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ABSOLUTE HELICITIES OF TWISTED 9,10-PHENANTHRENEQUINONES.

CIRCULAR DICHROISM AND CHEMICAL CORRELATION TO BIPHENYLS[1]

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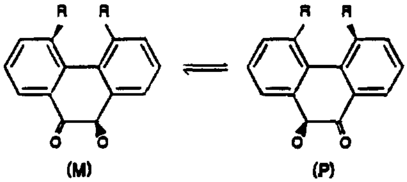
Dedicated to the late Professor Dr. Dr. h.c. Günther Snatzke

Abstract: The absolute configuration of the non-planar 9,10-phenanthrenequinone $(-)_{546}$-$\underline{\underline{18}}$ was determined to be (M) by a four-step chemical correlation (Scheme 2) to the bridged biphenyl $(-)_{365}$-$\underline{\underline{10}}$, the (M) helicity of which was proven via the circular dichroism of the conjugation band. The last step of the correlation consisted of the acyloin condensation of the diphenic ester $(-)_{365}$-(M)-$\underline{\underline{6}}$, during which partial loss of optical purity was observed. An intermediate 9,10-bis(trimethylsiloxy)phenanthrene is thought to racemize at a moderate rate, thereby causing some loss of activity. ------ The relative configurations of twisted 9,10-phenanthrenequinones can be determined by means of a series of weak Cotton effects between ca. 370 and 500 nm (Tables 2 and 3). These are negative for (M) quinones, as shown by the above mentioned correlation to a bridged biphenyl. --------Liquid chromatography on optically active sorbents served for most of the semipreparative separations of enantiomers and determinations of enantiomeric purity.

INTRODUCTION

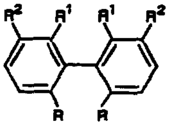
9,10-Phenanthrenequinones which are substituted in their 4- and 5-positions are twisted and therefore helical. Their enantiomers (M) and (P) were recently separated and characterized for the first time.[2,3,4]



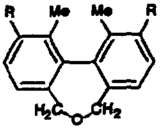
There are several points of interest related to the nonplanarity of this class of molecules. First of all, the barriers[4] to thermal racemization are higher than the ones for the corresponding phenanthrene hydrocarbons by approx. 20 kJ/mol. -------- Secondly, the half-wave potentials for the reduction to semiquinone monoanions and, subsequently, to hydroquinone dianions become more negative for less planar phenanthrenequinones.[5,6] The UV/VIS[7] and, particularly, the circular dichroism[8] (CD) spectra of these anions should also depend upon the angle of twist between the two external benzene rings. For semiquinone monoanions, ESR and ENDOR investigations resulted in a dependence of coupling constants upon twist[9] and in a proof of chirality.[10] ----- Finally, reactions leading to or starting from the quinones will result in complete conservation of enantiomeric purity or in partial or complete[11] loss of it. The fate of helicity during such reactions depends upon the mechanisms or, more specifically, upon the properties of the intermediates.

Because of these points of interest into 9,10-phenanthrenequinones, knowledge of relative and absolute configurations is highly desirable. The relative helicities of a few representatives, determined by CD, were briefly reported[3] but generalization is definitely required. Unfortunately, the chance for successful anomalous X-ray scattering is low because even *normal* X-ray analysis of the parent compound and some 4,5-disubstituted derivatives failed.[4] Therefore, *chemical* correlation seems to be the best way of establishing absolute helicity in this case.

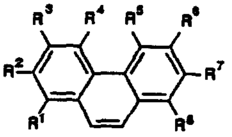
Thus, the present paper describes chemical correlations to some optically active substituted biphenyls, the CD spectra of these reference compounds in relation to their absolute configurations, and the CD behaviour of 9,10-phenanthrenequinones with a view to their relative helicities. For these purposes, we prepared the biphenyl derivatives **1** - **10**, the phenanthrene hydrocarbons **11** - **13**, the cis-9,10-dihydro-9,10-dihydroxy compounds **14** - **15**, the symmetrically substituted quinones **16** - **22** (Scheme 1), and the asymmetrically substituted ones **23** - **25** (formulae to be given in Table 2). Most of these compounds were investigated as preparatively enriched or pure enantiomers.



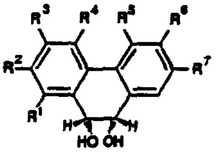
	R	R^1	R^2
1	CO_2H	Me	H
2	CO_2H	Et	H
3	CO_2H	Me	Me
4	CO_2Me	Me	H
5	CO_2Me	Et	H
6	CO_2Me	Me	Me
7	CH_2OH	Me	H
8	CH_2OH	Me	Me



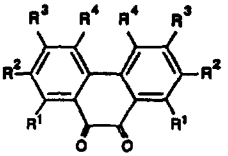
	R
9	H
10	Me



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
11	H	tBu	H	tBu	OMe	OMe	OMe	H
12	H	H	benzo		Me	H	H	Me
13	Me	H	benzo		tBu	H	tBu	H



	R^1	R^2	R^3	R^4	R^5	R^6	R^7
14	H	tBu	H	tBu	OMe	OMe	OMe
15	Me	H	benzo		tBu	H	tBu



	R^1	R^2	R^3	R^4
16	H	H	H	Me
17	H	H	H	Et
18	H	H	Me	Me
19	H	Me	Me	Me
20	Me	H	Me	Me
21	Me	Me	Me	Me
22	Cl	Cl	Cl	Cl

