## Helical Phenanthrenes, 3[1]

# Syntheses, Enrichment of Enantiomers, and Barriers to Racemization of Twisted 9,10-Phenanthrenequinones☆

**Rainer Fritsch, Erwin Hartmann, Doris Andert, and Albrecht Mannschreck***

Institut für Organische Chemie, Universität Regensburg,
Universitätsstraße 31, W-8400 Regensburg, F.R.G.

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The known syntheses of the 9,10-phenanthrenequinones **10a–c** were improved by the chlorotrimethylsilane modification of the acyloin condensation of biaryl diesters. The novel quinones **4a**, **4b**, and **12** were prepared. For the first time, enantiomers (*M* and *P*) of this class of compounds were enriched semipreparatively by liquid chromatography on optically active sorbents. The barriers to thermal racemization amount to 90–130 kJ mol$^{-1}$ (Table 2) and are thus higher than the barriers for the corresponding phenanthrene hydrocarbons by roughly 20 kJ mol$^{-1}$. The reasons for this increase are discussed in terms of repulsive interactions in the transition state of helix inversion.

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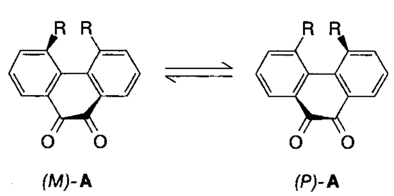
Wittig and Zimmermann[2] were the first to consider that 4,5-dimethyl-9,10-phenanthrenequinone (**A**, R = Me) might be twisted, i.e. chiral. However, its synthesis from an optically active biphenyl derivative at room temperature yielded only inactive material[2]. Newman and his coworkers[3] interpreted the polarographic half-wave potentials for the reduction of some quinones **A** ($R \neq H$) in terms of non-coplanar carbonyl groups, their twist being generated by the substituents in 4- and 5-positions. In 5,6-[6]helicenequinone, too, a torsion about the 5,6-dione fragment was assumed[4]. Apparently, no further results concerning twisted *ortho*-quinones have been published. Therefore, we studied the separability of the enantiomers (*M*)-**A** and (*P*)-**A** with suitable substitution, the aim being the determination of the unknown rates of racemization[5].

For this purpose, the known syntheses[2,3,6,7,8] of methyl-substituted 9,10-phenanthrenequinones which contain nontrivial steps had to be repeated and, if possible, improved. In view of the rates of racemization, it was desirable to prepare some novel representatives of this class of compounds which might help to understand the factors affecting the heights of the barriers.

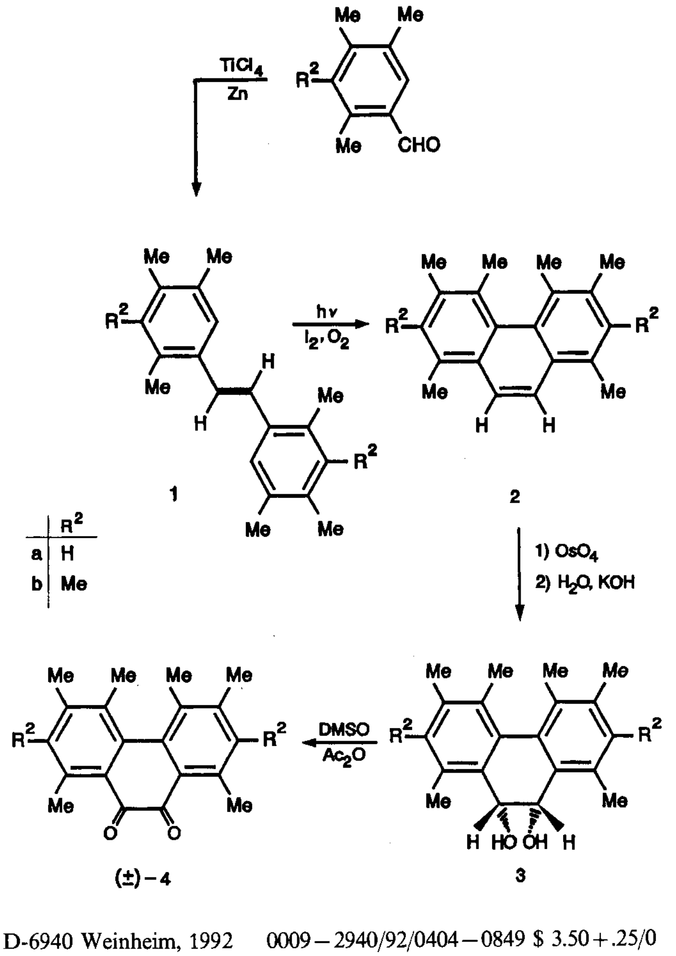


(*M*)-**A** (*P*)-**A**

## Syntheses

Initially, we preferred routes to 9,10-phenanthrenequinones which, in addition, give access to the corresponding hydrocarbons because the chirality of the latter is also of interest. Photocyclization and dehydrogenation, e.g. the conversion of **1** into **2** (Scheme 1), can be performed in spite of hindering substituents[9]. If the phenanthrene molecule is

