⁾. The crystalline enriched enantiomers were characterized by their retention and racemization data

Table 1. Properties related to the chirality of 4,5-disubstituted phenanthrenes

	Relative Retent. ^{a)}	ΔG^\ddagger ^{c)} [kJ/mol]	<i>T</i> [°C]	Method	Solvent
2	3.0	95.8 ± 0.2	+ 30	d)	CHCl ₃
7		47.3 ± 0.8	- 49	e)	[D ₆]acetone/C ₆ D ₅ CD ₃ , 1:1
8	b)	80.9 ± 0.4	+ 103	e)	[D ₃]nitrobenzene
9	2.0	111.3 ± 0.4	+ 80	d)	(<i>n</i> BuOCH ₂ CH ₂) ₂ O
10		60.2 ± 0.4	- 14	e)	[D ₆]acetone/C ₆ D ₅ CD ₃ , 1:1
11	1.4	118.0 ± 0.4	+ 80	d)	(<i>n</i> BuOCH ₂ CH ₂) ₂ O
12		70.6 ± 0.8	+ 63	e)	Cl ₂ CDCDCl ₂
13	1.2	95.2 ± 0.1	+ 27	d)	CHCl ₃
14	1.4	95.1 ± 0.1	+ 30	d)	CHCl ₃
15	1.3	129.9 ± 0.6	+ 130	d)	(<i>n</i> BuOCH ₂ CH ₂) ₂ O
16	1.5	162 ± 1	+ 200	d)	(<i>n</i> BuOCH ₂ CH ₂) ₂ O

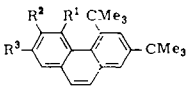
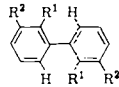
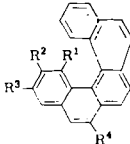
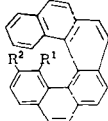
a) Relative retention $(v_+ - v_0)/(v_- - v_0)$ on triacetylcellulose¹⁰⁾ at +22 °C in EtOH/H₂O, 96:4. v_+ , v_- , v_0 : Retention volumes of the (+)₄₃₆- and (-)₄₃₆-enantiomers and of ethyltriphenylphosphonium bromide which we assume not to be retained. - b) Polarimetric detection shows no separation of enantiomers. - c) Enantiomerization barrier at temperature *T*, measured by the method given. - d) Thermal racemization of an enriched enantiomer, monitored by polarimetry. - e) Coalescence of a ¹H NMR CH_AH_B absorption. ²*J*_{AB} ranged from 11 to 13 Hz and $\delta_A - \delta_B$ (extrapolated to the coalescence temperatures) from 0.12 to 0.26.

(Table 1) as well as by specific rotations referring to unknown enantiomeric purities (see Experimental Part).

Discussion of Barriers to Enantiomerization

The barriers (Table 1) cannot yet be given for common temperatures of comparison. If *small* ΔS^* -values^{3,7)} are assumed, some useful semiquantitative comparisons are justified anyway. For this purpose, the barriers of phenanthrenes **2**, **7**, **8**, and **9** (type **A**), benzo[*c*]phenanthrenes **10** and **11** (type **B**), and benzo[*g*]chrysenes **12**, **13**, **14**, and **15** (type **B**) can be compared. For groups R in **A** and **B** the expected order $\text{CMe}_3 > \text{Br} > \text{Me} \approx \text{Cl} > \text{OBz}$ of decreasing nonbonding repulsion ("hindrance") in the transition state is found. The effect of annelated benzo rings instead of R is relevant to helicene stereochemistry. Such rings fit into the above order between CMe_3 and Br, as shown, inter alia, by the barriers (Table 1) of **8**, **10**, and **7**. An order benzo > Me seems to hold for biaryls and the smaller helicenes **11** and **9**, but is reversed for larger ones (Table 2,

Table 2. ΔG^\ddagger -values [kJ/mol] for enantiomerization of hydrocarbons bearing benzo and Me as hindering fragments. R^2 and R^4 are not specified, as they are unimportant for the barriers