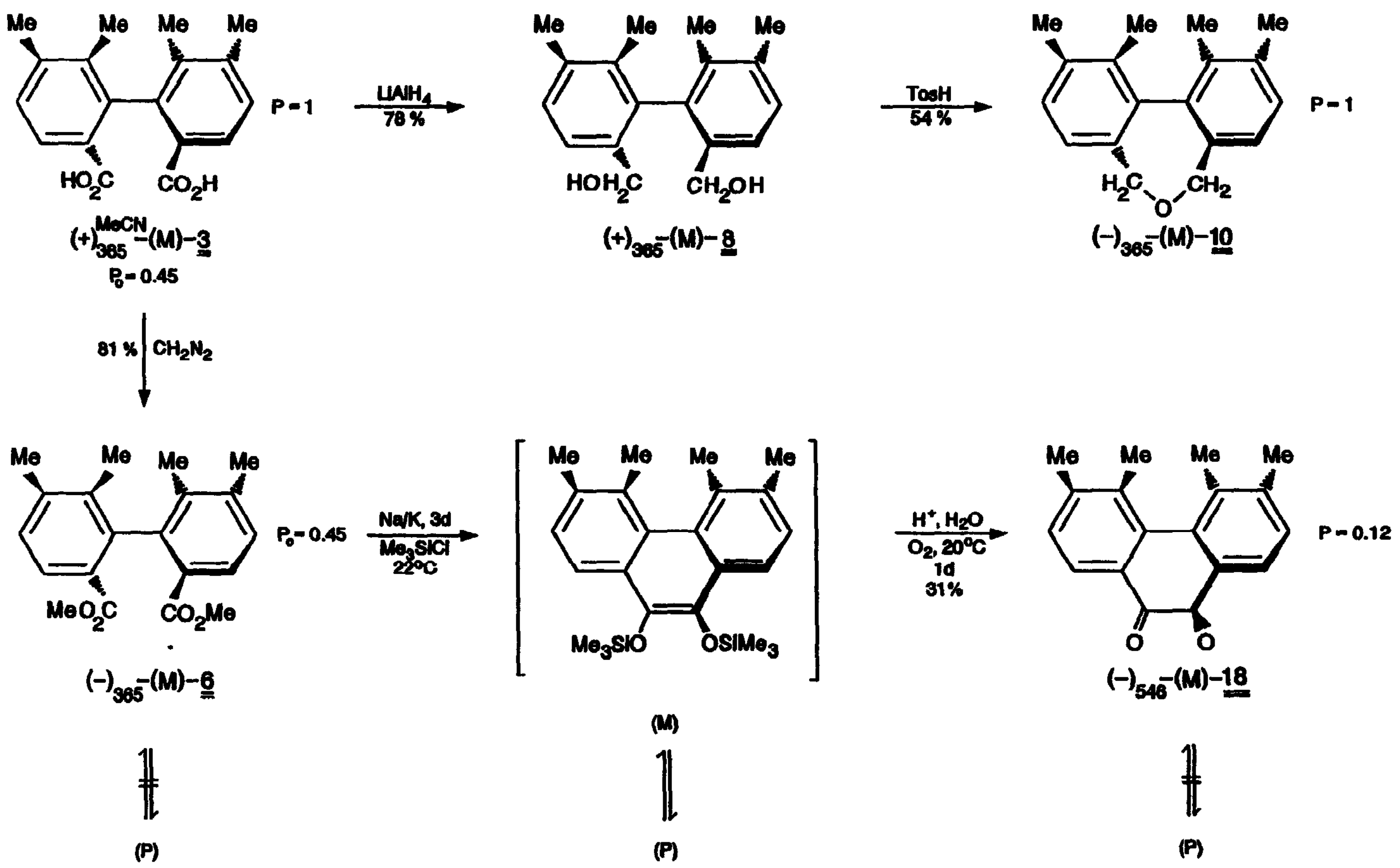
Scheme 1. Compounds prepared and investigated, including the symmetrically substituted quinones 16 - 22. (The formulae of the asymmetrically substituted quinones 23 - 25 will be given in Table 2.)

CHEMICAL CORRELATION OF 9,10-PHENANTHRENEQUINONES TO BIPHENYLS

The acyloin condensation of biaryl diesters was chosen for this purpose because its chlorotrimethylsilane modification[12] at approx. 120°C during 5h had given acceptable yields of racemic phenanthrenequinones.[4] However, optically active **4**, the simplest possible starting material for a correlation, had yielded[11] optically *inactive* quinone **16** at approx. 20°C during 4d (although without use of $ClSiMe_3$). Meantime, the barrier to enantiomerization of **16** is known[4] to amount to $\Delta G^{\ddagger} = 90.2$ kJ/mol, corresponding to a half-life of its enantiomers of only 22 min at 20°C. Thus, it turns out that the experiment of Wittig and Zimmermann[11] had failed because the product **16** racemizes during the reaction.

Therefore a quinone had to be used for correlation which enantiomerizes more slowly. The barrier[4] of **18**, $\Delta G^{\ddagger} = 111.5$ kJ/mol, corresponds to a half-life of 19 d at 22°C, the temperature at which our acyloin condensation, the hydrolysis, and the oxidation on air took place during 4d (Scheme 2). This means that $(-)_{546}$ - **18** did not racemize appreciably. The decrease of optical purity when going from $(-)_{365}$ - **6**, $P_o = 0.45$, to $(-)_{546}$ - **18**, enantiomeric purity $P = 0.12$, i.e. an approximate half-life of 2d at 22°C, must have other reasons. Partial racemization of the intermediate 3,4,5,6-tetramethyl-9,10-bis(trimethylsiloxy)phenanthrene (Scheme 2) is a possibility. A somewhat related molecule, 9,10-dimethoxy-3,4,5,6-tetramethylphenanthrene[15] shows a barrier[15] of $\Delta G^{\ddagger} = 99.4 \pm 0.1$ kJ/mol, 44.9°C, EtOH, corresponding to a half-life of 1.2 d at 22°C. Since there is no reason to assume net inversion of helicity during the acyloin condensation sequence of Scheme 2, the optical activity of its product must mean *retention*. Therefore, the reaction product $(-)_{546}$ - **18** and the starting material $(-)_{365}$ - **6** (Scheme 2) have the same configuration. It will be shown in the paragraph on CD of biphenyls that this method assigns with some confidence the (M) helicity, identical[17] with the (R) configuration, to $(-)_{365}$ - **6**.

This assignment will now be confirmed by the following chemical correlation[16] of the non-bridged $(-)_{365}$ - **6** with the bridged biphenyl $(-)_{365}$ - **10** (Scheme 2). The reactions with CH_2N_2, $LiAlH_4$, and TosH occurred without noticeable loss of enantiomeric purities. The assumption that no net helix inversions have happened during these reactions again means *retention* of configurations from $(-)_{365}$-**6** to $(-)_{365}$ - **10**. The next paragraph will assign unquestionably the (M) helicity to the latter bridged biphenyl and thus to *all* molecules depicted in Scheme 2.