Scheme 1



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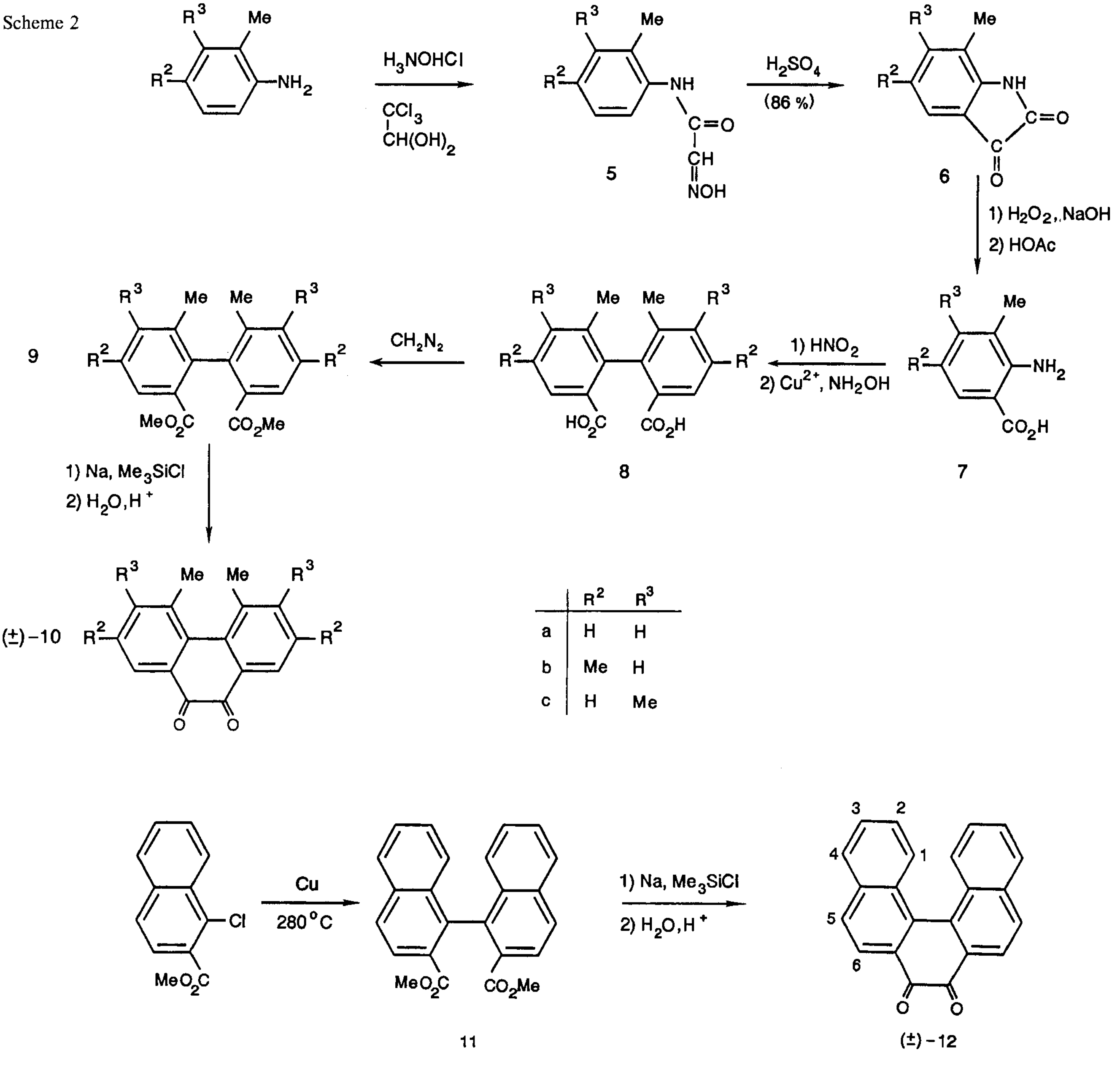
symmetrically substituted the required stilbenes, e.g. **1**, are more easily prepared by the McMurry reaction[10] (Scheme 1) than by the Wittig synthesis which we had used[9] for the less symmetrical stilbenes. The oxidation of hindered hydrocarbons to their quinones had been performed by Newman et al.[3,6–8] by chromium trioxide, attaining yields of up to 30%, or by the less convenient procedure via a 9,10-dihydro-9,10-dihydroxyphenanthrene intermediate (cf. **3**, Scheme 1). We preferred the latter route because the corresponding overall yields are more satisfactory. In the present context of stereodynamics, the preparation via the phenanthrene hydrocarbon (Scheme 1) had to be described for the novel quinones (±)-**4a** and (±)-**4b**, exclusively.

In cases where the hydrocarbon is not required itself, or is *not* easily available, the reaction[11] of benzil with $C_8K$ might be used. However, this procedure did not provide hindered methyl-substituted 9,10-phenanthrenequinones[12]. Therefore, (±)-**10** and (±)-**12** were synthesized by an acyloin condensation of the biaryl diesters **9** and **11** (Scheme 2). This reaction had been used for the same purpose by Wittig and Zimmermann[2] and by Newman et al.[3], their yields ranging from 29 to 45%. We modified their procedure, mainly by adding chlorotrimethylsilane according to Rühlmann[13] and attained yields between 28 and 75% (Scheme 2). The required biphenyl diesters **9** were obtained by reductive coupling[8,14] of the diazonium salts derived from anilines **7**. We also prepared the unknown [5]helicene quinone (±)-**12** in 47% yield by the $Me_3SiCl$-modified acyloin condensation (Scheme 2).

## Liquid Chromatography on Optically Active Sorbents

With the exception of (±)-**10c** (Figure 1), the separations on microcrystalline triacetylcellulose at 22 °C are weak (Ta-

Scheme 2



| | $R^2$ | $R^3$ |
|---|---|---|
| a | H | H |
| b | Me | H |
| c | H | Me |

ble 1); the semipreparative enrichment was difficult or, in the case of (±)-**10a** and (±)-**10b**, impossible. Apparently, the main reasons for this situation are the low overall retentions, i.e. the low absolute values of the capacity factors. Corresponding hydrocarbons[9] show higher retentions (and also more efficient separations), probably because they are more lipophilic. In the case of (±)-**10a** another reason may exist because no polarimetric detection at all was monitored after LC (Table 1). Its low barrier to helix inversion (90.2 kJ $mol^{-1}$, Table 2) may cause coalescence of the two peaks, a phenomenon observed in many similar cases[15].

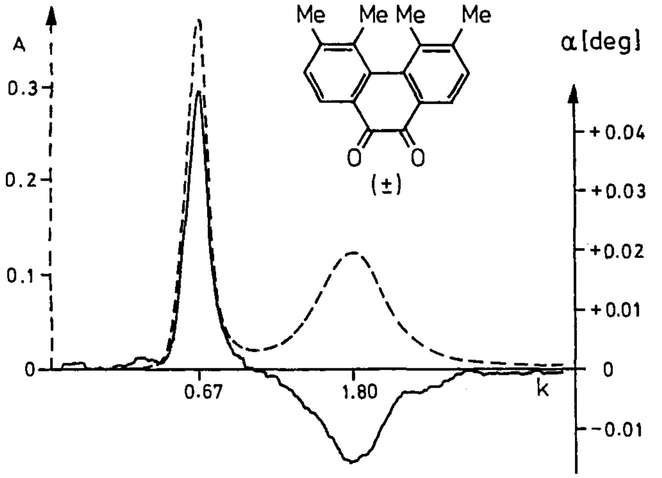


Figure 1. LC of 0.82 mg of (±)-**10c** in $EtOH/H_2O$ (96:4) on microcrystalline triacetylcellulose at ≈2 bar and 22°C. *A*: Absorbance at 278 nm. α: Polarimetric rotation angle at 546 nm. *k*: Capacity factor