	$\text{R}^2/\text{R}^1 =$ benzo	$\text{R}^2 = \text{H},$ $\text{R}^1 = \text{Me}$	$T [^\circ\text{C}]$
	118.0 (11)	111.3 (9)	+ 80
	96 ¹⁶⁾	72.9 ¹⁷⁾	-35
	155 ¹²⁾	162 (16)	+ 200
	178 ¹²⁾	183.2 ¹³⁾	+ 269

lower part). We relate this differing behaviour to unequal enantiomerization mechanisms: Larger helicenes planarize only *one* moiety¹²⁻¹⁴⁾ while turning it close to the non-planar one, whereas *both* moieties of smaller helicenes¹⁴⁾ are probably coplanarized in the transition state. Semi-empirical calculations¹⁵⁾ with respect to these mechanisms for the enantiomerization of our phenanthrenes are in progress.

We cannot compare the barriers in Table 1, including the one for **2**, with the few relevant literature data^{2,3,6)} mentioned above. This would be possible if the barriers for

3, 5, and similar simple helicenes were known. However, we have not been able to determine such barriers as yet.

Professor *M. S. Newman*, Columbus, kindly provided the sample of **2**. We are grateful to Professor *R. H. Martin*, Brussels, and to Dr. *W. Offermann*, Regensburg, for stimulating discussions. Dr. *T. Burgemeister*, Regensburg, contributed most of the NMR spectra, Professor *H. J. Lindner*, Darmstadt, the X-ray structure analysis of (–)-**9**. We thank "Deutsche Forschungsgemeinschaft" and "Fonds der Chemischen Industrie" for their support.

Experimental Part

Melting points: Büchi SMP 20 instrument; not corrected. – ^1H NMR spectra: Varian T-60 (CW mode, 60 MHz), Bruker WH-90 and WM-250 (PFT mode, 90 and 250 MHz, respectively). Temperature measurement for the latter two spectrometers was performed using methanol or glycol and the Van Geet formula. $[\text{D}_8]\text{Cyclosilane}$ (Merck AG, Darmstadt) was used as internal standard for NMR at higher temperatures (Table 1). – ^{13}C NMR spectra: PFT mode, 22.63 MHz, Bruker WH-90; proton noise or off-resonance decoupling. – UV spectra: Beckman Model 24. – Specific rotations: Perkin-Elmer Polarimeter 241. – MS spectra: Varian MAT 311 A and CH5, both at 70 eV.

(3,5-Dichlorobenzyl)triphenylphosphonium bromide: Obtained from 3,5-dichlorobenzylbromide¹⁸⁾ and triphenylphosphine in boiling benzene. M. p. 310–317 °C. – ^1H NMR (CDCl_3): $\delta = 5.18$ (CH_2 , d, $^2J = 14$ Hz), 6.92 and 7.13 (3H, A_2B , $^4J \approx 2$ Hz), 7.4–7.8 (15H, m).

Further educts: 2-Formylnaphthalene, 9-formylphenanthrene, and 3-acetylphenanthrene are available from EGA-Chemie, Steinheim. 3,5-Di-*tert*-butylbenzaldehyde¹⁹⁾, 2-benzyloxy-3,5-dibromobenzaldehyde²⁰⁾, 3,5-dimethylbenzaldehyde⁸⁾, (3,5-di-*tert*-butylbenzyl)-**9**), (3,5-dimethylbenzyl)-**8**), and (3,5-dibenzyloxybenzyl)triphenylphosphonium bromide²¹⁾ were synthesized according to the literature.

Wittig reactions of aldehydes and phosphonium bromides: Common procedures²²⁾ yielded crude alkenes which were purified by vacuum distillation or by chromatography on silica gel or neutral alumina. The mixtures of (*E*)- and (*Z*)-1,2-diarylethenes were found by ^1H NMR to be pure and were directly used for the photocyclizations.