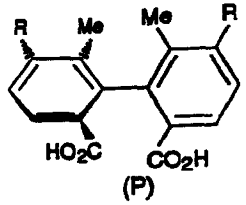
Scheme 2. Chemical correlation[16] of quinone $(-)_{546}$ - 18 to biphenyl $(-)_{365}$-10. P, P_o: Enantiomeric and optical purities, respectively.

1,3,4,5,6,8-Hexamethyl-9,10-phenanthrenequinone[4] (20) and 1,4,5,8-tetramethyl-9,10-phenanthrenequinone were chemically correlated[18] to the corresponding cis-9,10-dihydro-9,10-dihydroxy compounds (cf. Scheme 1 for formulae of similar diols 14 and 15). The (M) helicities of the latter were assigned by CD on the basis of the findings of Armstrong and coworkers.[19,20] The dehydrogenation of these diols by dimethylsulfoxide/acetic anhydride at 20°C resulted in the two quinones mentioned above, the configurations of which should therefore be (M), too. The CD spectra of these reaction products were in agreement with the features to be described below for (M) quinones (e.g. for $(-)_{546}$ - (M) - 20 in Table 3). These experiments[18] represent independent proof for the absolute helicities of 9,10-phenanthrenequinones derived via Scheme 2.

CIRCULAR DICHROISM OF BIPHENYLS USED FOR CORRELATION

The first possibility of assigning absolute helicity to $(-)_{546}$-18 consisted in finding the configuration of the diphenic acid $(+)^{\mathrm{MeCN}}_{365}$- 3 (Scheme 2), i.e. to compare its CD spectrum with the one of $(+)^{\mathrm{MeCN}}_{365}$- 1. For the latter, the (P) configuration has been proven[21]; its polarimetric signs for dioxane and MeCN as solvents are identical (see Experimental). Although the two curves for the above acids represent approximate mirror images (cf. Table 1), this fact was not considered sufficient proof of opposite helices. In addition, we were cautious because of their polarimetric behaviour (see Experimental). For instance, the enantiomer of 1 mentioned above is *levo*rotatory in $CHCl_3$. $(+)^{\mathrm{MeCN}}_{365}$- 3, on the other hand, is *levo*rotatory in dioxane! These and similar[22,23] observations that the polarimetric sign of biphenyls may or may not depend upon solvent and wavelength lead us to state both upon naming enantiomers. The above behaviour is probably caused by the association of the acids with themselves or with the solvents. In conclusion, we did not decide by CD about the absolute helicity of the diphenic acid 3.

Table 1. CD Spectra of (P)-Diphenic Acids in MeCN. λ_{max} in nm; $\Delta\epsilon_{max}$ in 1 $mol^{-1}cm^{-1}$



	R	λ_{max} ($\Delta\epsilon_{max}$)		
$(+)^{\mathrm{MeCN}}_{365}$-1	H	213 (+6.1)	239 (-6.5)	-
$(-)^{\mathrm{MeCN}}_{365}$-3	Me	219 (+6.0)	234 (-7.8)	265 (+0.2)

As a second possibility, the diphenic ester $(-)_{365}$-**6** (Scheme 2) was tried for this purpose. Its CD in MeCN is similar to the one of $(-)_{365}$-**4** (Fig.1) for which a spectrum[24] in dioxane and the (M) configuration[21,25] were known. Therefore, it can be concluded with some confidence that the ester $(-)_{365}$ - **6** has (M) helicity, too.

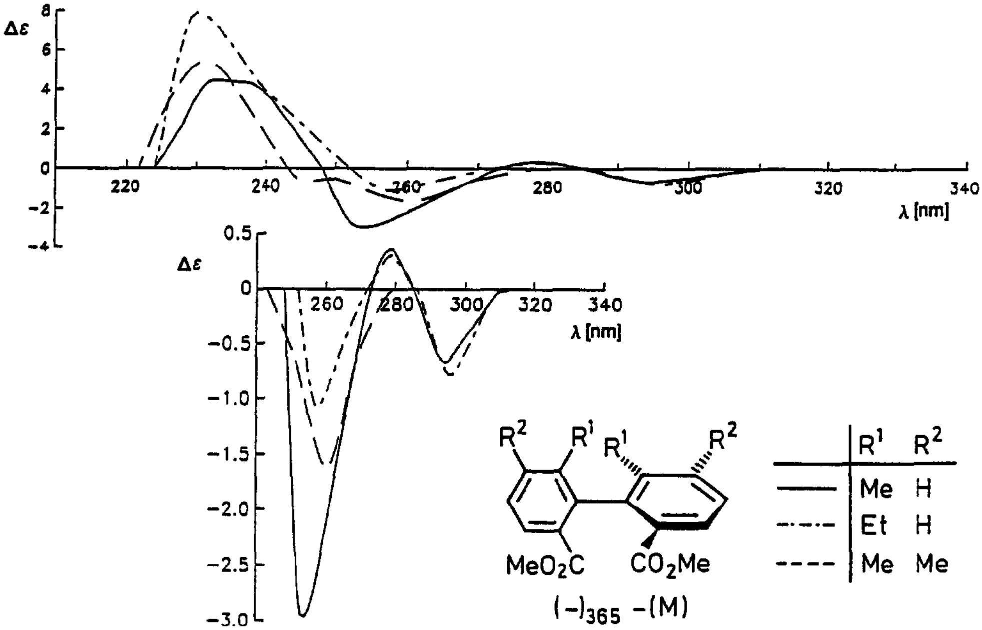


Fig. 1. CD spectra of diphenic esters (M)-**4** (———), -**5** (- - - -) and -**6** (-----) in MeCN. Δε in l mol^{-1}cm^{-1}

Finally, we correlated (Scheme 2) the above non-bridged biphenyl to the bridged-biphenyl $(-)_{365}$ - **10** by chemical means and tried to obtain the configuration of the latter. The CD spectra of $(+)_{365}$ - **10** and-**9** (Fig.2) suggest identical helicities. In addition, for the latter bridged biphenyl a spectrum[26] in dioxane and the (P) configuration[21] were known. To both compounds, an empirical rule, given by Mislow, Djerassi and coworkers[21], can be applied successfully. Its reliability has been shown by later investigations including the ones by Sandström and collegues[27]. It states that bridged biphenyls with the (S), identical to (P), configuration and an inter-ring angle of ca. 45° will have a negative Cotton effect centered at 240-250 nm and corresponding to the biphenyl conjugation band ($\epsilon \approx 10^4 lmol^{-1}cm^{-1}$). These bands are present in the UV spectra of **9**[26] and **10** (Experimental Part) and the negative Cotton effects around 240 nm in Fig.2 prove the (P) helicity for $(+)_{365}$-**9** and **10**. This result shows that *all* molecules depicted in Scheme 2 have the (M) configuration.