Table 1. Capacity factors $k_1$ and $k_2$ of enantiomers of phenanthrenequinones upon analytical LC. If not indicated otherwise, microcrystalline triacetylcellulose[18] at +22°C served as sorbent and $EtOH/H_2O$ (96:4) as eluent at 2 bar. Different specimens of columns, prepared in virtually identical ways, were used for the determination of *k* values; therefore, the latter are not necessarily comparable among themselves. (*) Sign of rotation for the enantiomer eluted first, as obtained by an on-line polarimeter; the sign refers to 436 nm for **10a** and to 546 nm for the other quinones

| Comp. No. | $R^1$ | $R^2$ | $R^3$ | $R^4$ | (*) | $k_1$ | $k_2$ |
|---|---|---|---|---|---|---|---|
| (±)-**10a** | H | H | H | Me | (+) | $\bar{k} = 1.3$ | |
| | | | | | (−) | 0.4 | 0.6[a] |
| (±)-**10b** | H | Me | H | Me | (−) | $\bar{k} = 0.6$ | |
| (±)-**10c** | H | H | Me | Me | (+) | 0.7 | 1.8 |
| (±)-**4a** | Me | H | Me | Me | (+) | $\bar{k} = 0.2$ | |
| | | | | | (+) | 2.5 | 3.2[b] |
| (±)-**4b** | Me | Me | Me | Me | (−) | 0.3 | 0.4 |
| | | | | | (+) | 3.6 | 4.5[c] |
| (±)-**12** | H | H | benzo | | (+) | $\bar{k} = 1.6$ | |
| | | | | | (−) | 0.1 | 1.1[d] |

[a] (+)-Poly(trityl methacrylate)/$SiO_2$[17], MeOH, 50 bar, −5°C. — [b] Microcrystalline tribenzoylcellulose[16], $EtOH/H_2O$ (96:4), 75 bar, +22°C. — [c] Microcrystalline tribenzoylcellulose[16], $EtOH/H_2O$ (96:4), 65 bar, +22°C. — [d] (+)-Poly(trityl methacrylate)/$SiO_2$[17], MeOH, 27 bar, +14°C.

Indeed, (±)-**10a** shows some separation of its enantiomers upon LC on (+)-poly(trityl methacrylate)/$SiO_2$ at −5°C (Table 1). On this sorbent the [5]helicene quinone (±)-**12** experiences an excellent separation which was used semipreparatively. However, the quantities of the enantiomers obtained were very small, because only an *analytical* column containing this sorbent is available.

The *k* values in Table 1 for (±)-**4a** and (±)-**4b** on triacetyl- and tribenzoylcellulose show semiquantitatively that the separations are somewhat more advantageous on the latter[16].

The solutions of the present quinones in EtOH at room temperature do not contain appreciable amounts of reaction products[5], e.g. hemiketals, as shown by LC and by UV.

The above separations represent the first proof of helicity of 4,5-disubstituted 9,10-phenanthrenequinones and the first semipreparative enrichments of their enantiomers.

## Barriers to Helix Inversion

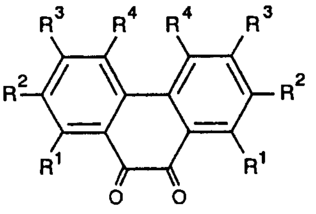
For experimental reasons, the barriers $\Delta G^{\neq}$ (Table 2, left part) had to be determined in different solvents. The barriers obtained with $EtOH/H_2O$ (96:4) are slightly higher than those obtained with *o*-dichlorobenzene, probably because of some stabilization of the quinone ground state by hydrogen bonds to the alcohol. Again for experimental reasons, the temperatures of the racemizations ranged from 23.8 to 140.9°C. The best way out of this situation is the measurement of rate constants at more temperatures for at least one of the compounds, an experiment which will be performed in the near future. If we assume the entropies of activation to be small (which is true for the hydrocarbons **13**[1] and **17**[19], related to phenanthrenequinones) we can compare the quinone $\Delta G^{\neq}$ values at least in a qualitative manner.

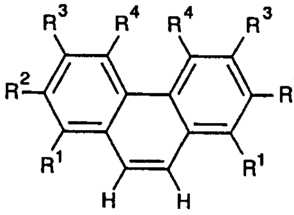
Thus, an effect of hindrance to the helix inversion (*M*)-**A** ⇌ (*P*)-**A** of roughly 17 kJ $mol^{-1}$ can be seen for **10a**/**13** and for **10c**/**4a**. A buttressing effect of ca. 22 kJ $mol^{-1}$ is observed by comparing **10a**/**10c** and **13**/**4a**.

As far as a comparison with the related hydrocarbons (Table 2, right part) is concerned, we *calculated* their $\Delta G^{\neq}$ values for the temperatures of the measurements of the quinones. These calculations were performed on the basis of the experimental $\Delta G^{\neq}$ values of the hydrocarbons (Table 3) and an entropy of activation of −17 J $mol^{-1}$ $K^{-1}$. The latter value was found experimentally for **14**[1] and **18**[19]. Table 2 finally lists values of $\Delta\Delta G^{\neq}$, i.e. differences between the free enthalpies of activation for a quinone and for a hydrocarbon. The barrier is higher in the quinones, partly because of oxygen/oxygen repulsion in the transition state of inversion. $\Delta\Delta G^{\neq}$ amounts to ca. +15 kJ $mol^{-1}$ when $R^1$ = H and to roughly +25 kJ $mol^{-1}$ when $R^1$ = Me which represents a repulsive interaction between $R^1$ = Me and the next oxygen atom in the transition state.

Changes of bonding, mainly of bond lengths, may also contribute indirectly to the $\Delta\Delta G^{\neq}$-values (Table 2). The C-9/C-10 length in 2,4,7-trinitro-9,10-phenanthrenequinone is 152 pm[23], in phenanthrene itself 134 pm[24]. This difference may mean for the transition states of the molecules in