Photocyclizations of 1,2-diarylethenes: A photoreactor with forced circulation, an unfiltered Hg high-pressure lamp TQ 150, and distilled cyclohexane were used. All other details are described^{8,9)}. The course of the reaction was easily followed by TLC on silica gel sheets coated with 2,4,5,7-tetranitrofluorenone²³⁾. When the reaction had finished the cyclohexane solution was washed with 100 ml of a saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried over Na_2SO_4 , and evaporated. The oily racemic phenanthrenes were worked up as described below. The yields of pure racemates varied from 10 to 40%.

(\pm)-3,4,5,6-Tetramethylphenanthrene (**2**)²⁴⁾: ^1H NMR (CDCl_3): $\delta = 2.42$ (4-Me/5-Me), 2.47 (3-Me/6-Me), 7.38 and 7.51 (2-H/7-H and 1-H/8-H, resp., AB, $^3J = 8$ Hz), 7.42 (9-H/10-H, s).

1,5,7-Tribenzyloxy-2,4-dibromophenanthrene (**7**): During photocyclization a pyrex filter was used. Dry-column chromatography on neutral alumina (2×30 cm) with cyclohexane as the eluent and recrystallization from cyclohexane yielded a white powder, m. p. 183–185 °C. – ^1H NMR (CDCl_3): $\delta = 5.03$, 5.12, and 5.20 (s, 6H, OCH_2Ph), 6.80 (broad s, 2H), 7.17–7.73 (m, 17H), 7.87 (s, 1H). – MS, molecular ion: Calcd. 652.0249, Found 652.0246.

2,4-Dibenzyloxy-5,7-di-*tert*-butylphenanthrene (**8**): By column chromatography on silica gel (2.5×30 cm) with toluene/30% petrolether as the eluent a colourless oil was obtained which

crystallized from petrolether. Recrystallization from ethanol yielded colourless crystals, m.p. 108–109°C. – $^1\text{H NMR}$ (CDCl_3): δ = 1.17 (s, 5-Me₃C), 1.43 (s, 7-Me₃C), 4.84 and 4.94 (AB, 2J = 9.8 Hz, 4-PhCH₂O), 5.13 (s, 2-PhCH₂O), 6.63 (d, 4J = 2 Hz, 3-H), 6.87 (d, 4J = 2 Hz, 1-H), 7.0–7.6 (m, 13H), 7.72 (d, 4J = 2 Hz, 6-H). – MS: m/e = 502 (32%, M⁺), 445 (4%, M – C₄H₉). – An X-ray structure analysis¹⁵ of 2,4-di-*tert*-butyl-5,7-dimethoxyphenanthrene, prepared in a way similar to **8**, confirms its constitution and its helical stereostructure.

C₃₆H₃₈O₂ (502.7) Calcd. C 86.01 H 7.62 Found C 85.92 H 7.56

(±)-2,4-Di-*tert*-butyl-5,7-dimethylphenanthrene (**9**): Triple column chromatography on silica gel (2.5 × 40 cm) with cyclohexane as the eluent gave a colourless oil which crystallized from ethanol. By recrystallization from methanol colourless needles were obtained, m.p. 90–91.5°C. – $^1\text{H NMR}$ (CCl₄): δ = 1.16 (s, 4-Me₃C), 1.40 (s, 2-Me₃C), 2.40 (s, 7-Me), 2.53 (s, 5-Me), 6.80 (broad s, 6-H), 7.15 (broad s, 3H), 7.28 (d, 4J = 2 Hz, 1-H), 7.58 (d, 4J = 2 Hz, 3-H). – $^{13}\text{C NMR}$ (CDCl₃): δ = 22.8 and 21.1 (5-Me and 7-Me, resp.), 31.4 (2-(H₃C)₃C), 33.3 (4-(H₃C)₃C), 34.4 (2-Me₃C), 39.9 (4-Me₃C), 120.6, 123.3, 124.9, 125.6, 126.3, and 127.4 (tertiary C-atoms), 125.2, 130.0, 133.4, 133.4, 134.8, 136.7, 147.8, and 148.4 (quarternary arene). – UV(CHCl₃): λ_{max} (lg ϵ) = 378 (sh, 2.31), 360 (2.50), 325 (3.86), 313 (3.96), 278 nm (4.66). – MS: m/e = 318 (42%, M⁺), 303 (8%, M – CH₃), 262 (23%, M – C₄H₉). – An X-ray structure analysis¹⁵ confirms the constitution and the helical stereostructure of (±)-**9**.