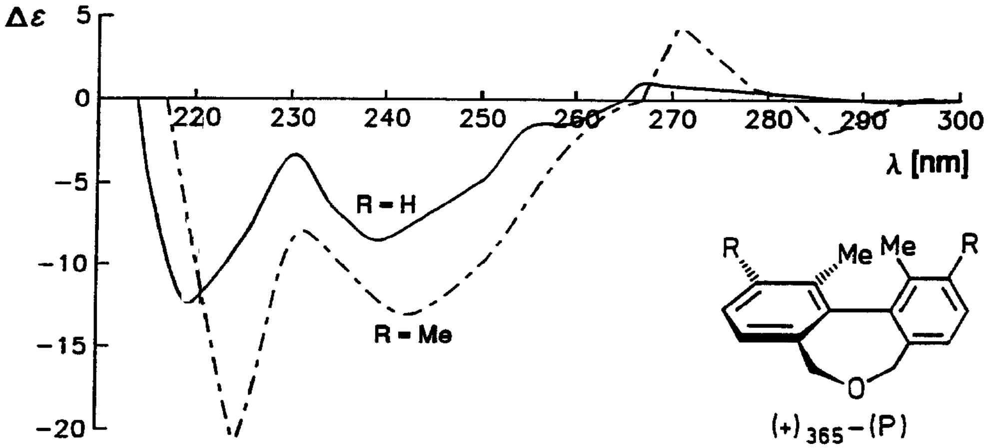


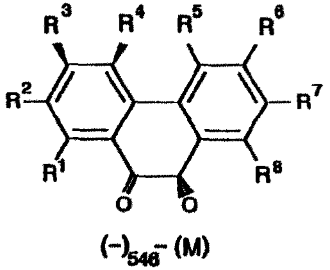
Fig. 2. CD spectra of bridged biphenyls (P)-**9** (R = H) and -**10** (R = Me) in MeCN. Δε in l mol^{-1}cm^{-1}

CIRCULAR DICHROISM AND RELATIVE HELICITIES OF 9,10-PHENANTHRENEQUINONES

Some intensities of the Cotton effects in Tables 2 and 3 are given as strong, medium, or weak. In these cases the differential absorption coefficients $\Delta\epsilon_{max}$ are *not* given because of two possible reasons: Either the dichrogram was only measured in terms of ΔA during stop of flow[2,28] of liquid chromatography or the $\Delta\epsilon_{max}$ values were not safe because of erroneous calibrations of the dichrograph. The latter statement may also be true for $\Delta\epsilon_{max}$ of four quinones given earlier[3], although the λ_{max} values and the signs reported[3] are correct.

Since the quinone $(-)_{546}$-**18** is assigned the (M) configuration by means of reactions (Scheme 2) and CD (Fig.3), it is of interest to connect the relative helicities of 9,10-phenanthrenequinones via their CD spectra to **18**. For this purpose, the most reliable feature is a series of weak negative Cotton effects between ca. 370 and 500 nm (Table 2) when MeOH or EtOH are the solvents. This is also shown in Fig.3, although for two (P) enantiomers. Less influence by the medium is expected for solutions in MeCN or $CHCl_3$. Indeed, these spectra (Fig.4 and Table 3) differ from the ones in Table 2, but again a similar series of characteristic weak negative Cotton effects between ca. 380 and 500 nm is observed for the (M) enantiomers. Fig. 5 generalizes the spectral behaviour.

Table 2. CD Spectra of (M)-9,10-Phenanthrenequinones in MeOH or EtOH. λ_{max} in nm; intensities Δi_{max} indicated by s (strong), m (medium), or w (weak)



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	$\lambda_{max}(\Delta i_{max})$				
16[a)]	H	H	H	Me	Me	H	H	H	280(-s)	330(+m)	370(-w)	400(-w)	475(-w)
17	H	H	H	Et	Et	H	H	H	285(-s)	325(+m)	375(-w)	400(-w)	460(-w)
18[a]	H	H	Me	Me	Me	Me	H	H	298(-m)	335(+w)		400(-w)	475(-w)
23	H	tBu	H	tBu	OMe	OMe	OMe	H	300(-s)	330(+m)	375(-w)	400(-w)	475(-w)
24[b)]	H	H	benzo		Me	H	H	Me	270(-m)	320(+w)	370(-w)	400(-w)	475(-w)
25	Me	H	benzo		tBu	H	tBu	H	275(-m)	330(+w)	385(-w)	400(-w)	475(-w)

a) Cf. Fig. 3 for values of $\Delta\epsilon_{max}$.

b) See Experimental Part for values of $\Delta\epsilon_{max}$.