Table 2. Comparison of barriers to helix inversion in phenanthrenequinones and hydrocarbons. The $\Delta G^{\neq}$ values of the quinones were determined by thermal racemizations of enriched enantiomers, monitored by polarimetry; the values measured in $EtOH/H_2O$ (96:4, ETW) as solvent were obtained on line (see Experimental), the others by using preparatively enriched enantiomers. The $\Delta G^{\neq}$ values of the hydrocarbons were calculated from the experimental free enthalpies $\Delta G_e^{\neq}$ (Table 3) and the experimental temperatures $T_e$ (Table 3) by means of the equation $\Delta G^{\neq} = \Delta G_e^{\neq} + \Delta S^{\neq}(T_e - T)$. An entropy of activation of $\Delta S^{\neq} = -17 \pm 4$ J $mol^{-1}$ $K^{-1}$ was used[19,21]. $\Delta\Delta G^{\neq}$: Difference between the free enthalpies of activation for a quinone and for a hydrocarbon. DCB: *o*-Dichlorobenzene





| $R^1$ | $R^2$ | $R^3$ | $R^4$ | T [°C] | Comp. No. | Sol-vent | $\Delta G^{\neq}$ [kJ $mol^{-1}$] | Comp. No. | $\Delta G^{\neq}$ [kJ $mol^{-1}$] | $\Delta\Delta G^{\neq}$ [kJ $mol^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|---|
| H | H | H | Me | 25.0 | **10a** | ETW | 90.2 ± 0.2 | **14** | 67 ± 6 | ≃23 |
| H | Me | H | Me | 23.8 | **10b** | ETW | 94.0 ± 0.2 | – | – | – |
| Me | H | H | Me | 61.7 | **13** | ETW | 107.2 ± 0.4[20] | **15** | 77.8 ± 1.0 | 29 |
| | | | | 63.4 | | DCB | 106.2 ± 0.2[20] | | – | – |
| H | H | Me | Me | 77.4 | **10c** | ETW | 112.0 ± 0.2 | **16** | 97.2 ± 0.3 | 15 |
| | | | | 74.4 | | DCB | 111.5 ± 0.2 | | – | – |
| Me | H | Me | Me | 123.9 | **4a** | DCB | 129.0 ± 0.3 | **17a** | 106.4 ± 0.7 | 23 |
| Me | Me | Me | Me | 140.9 | **4b** | DCB | 131.3 ± 0.5 | **17b** | 110.3 ± 1.0 | 21 |
| H | H | benzo | | 55.7 | **12** | $CHCl_3$ | 116.7 ± 0.2 | **18** | 101 | 16 |

Table 3. Barriers $\Delta G_e^{\neq}$ to helix inversion in phenanthrene hydrocarbons, determined by thermal racemizations of enriched enantiomers, monitored at $T_e$ by polarimetry. The $\Delta G_e^{\neq}$ value for **14** was obtained off line according to ref.[21], the one for **15** and **16** on line in alcohols (see Experimental), the other ones by using preparatively enriched enantiomers

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Comp. No. | Solvent | $T_e$ [°C] | $\Delta G_e^{\neq}$ [kJ $mol^{-1}$] |
|---|---|---|---|---|---|---|---|
| H | H | H | Me | **14** | $n$-$C_6H_{14}$ | 25.0 | 67 ± 6[21] |
| Me | H | H | Me | **15** | MeOH | −10.8 | 76.6 ± 0.7[22] |
| H | H | Me | Me | **16** | $EtOH/H_2O$ (96:4) | 29.9 | 96.4 ± 0.2 |
| | | | | | $CHCl_3$ | 30.0 | 95.8 ± 0.2[9] |
| Me | H | Me | Me | **17a** | $CHCl_3$ | 49.5 | 105.1 ± 0.4[5] |
| Me | Me | Me | Me | **17b** | $CHCl_3$ | 53.7 | 108.8 ± 0.6[5] |
| H | H | benzo | | **18** | $CHCl_3$ | 40 | 101[19] |

Table 2 that the substituents in 4- and 5-positions in a quinone suffer stronger mutual repulsion than in a hydrocarbon.

Although there are reasons to assume that the 4-nitro group and 5-H in the trinitro compound do not interact strongly, the above choice of reference molecules is by no means an ideal one. However, we are not aware of any further bond length information about 9,10-phenanthrenequinone or its substitution products. Attempts of X-ray analyses of the parent compound, of (±)-**4a** and of (±)-octachloro-9,10-phenanthrenequinone[5] failed[25], mainly because none of the crystals hitherto investigated produced a sufficient number of reflexes.

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## Experimental

Melting points are not corrected. – $^1H$ NMR: Varian T60A or Bruker WM250; for lanthanoid-induced splittings, see ref.[26]. – UV: Beckman, Model 24, at $10^{-3}$ to $10^{-4}$ mol/l. – MS: Varian CH5 at low resolution. – Specific rotations: Polarimeter Perkin-Elmer 241; the cell temperature was fixed by a thermostat.

*Low-Pressure Liquid Chromatography on Microcrystalline Triacetylcellulose:* The sorbent[18], particle sizes 20–30 μm, was prepared, swollen, and filled into glass columns (25 × 300 nm) according to ref.[26]. The LC detectors are given in ref.[26]. This setup served for analytical (Table 1) as well as for semipreparative LC. The capacity factors were calculated from $k_i = (v_i - v_0)/v_0$, $v_0$ being the retention volume of 1,3,5-tri-*tert*-butylbenzene[18].

*High-Pressure Liquid Chromatography on Optically Active Sorbents:* Microcrystalline tribenzoylcellulose[16], particle sizes 10–15 μm, was prepared, swollen, and filled into steel columns (8 × 250 mm) according to ref.[16]. The capacity factors refer to 1,3,5-tri-*tert*-butylbenzene. – (+)-Poly(trityl methacrylate)/$SiO_2$[17] from Daicel, Himeji, Japan, was filled into steel columns (4 × 250 mm). The capacity factors refer to water. This column served for analytical (Table 1) and for semipreparative LC. – The photometer ERC 7210 (ERMA Optical Works, Ltd., Tokyo) and the polarimeter 241 (Perkin-Elmer, Überlingen) were used as LC detectors.

*Thermal Racemizations of Enriched Enantiomers:* Racemizations in alcohols were performed on line[15], i.e. LC was stopped on a peak, the polarimeter cell was thermostated to a suitable temperature and the decrease of the angle of rotation was monitored. Racemizations in *o*-dichlorobenzene or in $CHCl_3$ were performed off line, i.e. semipreparatively enriched enantiomers were dissolved in these solvents. In the cases of **10c** and **12**, the solutions remained in the polarimeter cell for racemization. In the cases of **4a** and **4b**, the solutions were thermostated in an external bath; at certain times, the samples were removed, cooled to room temp. and placed into the polarimeter for measurement. The racemizations of the enantiomers of **4a** and **4b** could only be monitored during one half-life; all other racemizations were measured during at least two half-lives.The $\Delta G^{+}$ values were calculated by means of the KINMIK or KINE computer programs[27].

*General Procedure*[10] *for the Preparation of Stilbenes* **1**: 76 mmol of zinc powder and 37 mmol of $TiCl_4$ were stirred in 350 ml of absol. THF under nitrogen. 35 mmol of aldehyde in 30 ml of absol. THF was added. After 16 h under reflux 200 ml of a satd. $Na_2CO_3$ solution was added to the brown-red mixture which was vigorously stirred for 15 min. The mixture was then extracted several times with diethyl ether and the united ethereal extracts were dried with $MgSO_4$. Dry-column chromatography on silica gel with petroleum ether (40–60°C) and crystallization from $CH_2Cl_2$/EtOH (5:1) resulted in colorless crystals.