C₂₄H₃₀ (318.5) Calcd. C 90.51 H 9.50 Found C 90.47 H 9.55

1,3-Bis(benzyloxy)benzo[*c*]phenanthrene (**10**): Dry-column chromatography on neutral alumina (2 × 40 cm) with petrolether/10% CHCl₃ as the eluent gave **10** as the first fraction which was twice recrystallized from ethanol: White needles, m.p. 130–131.5°C. – $^1\text{H NMR}$ (CCl₄): δ = 5.17 (s, 1-PhCH₂O), 5.40 (s, 3-PhCH₂O), 6.83–8.67 (m, 20H). – MS, molecular ion: Calcd. 440.1776, Found 440.1772. From the second fraction the corresponding benz[*a*]anthracene derivative was isolated.

(±)-1,3-Di-*tert*-butylbenzo[*c*]phenanthrene (**11**): Obtained by dry-column chromatography on silica gel (3.5 × 50 cm) with petrolether as the eluent. Recrystallization from methanol gave colourless needles, m.p. 137.5–139°C. – $^1\text{H NMR}$ (CCl₄): δ = 1.00 (s, 1-Me₃C), 1.50 (s, 3-Me₃C), 7.17–7.83 (m, 9H), 8.33 (m, 12-H). – UV (CHCl₃): λ_{max} (lg ϵ) = 395 (2.20), 373 (2.57), 335 (3.76), 300 (4.62), 290 nm (sh, 4.52).

C₂₆H₂₈ (340.5) Calcd. C 91.71 H 8.29 Found C 91.68 H 8.15

12,14-Bis(benzyloxy)benzo[*g*]chrysene (**12**): The crude product was chromatographed on silica gel (2 × 30 cm) with toluene. The obtained yellow crystals were washed with ether and recrystallized from ethanol/toluene (10:1): White needles, m.p. 139–140.5°C. – $^1\text{H NMR}$ ([D₆]acetone): δ = 5.12 and 5.31 (AB, 2J = 12.8 Hz, 14-PhCH₂O), 5.34 (s, 12-PhCH₂O), 6.90–8.20 (m, 18H), 8.60–8.80 (m, 4H). – MS, molecular ion: Calcd. 490.1933, Found 490.1936.

(±)-12,14-Dichlorobenzo[*g*]chrysene (**13**): Dry-column chromatography on silica gel (3 × 40 cm) with petrolether as the eluent gave brown crystals which were washed with ether and recrystallized from methanol/toluene (10:1): Colourless needles, m.p. 138–139°C. – $^1\text{H NMR}$ (CCl₄): δ = 7.33–8.67 (m). – UV (CHCl₃): λ_{max} (lg ϵ) = 383 (2.71), 350 (3.88), 328 (4.00), 297 (4.77), 287 (4.69), 276 (4.60), 257 nm (4.56).

C₂₂H₁₂Cl₂ (347.2) Calcd. C 76.09 H 3.49 Cl 20.42 Found C 75.91 H 3.55 Cl 20.23

(±)-12,14-Dimethylbenzo[*g*]chrysene (**14**): Double column chromatography on silica gel (2 × 25 cm) with petrolether/40% toluene and petrolether, respectively, being the eluents gave a white powder which was recrystallized from petrolether/methanol (1:1): Colourless plates, m.p. 151.5–153°C. – $^1\text{H NMR}$ (CDCl₃): δ = 2.33 (s, 14-Me), 2.57 (s, 12-Me), 7.17–8.10 (m, 8H),

8.20–8.83 (m, 4H). – UV (CHCl₃): λ_{\max} (lg ϵ) = 382 (2.89), 346 (3.98), 330 (4.06), 295 (4.86), 285 (4.83), 276 (sh, 4.70), 253 nm (4.56). – MS, molecular ion: Calcd. 306.1409, Found 306.1408.