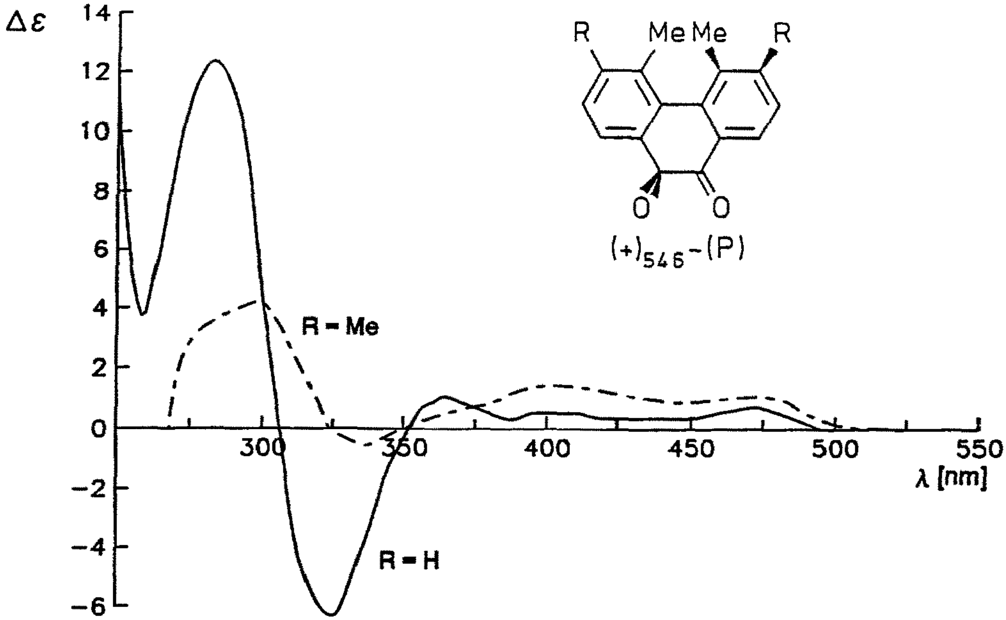


Fig. 3. CD spectra of 9,10-phenanthrenequinones (P)-16 (R = H) and -18 (R = Me) in MeOH. The spectrum[30] of (P)-16 was obtained at -20°C during stop of liquid chromatography of (MP)-16 on (+)-poly(trityl methacrylate)/SiO_2 and subsequent calibration[30] for Δε. The spectrum of (P)-18 was obtained at +22°C after dissolving this sample. Δε in $1\ mol^{-1}cm^{-1}$

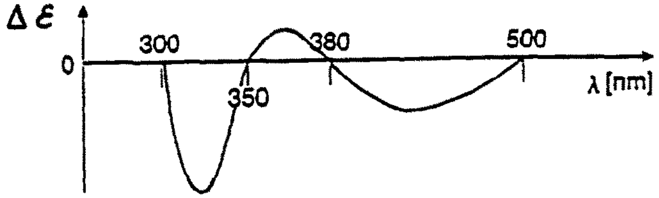


Fig. 5. Generalized CD spectra of (M)-9,10-phenanthrenequinones in MeCN or $CHCl_3$

An empirical rule[31] states that an enantiomer which owns a C_2 axis and is less retained upon liquid chromatography on (+)-poly(trityl methacrylate) has (M) configuration. From our corresponding results (Table 4), it must be concluded that quinones $(-)_{546}$-16 and -18 represent (M) helices. This finding independently confirms our assignments in Table 2 and Scheme 2.

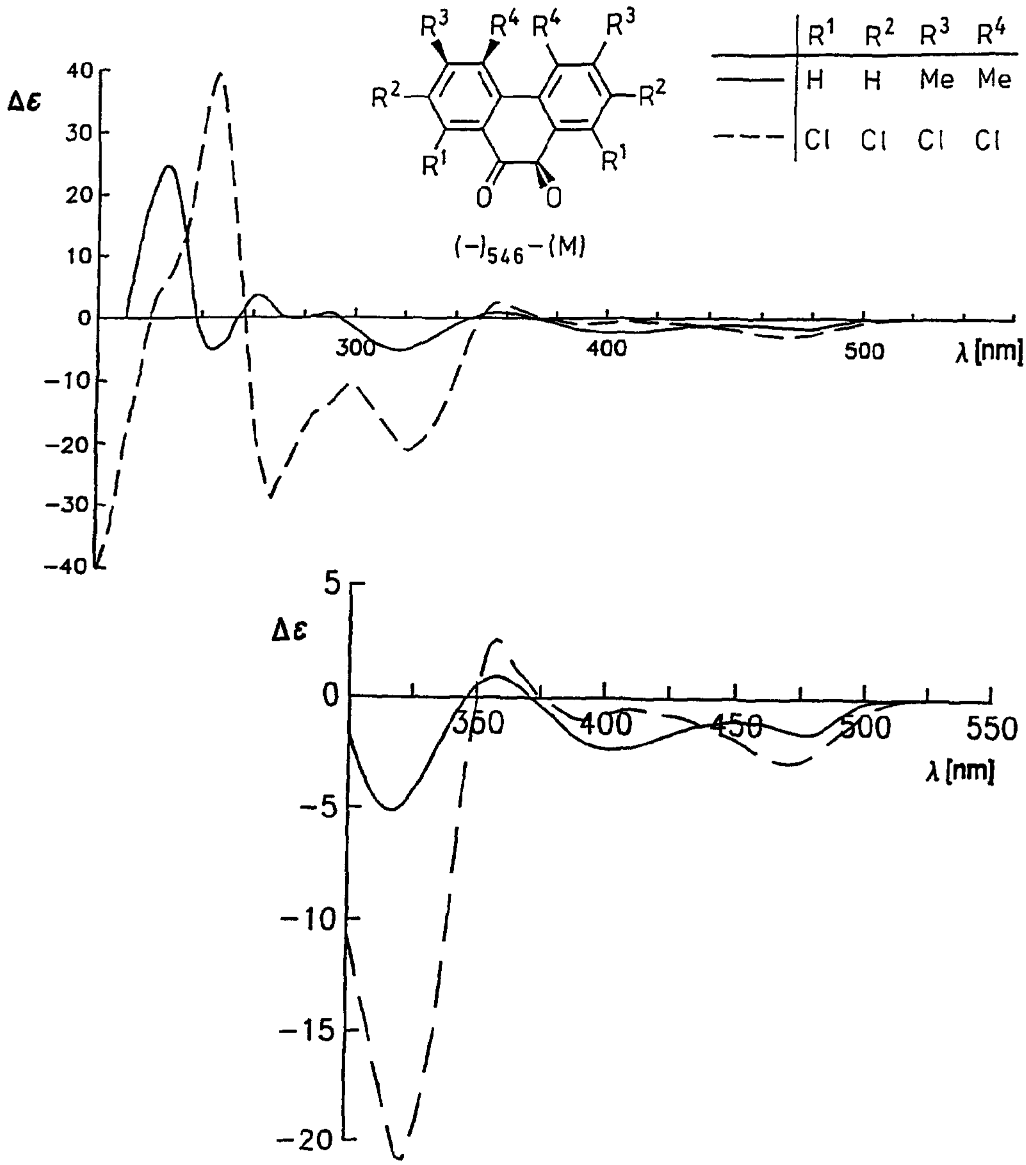
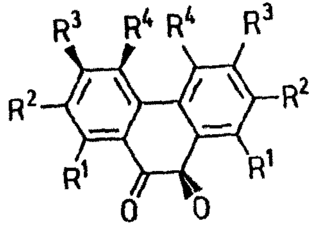