*2,2',4,4',5,5'-Hexamethylstilbene*[28] (**1a**): From 5.8 g (39 mmol) of 2,4,5-trimethylbenzaldehyde[29] according to the general procedure: 3.8 g (74%), m.p. 165–167°C. – $^1H$ NMR ($CDCl_3$): δ = 2.26, 2.35 (2 s, 18H, $CH_3$), 6.91 (s, 2H, alkene H), 7.10, 7.35 (2 s, 4H, arene H).

*2,2',3,3',4,4',5,5'-Octamethylstilbene*[28] (**1b**): From 3.0 g (20 mmol) of 2,3,4,5-tetramethylbenzaldehyde[30] according to the general procedure: 1.9 g (64%), m.p. 162–163°C. – $^1H$ NMR ($CDCl_3$): δ = 2.23, 2.28 (2 s, 24H, $CH_3$), 7.05, 7.16 (2 s, 4H, alkene and arene H).

*General Procedure*[29] *for the Preparation of Phenanthrenes* **2**: A procedure given earlier[9] was modified by the following details: A falling-film apparatus (Dema, Bornheim, Germany) of 0.5–2.0 l volume and a 500-W high-pressure Hg lamp (Hanau, TQ 718) with a Z2 filter were used for up to 3 mmol/l of a stilbene during 60 min. Dry-column chromatography on silica gel with petroleum ether (40–60°C) resulted in viscous oils which crystallized from ethanol.

*(±)-1,3,4,5,6,8-Hexamethylphenanthrene*[28] (**2a**): From 1020 mg (3.86 mmol) of **1a** according to the general procedure: Colorless leaves, m.p. 175–177°C, 405 mg (40%). – $^1H$ NMR ($CDCl_3$): δ = 2.36 (s, 6H, 4-$CH_3$), 2.43 (s, 6H, 3-$CH_3$), 2.67 (s, 6H, 1-$CH_3$), 7.20 (s, 2H, 2-H), 7.64 (s, 2H, 9-H).

$C_{20}H_{22}$ (262.4) Calcd. C 91.55 H 8.45
Found C 91.11 H 8.51

*(±)-1,2,3,4,5,6,7,8-Octamethylphenanthrene*[28] (**2b**): From 790 mg (2.71 mmol) of **1b** according to the general procedure: Colorless powder, m.p. 177–179°C, 157 mg (20%). – $^1H$ NMR ($CDCl_3$): δ = 2.40 (s, 3H, 1-$CH_3$), 2.41, 2.46 (2 s, 6H, 2-$CH_3$, 3-$CH_3$), 2.65 (s, 3H, 4-$CH_3$), 7.74 (s, 2H, 9-H). – MS (70 eV): *m/z* (%) = 290 (100) [$M^+$], 275 (41) [$M^+ - CH_3$], 260 (43) [$M^+ - 2\ CH_3$], 245 (26) [$M^+ - 3\ CH_3$], 230 (9) [$M^+ - 4\ CH_3$].

$C_{22}H_{26}$ (290.4) Calcd. C 90.98 H 9.02
Found C 90.81 H 9.36

*(±)-9,10-Dihydro-cis-9,10-dihydroxy-1,3,4,5,6,8-hexamethylphenanthrene* (**3a**): 250 mg (0.95 mmol) of **2a** was allowed to react for 1 week with a slight excess of $OsO_4$; workup was performed according to the method described in refs.[31,32]; CC on silica [petroleum ether (40–60°C)/ethyl acetate, 4:1] and its repetition (v:v, 4:3) furnished colorless crystals, m.p. 153–154°C (cyclohexane), 219 mg (78%). – $^1H$ NMR ($CDCl_3$): δ = 1.57 (br. m, 2H, OH), 1.96, 2.04, 2.27, 2.51, 2.56 (5 s, partially overlapped, 18H, $CH_3$), 4.75 (br., 1H, 9- or 10-H), 4.84 (br. d, *J* = 9 Hz, 1H, 9- or 10-H), 6.98 (s, 2H, 2-H, 7H). – UV ($CHCl_3$): $\lambda_{max}$ (lg ε) = 244 (4.30), 272 nm (4.10).

$C_{20}H_{24}O_2$ (296.4) Calcd. C 81.04 H 8.16
Found C 81.06 H 8.06

*(±)-9,10-Dihydro-cis-9,10-dihydroxy-1,2,3,4,5,6,7,8-octamethylphenanthrene* (**3b**): 450 mg (1.55 mmol) of **2b** was treated for 1 week with a slight excess of $OsO_4$; workup according to the method reported in refs.[31,32]; CC on silica [petroleum ether (40–60°C)/ethyl acetate, 4:1] and two recrystallizations from cyclohexane afforded colorless crystals, m.p. 236–238°C, 171 mg (34%). – $^1H$ NMR ($CDCl_3$): δ = 1.55 (br. s, 1H, OH), 1.98, 2.07, 2.26, 2.27, 2.29, 2.41, 2.50 (7 s, partially overlapped, 24H, $CH_3$), 2.61 (br. d, $^3J$ = 10 Hz, 1H, OH), 4.85 (br. m, 2H, 9-, 10-H). – UV ($CHCl_3$): $\lambda_{max}$ (lg ε) = 232 (4.44), 275 (4.16), 311 nm (sh).

$C_{22}H_{28}O_2$ (324.4) Calcd. C 80.40 H 8.34
Found C 80.43 H 8.69

*(±)-1,3,4,5,6,8-Hexamethyl-9,10-phenanthrenequinone* (**4a**): 219 mg (0.74 mmol) of **3a** was treated for 24 h with DMSO and $Ac_2O$ according to the method reported in ref.[7]; CC on silica [petroleum ether (40–60°C)/ethyl acetate, 4:1] resulted in yellow crystals, m.p. 244.5–248.5°C, 43 mg (20%). – $^1H$ NMR ($CDCl_3$): δ = 2.07 (s, 3H, 4-$CH_3$), 2.35 (s, 3H, 3-$CH_3$), 2.56 (s, 3H, 1-$CH_3$), 7.05 (s, 2H, 2-H). – MS (70 eV): *m/z* (%) = 292 (15) [$M^+$], 264 (100) [$M^+ - CO$], 249 (55) [$M^+ - CO - CH_3$], 221 (24) [$M^+ - 2\ CO - CH_3$], 206 (22) [$M^+ - 2\ CO - 2\ CH_3$].