(\pm)-12,14-Di-*tert*-butylbenzo[*g*]chryse (15): The crude product was dissolved in 150 ml of methylenechloride and filtered through 30 g of neutral alumina. After evaporation 15 was washed with methanol and recrystallized from benzene: Colourless crystals, m.p. 180–181.5°C. – ¹H NMR (CCl₄): δ = 1.00 (s, 14-Me₃C), 1.46 (s, 12-Me₃C), 7.26–7.83 (m, 8H), 7.93–8.60 (m, 4H). – ¹³C NMR (CDCl₃): δ = 31.4 (12-(H₃C)₃C), 33.4 (14-(H₃C)₃C), 34.6 (12-Me₃C), 39.3 (14-Me₃C), 147.9 and 149.5 (Me₃C–C), 120–134 (further arene C-atoms). – UV (CHCl₃): λ_{\max} (lg ϵ) = 386 (2.98), 338 (3.94), 304 (4.80), 292 (4.67), 282 (sh, 4.51), 273 (sh, 4.45), 255 nm (4.52). – MS: *m/e* = 390 (100%, M⁺).

C₃₀H₃₀ (390.5) Calcd. C 92.26 H 7.74 Found C 92.26 H 7.80

(\pm)-1,3,6-Trimethyl[5]helicene (16): Double dry-column chromatography on neutral alumina (3.5 × 50 cm) with cyclohexane/10% CHCl₃ as the eluent gave 16 as the first fraction. Recrystallization from *n*-propanol yielded faintly yellow plates, m.p. 171–172.5°C. – ¹H NMR (CDCl₃): δ = 1.45 (s, 1-Me), 2.55 (s, 3-Me), 2.81 (s, 6-Me), 6.95 (broad s, 2-H), 7.09–7.16 (m, 1H), 7.41–7.47 (m, 1H), 7.56 (broad s, 4-H), 7.66 (broad s, 5-H), 7.82–8.10 (m, 6H). – UV (CHCl₃): λ_{\max} (lg ϵ) = 408 (2.45), 388 (2.63), 315 (4.52), 275 (4.36), 238 nm (4.65). – MS, molecular ion: Calcd. 320.1565, Found 320.1569. – From the second fraction the corresponding dibenz[*a,h*]anthracene derivative was isolated.

Semipreparative liquid chromatography of racemic phenanthrenes on triacetylcellulose: The equipment has been described²⁵). 5 times 10 mg of racemic phenanthrene were injected. The relative retentions are given in Table 1. Fractionation yielded the crystalline enriched enantiomers. Because of the small amounts, the specific rotation [α_m]₄₃₆²⁵ (*c* = 1 to 2 g/l CHCl₃) was measured for one of the enantiomers only:

	(+)-2	(-)-9	(+)-11	(+)-13	(-)-14	(-)-15	(-)-16
[α_m] ₄₃₆ ²⁵	+ 23 ± 3	- 178 ± 9	+ 369 ± 9	+ 122 ± 8	- 73 ± 5	- 83 ± 4	- 4820 ± 83

Thermal racemizations of phenanthrenes, monitored by polarimetry: Racemizations below 80°C were performed as described in ref.¹⁰). Otherwise, the solution was kept in an oil bath with controlled temperature for a definite time, taken out, and cooled in an ice bath. After determination of the rotation angle, heating was continued. The evaluation of first-order rate constants and ΔG^\ddagger -values (Table 1) corresponds to ref.²⁶).

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