Fig. 4. CD spectra of 9,10-phenanthrenequinones (M)-**18** (———) and -**22** (-----) in MeCN. $\Delta\varepsilon$ in l mol^{-1}cm^{-1}

Table 3. CD Spectra of (M)-9,10-Phenanthrenequinones. λ_{max} in nm; $\Delta\epsilon_{max}$ in l mol^{-1}cm^{-1} or indicated by s (strong), m (medium), or w (weak)



$(-)_{546}-(M)$

	R^1	R^2	R^3	R^4	Solvent	$\lambda_{max}(\Delta\epsilon_{max})$					
18[a)]	H	H	Me	Me	MeCN		290(+0.8)	316(-4.8)	358(+0.8)	405(-1.8)	475(-1.5)
19[29]	H	Me	Me	Me	MeCN	282(-1.9)	301(+1.1)	323(-1.7)	358(+1.5)		483(-2.1)
20	Me	H	Me	Me	$CHCl_3$			319(-s)	~360(+w)	385(-w)	466(-m)
21	Me	Me	Me	Me	$CHCl_3$			325(-m)	~360(+w)	395(-w)	458(-m)
22[a)]	Cl	Cl	Cl	Cl	MeCN	270(-27)		321(-21)	359(+3)	389(-2)	468(-3)

a) Cf. Fig. 4.

Table 4. Capacity Factors k' upon Liquid Chromatography of 9,10-Phenanthrenequinones on (+)-Poly(trityl methacrylate)/SiO_2 in MeOH. Signs of polarimetric detection at 546 nm given in parentheses

	Substituents	k'(-)	k'(+)	T
<u>16</u>	4,5-Me_2	0.4	0.6	- 5°C
<u>18</u>	3,4,5,6-Me_4	0.4	0.7	-15°C

EXPERIMENTAL PART

Liquid Chromatography (LC) on Microcrystalline Triacetylcellulose at Low Pressure[4]

The sorbent[32], particle sizes 20-30μm, was prepared, swollen and filled into glass columns (25 x 300 nm) according to ref. 33. The LC detectors are given in ref. 33. This setup served for analytical as well as for semipreparative LC. The capacity factors were calculated from $k' = (v - v_o)/v_o$, v_o being the retention volume of 1,3,5-tri-tert-butylbenzene.[32] (+) or (-) stands for the signs in polarimetry, [+] or [-] for the signs in CD.

High-Pressure Liquid Chromatography on Optically Active Sorbents[30]

Microcrystalline triacetylcellulose, particle sizes 10-20 μm, was prepared in a way similar to ref. 34, but starting from Avicel 2330 (E.Merck), wind-sieved, swollen and slurry-packed at 214 bar into a 8 x 250 nm Knauer column. The capacity factors k' refer to 1,3,5-tri-tert-butylbenzene.[32] (+)-Poly(trityl methacrylate)/SiO_2[35] was filled into a Knauer column (4 x 250 mm). The capacity factors refer to water. LC was performed with the injector Rheodyne 7125 and the pump Irica Σ - 871 (ERMA Optical Works, Tokyo, Japan) at pressures of 103 to 168 bar. Additional cooling of the columns was achieved by using the thermostates of Colora Meßtechnik and Haake Meß-Technik as well as homemade column jackets.

Circular Dichroism

Off-line CD spectra were recorded at 20°C on JASCO J-40A or J-41A instruments. Detection of on-line CD spectra was performed on a JASCO J-40A spectrometer with a flow-through cell of Hellma GmbH (10 mm light path and 1 mm diameter; volume of 8 μl) and an additional homemade beam condenser[28]. Calibrated on-line CD spectra were obtained by the method described in ref. 30. Evaluations and plots of on- and off-line CD data were performed by the computer program[36] CD/UV, which takes the experimental baseline into account and achieves a smoothing of the spectra. $\Delta\epsilon_{max}$ values were calculated for the optical purity of P_o = 100 %.

Further Instruments

Melting points: Büchi 530 instrument; the results are not corrected. -^{1}H-NMR: Varian T 60 A, Bruker AW 80 or Bruker WM 250 (δ in ppm, J in Hz); for lanthanoid-induced splittings, see ref. 33. - UV: Beckman Model 24 at 10^{-3} to 10^{-4}mol/l. - MS: Varian CH 5 at low resolution. - IR: Acculab-1 (Beckman). - Specific rotation: Polarimeter Perkin-Elmer 241; the cell temperature was kept at 22°C by a thermostat.

Table 5. $[\alpha]^{22}$ of Diphenic Acids, Calculated for Optical Purities of 100 %

	Solvent	Conc. [g/100ml]	λ [nm] 365	436	546	578
$(+)^{MeCN}_{365}$-1	MeCN	0.05	+28±5	+25±3	+17±3	+15±2
	dioxane	0.06	+75±9	+41±6	+22±5	+21±5
	$CHCl_3$	0.09	-69±8	-21±3	- 4±1	- 3±1
$(-)^{MeCN}_{365}$-3	MeCN	0.03	-47±6	-27±5	- 8±1	- 5±1
	dioxane	0.44	-	+11±1	+ 6±1	+ 5±1

(±)-6,6-Dimethyldiphenic Acid (1)[4]

$(+)^{MeCN}_{365}$-6,6-Dimethyldiphenic Acid (1)[11]

[α] see Table 5.

$(-)^{MeCN}_{365}$-6,6-Dimethyldiphenic Acid (1)[11]

[α] see Table 5.