$C_{20}H_{20}O_2$ (292.4) Calcd. C 82.16 H 6.89
Found C 81.74 H 7.00

*(+)-1,3,4,5,6,8-Hexamethyl-9,10-phenanthrenequinone* (**4a**): From LC on triacetylcellulose (EtOH/$H_2O$, 96:4). M.p. 233–240°C. – $^1H$ NMR identical to that of (±)-**4a**. – Enantiomeric purity *P* = 47% (LC, tribenzoylcellulose, EtOH/$H_2O$, 96:4, +22°C, cf. Table 3). $[\alpha]_{546}^{22}$ = +2340 ± 170 (0.056 g/100 ml $CHCl_3$) for *P* = 100%.

*(−)-1,3,4,5,6,8-Hexamethyl-9,10-phenanthrenequinone* (**4a**): From LC on triacetylcellulose (EtOH/$H_2O$, 96:4). M.p. 237–243°C. – $^1H$ NMR identical to that of (±)-**4a**. – Enantiomeric purity *P* = 31% ⟨$^1H$ NMR, 0.5–0.6 equivalents of (+)-tris[3-heptafluorobutyryl-D-camphorato]europium(III)⟩. $[\alpha]_{546}^{22}$ = −2340 ± 240 (0.028 g/100 ml $CHCl_3$) for *P* = 100%.

*(±)-Octamethyl-9,10-phenanthrenequinone* (**4b**): 171 mg (0.53 mmol) of **3b** was treated for 24 h with DMSO and $Ac_2O$ according to the method described in ref.[7]; CC on silica gel ($CHCl_3$) and its repetition ($CH_2Cl_2$) resulted in yellow crystals, m.p. 280–284°C, 70 mg (41%). – $^1H$ NMR ($CDCl_3$): δ = 2.07 (s, 6H, 4-$CH_3$), 2.29, 2.32 (2 s, 12H, 2-$CH_3$, 3-$CH_3$), 2.55 (s, 6H, 1-$CH_3$). Small additional peaks visible. – UV ($CHCl_3$): $\lambda_{max}$ (lg ε) = 262 (3.99), 286 (3.76), 341 nm (3.35). – MS (70 eV): *m/z* (%) = 320 (10) [$M^+$], 292 (100) [$M^+ - CO$], 277 (41) [$M^+ - CO - CH_3$], 249 (14) [$M^+ - 2\ CO - CH_3$], 234 (12) [$M^+ - 2\ CO - 2\ CH_3$]; two additional peaks at *m/z* = 334 and 336.

*(+)-Octamethyl-9,10-phenanthrenequinone* (**4b**): From LC on triacetylcellulose (EtOH/$H_2O$, 96:4). M.p. 273–280°C. – $^1H$ NMR identical with that of (±)-**4b**. – Enantiomeric purity *P* = 41%

⟨$^1$H NMR, 0.5–0.6 equivalents of (+)-tris[3-heptafluorobutyryl-D-camphorato]europium(III)⟩. $[\alpha]^{22}_{546} = +1650 \pm 150$, $[\alpha]^{22}_{578} = +1190 \pm 140$ (0.024 g/100 ml $CHCl_3$) for $P = 100\%$.

*General Procedure*[33] *for the Preparation of 2,3-Indolediones* **6**: 70 mmol of isonitrosoacetanilide **5**, prepared[14] from the corresponding aniline, chloral hydrate and hydroxylammonium chloride, was added during 20 min to 63 ml of $H_2SO_4$ (86%), the temperature being held strictly at 55°C. After 10 min the mixture was heated to 75°C for 30 min. After cooling it was poured into 600 ml of ice/water. The red precipitate was removed by filtration and dried at 80°C: Deep-red crystals from HOAc. Yields 61–78%.

*7-Methyl-2,3-indoledione* (**6a**): M.p. 268–270°C (ref.[8] 269–271°C). – $^1$H NMR ($[D_6]$DMSO): $\delta$ = 2.17 (s, 3H, Me), 6.8–7.6 (m, 3H, arene H), 11.0 (s, 1H, NH).

*5,7-Dimethyl-2,3-indoledione* (**6b**): M.p. 247–249°C (ref.[14] 249–251°C). – $^1$H NMR ($[D_6]$acetone): $\delta$ = 2.31 (s, 6H, Me), 6.59, 7.08 (2 s, 2H, arene H), 11.05 (s, 1H, NH).

*6,7-Dimethyl-2,3-indoledione* (**6c**): M.p. 250–255°C (ref.[14] 255–258°C). – $^1$H NMR ($[D_6]$DMSO): $\delta$ = 2.12 (s, 3H, Me), 2.33 (s, 3H, Me), 6.80, 7.26 (2 d, 2H, $^3J$ = 7.8 Hz, arene H), 11.05 (s, 1H, NH).

*General Procedure*[34] *for the Preparation of Diphenic Acids* **8**: *Diazonium Salt:* 19.0 mmol of 2-aminobenzoic acid **7**, prepared[8,14] from 2,3-indoledione **6**, $H_2O_2$, and NaOH, was dissolved in 30 ml of $H_2O$ with 25.0 mmol of NaOH. After cooling the solution to 10°C and adding 18.8 mmol of $NaNO_2$, it was dropped into 40 ml of HCl (10%), the temperature being held below 2°C. The mixture was stirred at 0°C for 30 min. *Copper(I) Salt:* 20.8 mmol of hydroxylammonium sulfate in 10 ml of $H_2O$, treated with 6 ml of 6 N NaOH at 10°C, was added dropwise at 10°C to 32.0 mmol of $CuSO_4 \cdot 5\,H_2O$ in 25 ml of $H_2O$, treated with 15 ml of $NH_3$ (30%) at 10°C. *Coupling reaction:* The diazonium salt solution was added dropwise at 10–12°C to the copper(I) salt solution with vigorous stirring. The addition of a few drops of $Et_2O$ prevented violent evolution of $N_2$. After 20 min the mixture was refluxed. Upon careful acidification with conc. HCl a yellow material precipitated which was collected and dried at 60°C. *Purification:* The crude acid in 30 ml of 2 N NaOH was boiled with 1 g of zinc dust, filtered, and the filtrate was acidified with conc. HCl. The formed precipitate was dried at 60°C, suspended in 300 ml of $Et_2O$, filtered and liberated from the ether.