(±)-6,6'-Diethyldiphenic Acid (2)[38]

(±)-5,5',6,6'-Tetramethyldiphenic Acid (3)[4]

$(-)^{MeCN}_{365}$-5,5',6,6'-Tetramethyldiphenic Acid (3)/(-)-Quinine

(cf. ref. 11)

2.48 g (8.4 mmol) of (±)-3 were dissolved in 100 ml of boiling EtOH, treated with 5.45g (16.8 mmol) of (-)-quinine and refluxed for 20 min. After cooling 100ml of Et_2O were added and the solution was kept for 6d in the refrigerator. The precipitate was filtered from the mother liquor and dried over P_2O_5: 3.02g (4.85 mmol) of colourless crystals. Yield 58%; m.p. 171-172°C.

$[\alpha]^{22}_{365} = -294 \pm 8$; $[\alpha]^{22}_{436} = -105 \pm 6$; $[\alpha]^{22}_{589} = -52 \pm 5$ (0.05g/100 ml MeCN).

$(+)^{MeCN}_{365}$-5,5',6,6'-Tetramethyldiphenic Acid (3)/(-)-Quinine

Evaporation of the above mother liquor afforded 2.45g (3.64 mmol) of slightly brownish crystals. Yield 43%; m.p. 136-142°C.

$[\alpha]^{22}_{365}$ = +147 ± 3; $[\alpha]^{22}_{436}$ = +56 ± 2; $[\alpha]^{22}_{589}$ = +12 ± 2 (0.15g/100ml MeCN).

$(-)^{MeCN}_{365}$-5,5',6,6'-Tetramethyldiphenic Acid (3) (cf. ref. 11)

$(-)^{MeCN}_{365}$-3/(-)-quinine was dissolved in 100 ml of $CHCl_3$ and extracted with 15% HCl (3 x 30 ml). Additional extraction of the organic layer with 2N NaOH (3 x 30 ml). The combined NaOH-layers were acidified with conc. HCl and the precipitated acid was separated. Drying over P_2O_5: 1.27g (4.26 mmol) of colourless crystals. Yield 88%; m.p. 231-234°C. ^1H NMR identical with the one of (±)-3. Enantiomeric purity P = 45% (^1H NMR after esterification to $(+)_{365}$ - 6; 1.0 equivalents of (+)-tris[3-heptafluorobutyryl-D-camphorato]europium (III)).

A further amount of $(-)^{MeCN}_{365}$-3 was provided by LC on optically active poly(L-menthylmethacrylate); m.p. 247-249°C. Optical purity P_o ≈ 100% (by comparison of [α] with the one of the sample described above).

[α] see Table 5.

$(+)^{MeCN}_{365}$-5,5',6,6'-Tetramethyldiphenic Acid (3)

Preparation from $(+)^{MeCN}_{365}$-3/(-)quinine as described for $(-)^{MeCN}_{365}$-3: 0.98g (3.28 mmol) of colourless crystals. Yield 90%; m.p. 233-236°C. ^1H NMR identical with the one of (±)-3. Optical purity P_o = 43% (by comparison of [α] with the one of $(-)^{MeCN}_{365}$ - 3).

[α] see Table 5.

Dimethyl (±)-6,6'-Dimethyldiphenate (4)[11]

Dimethyl $(-)_{365}$-6,6'-Dimethyldiphenate (4)[11]

$[\alpha]^{22}_{365}$ = -104±11; $[\alpha]^{22}_{436}$ = -87±6; $[\alpha]^{22}_{578}$ = -26±3 (0.19g/100ml MeCN; P = 100%). $[\alpha]^{22}_{365}$ = -139±11; $[\alpha]^{22}_{436}$ = -78±8; $[\alpha]^{22}_{578}$ = -38±5 (0.07g/100ml dioxane; P = 100%).

Dimethyl (±)-6,6'-Diethyldiphenate (5)[38]

Dimethyl $(-)_{365}$-6,6'-Diethyldiphenate (5)

From semipreparative LC on triacetylcellulose (EtOH/H_2O, 96:4). Colourless oil. k' = 0.4 (-) at 365 nm. P = 100% (LC on triacetylcellulose (EtOH/H_2O, 96:4)).

$[\alpha]^{22}_{365}$ = -112±9; $[\alpha]^{22}_{436}$ = -56±7; $[\alpha]^{22}_{578}$ = -23±6 (0.04g/100ml MeCN).

Dimethyl (±)-5,5',6,6'-Tetramethyldiphenate (6)[4]

Dimethyl $(+)_{365}$-5,5',6,6'-Tetramethyldiphenate (6)

Esterification of 1.0g (3.36 mmol) of $(-)^{\mathrm{MeCN}}_{365}$- 3 (P = 45%) with CH_2N_2 gave 0.88g (2.68 mmol) of colourless crystals. Yield 80%; m.p. 95-97°C. ^{1}H NMR identical with the one of (±)-6. P = 45% (^{1}H NMR, 1.0 equivalents of (+)-tris[3-heptafluorobutyryl-D-camphorato]europium(III).

Dimethyl $(-)_{365}$-5,5',6,6'-Tetramethyldiphenate (6)

Esterification of 0.98g (3.28 mmol) of $(+)^{\mathrm{MeCN}}_{365}$-3 ($P_o$ = 45%) with CH_2N_2 afforded 0.86g (2.63 mmol) of colourless crystals. Yield 81%; m.p. 88-89°C. ^{1}H NMR identical with the one of (±)-6. P_o = 45% (by comparison of $[\alpha]$ and $\Delta\epsilon$ with the ones of $(+)_{365}$-6.

$[\alpha]^{22}_{365}$ = -42±4; $[\alpha]^{22}_{436}$ = -21±3; $[\alpha]^{22}_{546}$ = -11±3 (0.10g/100ml MeCN; calculated for P_o = 100%).