*6,6'-Dimethyldiphenic Acid* (**8a**): From 3.01 g (20.0 mmol) of 3-methylanthranilic acid; colorless crystals, m.p. 230°C (ref.[36] 230°C), 1.25 g (46%). – $^1$H NMR ($[D_6]$DMSO): $\delta$ = 1.84 (s, 6H, 6-$CH_3$, 6'-$CH_3$), 7.32 (t, 2H, $^3J$ = 8.0 Hz, 4-, 4'-H), 7.45 (d, 2H, $^3J$ = 8.0 Hz, 5-, 5'-H), 7.89 (d, 2H, $^3J$ = 8.0 Hz, 3-, 3'-H), 12.2 (br. s, 2H, $CO_2H$).

*4,4',6,6'-Tetramethyldiphenic Acid* (**8b**): From 3.3 g (20 mmol) of 3,5-dimethylanthranilic acid; colorless crystals, m.p. 274–278°C (ref.[14] 275–282°C), 2.1 g (78%) (ref.[14] 80%). – $^1$H NMR ($[D_8]$THF): $\delta$ = 1.80 (s, 6H, $CH_3$), 2.30 (s, 6H, $CH_3$), 7.10, 7.50 (2 s, 4H, arene H), $CO_2H$ not visible.

*5,5',6,6'-Tetramethyldiphenic Acid* (**8c**): From 3.06 g (19.0 mmol) of 3,4-dimethylanthranilic acid; yellowish crystals, m.p. 248–250°C (ref.[14] 252°C), 1.36 g (48%) (ref.[14] 55.2%). – $^1$H NMR ($[D_6]$DMSO): $\delta$ = 1.69 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 7.10, 7.54 (2 s, 4H, $^3J$ = 8.4 Hz, arene H), 11.4 (s, 2H, $CO_2H$).

*General Procedure*[37] *for the Preparation of Dimethyl Diphenates* **9**: They were obtained from diphenic acids **8** and $CH_2N_2$. Column chromatography on silica gel ($CCl_4$/$Et_2O$, 5:1) or recrystallization from EtOH yielded 73–80% of colorless crystals.

*Dimethyl 6,6'-Dimethyldiphenate* (**9a**): M.p. 51–52°C (ref.[2] 52–53°C). – $^1$H NMR ($CDCl_3$): $\delta$ = 1.90 (s, 6H, $C-CH_3$), 3.57 (s, 6H, $OCH_3$), 7.34 (t, 4H, $^3J$ = 7.7 and 7.5 Hz, arene H), 7.43 (d, 4H, $^3J$ = 7.7 Hz, arene H), 7.85 (d, 4H, $^3J$ = 7.5 Hz, arene H).

*Dimethyl 4,4',6,6'-Tetramethyldiphenate* (**9b**): M.p. 147–148°C (ref.[3] 155.5–156.5°C). – $^1$H NMR ($CDCl_3$): $\delta$ = 1.87 (s, 6H, $C-CH_3$), 2.36 (s, 6H, $C-CH_3$), 3.55 (s, 6H, $OCH_3$), 7.23 (s, 2H, arene H), 7.63 (s, 2H, arene H).

*Dimethyl 5,5',6,6'-Tetramethyldiphenate* (**9c**): M.p. 98–103°C (ref.[3] 106–107°C). – $^1$H NMR ($CDCl_3$): $\delta$ = 1.76 (s, 6H, $C-CH_3$), 2.31 (s, 6H, $C-CH_3$), 3.48 (s, 6H, $OCH_3$), 7.11, 7.68 (2 d, 4H, $^3J$ = 8.4 Hz, arene H).

*Dimethyl 1,1'-Binaphthyl-2,2'-dicarboxylate* (**11**): 5.06 g (23.0 mmol) of methyl 1-chloro-2-naphthoate[38] was heated with 10.0 g (158 mmol) of freshly activated copper[39] ("Naturkupfer C" from BASF AG, Ludwigshafen) and a trace of $I_2$ under $N_2$ in a sand bath to 280–300°C for 45 min. The acetone extract of the mixture was refluxed with Norit and furnished, after evaporation of acetone, a yellow product. Colorless crystals (MeOH), m.p. 155–157°C (ref.[38] 157–158°C), 1.06 g (25%). – $^1$H NMR ($CDCl_3$): $\delta$ = 3.48 (s, 6H, $OCH_3$), 7.07 (d, 2H, $^3J$ = 8.3 Hz, 8-, 8'-H), 7.24 (dd, 2H, 7-, 7'-H), 7.52 (dd, 2H, 6-, 6'-H), 7.94 (d, 2H, $^3J$ = 8.4 Hz, 5-, 5'-H), 8.01, 8.18 (2 d, 4H, $^3J$ = 8.7 Hz, 3-, 3'-, 4-, 4'-H).

*General Procedure for the Preparation of 9,10-Phenanthrenequinones* (±)-**10** *and* (±)-**12**: After preparing a suspension of sodium[13a] from 43.5 mmol of Na and 70 ml of absol. toluene by use of a mechanical stirrer, the mixture was refluxed for 45 min in order to obtain absolutely dry toluene. The acyloin condensation was performed as described[13a] with 27.6 mmol of $Me_3SiCl$ and 3.1 mmol of dimethyl diphenate **9** or dimethyl binaphthyldicarboxylate **11**. The 1,2-bis(trimethylsiloxy) derivative was hydrolyzed[13b], and the resulting crude quinone was isolated[2].

*(±)-4,5-Dimethyl-9,10-phenanthrenequinone* (**10a**): From 1.50 g (4.99 mmol) of **9a**. CC on silica gel ($CHCl_3$) and recrystallization from EtOH resulted in orange crystals, m.p. 160–161°C (ref.[2] 162–162.5°C), 325 mg (28%) (ref.[2] 35.7%). – $^1$H NMR ($CDCl_3$): $\delta$ = 2.30 (s, 6H, $CH_3$), 7.40 (t, 2H, $^3J$ = 7.0 Hz, 2-H), 7.53 (d, 2H, $^3J$ = 7.0 Hz, 3-H), 7.87 (d, 2H, $^3J$ = 7.0 Hz, 1-H). – UV ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$) = 344 (3.66), 284 (3.93), 262 (4.23), 228 nm (4.40).

*(±)-2,4,5,7-Tetramethyl-9,10-phenanthrenequinone* (**10b**): From 1.00 g (3.07 mmol) of **9b**. Dry-column chromatography on silica ($CHCl_3$) afforded orange crystals, m.p. 195–198°C (ref.[3] 195–200°C), 610 mg (75%) (ref.[3] 45%). – $^1$H NMR ($CDCl_3$): $\delta$ = 2.27 (s, 6H, 4-$CH_3$), 2.35 (s, 6H, 2-$CH_3$), 7.33, 7.67 (2 s, 4H, arene H). – UV ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$) = 425 (3.17), 340 (3.67), 262 (4.50), 229 nm (4.51).

*(±)-3,4,5,6-Tetramethyl-9,10-phenanthrenequinone* (**10c**): From 1.00 g (3.07 mmol) of **9c**. CC on silica gel ($CH_2Cl_2$) afforded orange crystals, m.p. 195–197°C (ref.[3] 197°C), 337 mg (42%) (ref.[3] 38%). – $^1$H NMR ($CDCl_3$): $\delta$ = 2.16 (s, 6H, 4-$CH_3$), 2.41 (s, 6H, 3-$CH_3$), 7.27, 7.81 (2 d, 2H, $^3J$ = 7.9 Hz, arene H). – UV ($CH_2Cl_2$): $\lambda_{max}$ (lg $\varepsilon$) = 344 (3.66), 284 (3.93), 262 (4.23), 228 nm (4.40).

*(+)-3,4,5,6-Tetramethyl-9,10-phenanthrenequinone* (**10c**): From LC on triacetylcellulose (EtOH/$H_2O$, 96:4), then thick-layer chromatography on silica gel ($CHCl_3$). M.p. 191–193°C. – $^1$H NMR identical with that of (±)-**10c**. Enantiomeric purity 100% ⟨$^1$H NMR, 0.8 equivalents of (+)-tris[3-heptafluorobutyryl-D-camphorato]europium(III)⟩. $[\alpha]^{22}_{365} = -1110 \pm 60$, $[\alpha]^{22}_{436} = +1040 \pm 60$, $[\alpha]^{22}_{589} = +510 \pm 40$ (0.024 g/100 ml $CH_3CN$).

*(−)-3,4,5,6-Tetramethyl-9,10-phenanthrenequinone* (**10c**): From LC on triacetylcellulose (EtOH/$H_2O$, 96:4). M.p. 188–191°C. –

$^1$H NMR identical with that of (±)-**10c** but showing an additional small peak at $\delta = 2.34$. Enantiomeric purity 100% ($^1$H NMR, as described for $(+)_{436}$-**10c**). $[\alpha]^{22}_{365} = +1120 \pm 60$, $[\alpha]^{22}_{436} = -1060 \pm 60$, $[\alpha]^{22}_{589} = -530 \pm 30$ (0.030 g/100 ml $CH_3CN$).

*(±)-Dibenzo[c,g]phenanthrene-7,8-quinone* (**12**): From 1.00 g (2.70 mmol) of **11**. Dry-column chromatography on silica ($CHCl_3$) afforded dark-red crystals, m.p. 224–226°C, 394 mg (47%). – $^1$H NMR ($CDCl_3$) (for numbering of protons, see Scheme 2): $\delta = 7.35$ (m, 2H, 2-H), 7.45 (m, 2H, 1-H), 7.66 (m, 2H, 3-H), 7.96 (m, 2H, 4-H), 8.02, 8.18 (AB, 4H, $^3J = 8.5$ Hz, 5-, 6-H). – UV ($CH_3CN$): $\lambda_{max}$ (lg ε) = 520 sh (2.40), 475 (2.55), 357 (3.17), 307 (3.8, sh), 285 nm (3.7, sh). – MS (70 eV), $T_E = 180$°C): $m/z$ (%) = 308 (100) [$M^+$], 280 (54) [$M^+ - CO$], 252 (66) [$M^+ - 2\ CO$].

$C_{22}H_{12}O_2$ (308.3) Calcd. C 85.68 H 3.92
Found C 85.58 H 3.92

*(+)-Dibenzo[c,g]phenanthrene-7,8-quinone* (**12**): From LC on (+)-poly(trityl methacrylate)/$SiO_2$ (MeOH, +15°C). Red oil. Enantiomeric purity $P = 95\%$ (LC, cf. Table 1). $[\alpha]^{22}_{436} = -8000 \pm 2500$, $[\alpha]^{22}_{546} = +7500 \pm 2300$, $[\alpha]^{22}_{578} = +4900 \pm 1600$ (0.001 g/100 ml $CH_3CN$) at $P = 100\%$.

*(–)-Dibenzo[c,g]phenanthrene-7,8-quinone* (**12**): From LC, see $(+)_{546}$-**12**. Red oil. Enantiomeric purity 100% (LC, cf. Table 1).

CAS Registry Numbers

(*E*)-**1a**: 138151-98-1 / (*E*)-**1b**: 138488-65-0 / (±)-**2a**: 138488-66-1 / (±)-**2b**: 138488-67-2 / (±)-**3a**: 138661-04-8 / *cis*-(±)-**3b**: 138488-68-3 / **4a**: 117745-51-4 / (±)-**4a**: 113506-95-9 / (+)-**4a**: 113459-79-3 / (–)-**4a**: 113459-80-6 / **4b**: 117745-52-5 / (±)-**4b**: 113459-81-7 / (+)-**4b**: 113459-84-0 / **5a**: 1132-03-2 / **5b**: 7343-12-6 / **5c**: 6579-44-8 / **6a**: 1127-59-9 / **6b**: 39603-24-2 / **6c**: 20205-43-0 / **7a**: 4389-45-1 / **7b**: 14438-32-5 / **7c**: 50419-58-4 / **8a**: 71871-11-9 / **8b**: 7343-14-8 / **8c**: 7343-07-9 / **9a**: 93878-26-3 / **9b**: 61881-53-6 / **9c**: 138488-69-4 / **10a**: 17825-37-5 / (±)-**10a**: 138488-71-8 / **10b**: 17825-38-6 / (±)-**10b**: 138488-72-9 / **10c**: 17825-40-0 / (±)-**10c**: 138488-73-0 / (+)-**10c**: 138488-74-1 / (–)-**10c**: 138488-75-2 / **11**: 85464-88-6 / **12**: 117745-57-0 / (±)-**12**: 113459-83-9 / (+)-**12**: 113459-86-2 / (–)-**12**: 138602-79-6 / **13**: 138488-76-3 / **14**: 3674-69-9 / **15**: 138488-77-4 / **16**: 7343-06-8 / **17a**: 138488-78-5 / **17b**: 138488-79-6 / **18**: 188-52-3 / Methyl 1-Chloro-2-naphthoate: 138488-70-7 / 2,4,5-trimethylbenzaldehyde: 5779-72-6 / 2,3,4,5-Tetramethylbenzaldehyde: 29344-95-4

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☆ Dedicated to Professor *Jürgen Sauer* on the occasion of his 60th birthday.

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