(±)-2,2'-Bis(hydroxymethylene)-6,6'-dimethylbiphenyl (7)[11]

$(-)_{365}$-2,2'-Bis(hydroxymethylene)-6,6'-dimethylbiphenyl (7)[11]

(±)-2,2'-Bis(hydroxymethylene)-5,5',6,6'-tetramethylbiphenyl (8)[39]

$(-)_{365}$-2,2'-Bis(hydroxymethylene)-5,5',6,6'-tetramethylbiphenyl (8)

To a suspension of 0.17g (4.5 mmol) of $LiAlH_4$ in 30ml of abs. THF 0.30g (1.0 mmol) of $(-)^{\mathrm{MeCN}}_{365}$-3 ($P_o$ ≈100%) in 20ml of abs. THF were dropped with external cooling. The solution was refluxed for 24h. After cooling 20ml of Et_2O, 20ml of H_2O and 10ml of HCl (15%) were carefully added; additional stirring for 60min. The organic layer was separated and extracted with 2N NaOH (3x20ml), washed with H_2O (3x20ml) and dried over Na_2SO_4. Evaporation of the solvent afforded 0.20g (0.74mmol) of colourless crystals. Yield 73%; m.p. 93-95°C. ^{1}H NMR identical with the one of (±)-8

$[\alpha]^{22}_{365}$ = -149±13; $[\alpha]^{22}_{436}$ = -98±11; $[\alpha]^{22}_{578}$ = -54±9 (0.03g/100ml MeCN).

(±)-1",4'-Dimethyl-2,7-dihydro-3,4,5,6-dibenzoxepine (9)[11]

$(+)_{365}$-1",4'-Dimethyl-2,7-dihydro-3,4,5,6-dibenzoxepine (9)[11]

(±)-1",2",3',4'-Tetramethyl-2,7-dihydro-3,4,5,6-dibenzoxepine (10)

0.2g(0.74mmol) of (±)-8 and 0.15g (0.79 mmol) of 4-toluenesulfonic acid were refluxed in 25 ml of abs. benzene for 24h. The solution was washed with 40ml of 6N NaOH, 40ml of H_2O and dried over Na_2SO_4. After evaporation of the solvent, purification by column chromatography on SiO_2 ($CHCl_3$, R_f = 0.41) afforded 0.1g (0.39 mmol) of colourless crystals. Yield 54%; m.p. 106-108°C.

IR (KBr): ν'_{CH}, 3020, 2960, 2940, 2880; $\nu'_{C=C}$, 1600; ν'_{CO}, 1060 cm^{-1}. ----^1H NMR (C_6D_6/TMS) δ: 1.92 (6H, s, 2 Me); 2.10 (6H, s, 2 Me); 4.06, 4.38 (4H, AB, CH_2, J_{AB} = 10.7 Hz); 7.00 (4H, s, arene H). ---- UV (MeCN) λ_{max} (lgϵ): 246 (4.02); 220 nm (4.60). ---- MS (70 eV, T_E = 180°C) m/z (%): 252 (100) [M^+]; 237 (58) [M^+ - Me]; 209 (50) [M^+ - Me - CO].

$(+)_{365}$-1",2",3',4'-Tetramethyl-2,7-dihydro-3,4,5,6-dibenzoxepine (10)

The reaction of 0.15g (0.47 mmol) of $(-)_{365}$ - 8 and 0.12g (0.63 mmol) of 4-toluenesulfonic acid was carried out as described for (±)-10. Column chromatography resulted in 0.060g (0.24 mmol) of colourless crystals. ^1H NMR identical with the one of (±)-10. P = 100% (LC on triacetylcellulose (EtOH/H_2O, 96:4)). k' = 0.4.

$[\alpha]^{22}_{365}$ = + 1074 ± 80; $[\alpha]^{22}_{436}$ = + 1005 ± 74; $[\alpha]^{22}_{578}$ = + 621 ± 50 (0.04g/100ml MeCN).

2,4-Di-tert.butyl-5,6,7-trimethoxyphenanthrene (11)[40]

1,4-Dimethylbenzo[c]phenanthrene (12)[40]

1,3-Di-tert.butyl-7-methylbenzo[c]phenanthrene (13)[40]

(±)-cis-9,10-Dihydro-9,10-dihydroxy-2,4-di-tert.butyl-5,6,7-trimethoxyphenanthrene (14)

0.77g (2.0 mmol) of 11 reacted with a slight excess of OsO_4 according to the procedure in refs. 41 and 42. Work-up as described.[41,42] Column chromatography on SiO_2 (petroleum ether 40/60/ethyl acetate, 4:1) and recrystallization from cyclohexane afforded 0.37g (0.88 mmol) of colourless crystals. Yield 44%; m.p. 162-163°C.

^1H NMR ($CDCl_3$/TMS) δ: 1.38, 1.43 (18H, 2s, 2 CMe_3); 3.20 (3H, s, OMe); 3.87 (3H, s, OMe); 3.90 (3H, s, OMe); 4.39 - 4.85 (2H, m, H9/10); 7.04 (1H, s, H-8); 7.17, 7.62 (2H, 2d, H-1/3, ^4J = 2.0Hz).

Anal. for $C_{25}H_{34}O_5$: Calc. C, 72.43%; H, 8.27%. Found C, 73.12%; H, 8.54%.

(±)-cis-9,10-Dihydro-9,10-dihydroxy-1,3-di-tert.butyl-7-methylbenzo[c]phenanthrene (15)

0.033g (0.093 mmol) of 13 reacted with a slight excess of OsO_4 according to the procedure in refs. 41 and 42. Work-up as described.[41,42] Column chromatography on SiO_2 ($CHCl_3$, R_f = 0.12) and recrystallization from MeOH afforded 0.01g (0.026 mmol) of colourless crystals. Yield 28%; m.p. 154-156°C.

^1H NMR ($CDCl_3$/TMS) δ: 1.30 (2H, bs, OH); 1.37 (9H, s, CMe_3); 1.45 (9H, s, CMe_3); 2.33 (3H, s, Me-7); 4.54 (1H, bs, H-9 or H-10); 4.86-4.94 (1H, m, H-9 or H-10); 7.17-8.40 (7H, m, arene+H). --- MS (70eV, T_E = 153°C) m/z (%): 388 (100) [M^+]; 331 (31) [$M^+-C_4H_9$].

(±)-4,5-Dimethyl-9,10-phenanthrenequinone (16)[4,30]

(±)-4,5-Diethyl-9,10-phenanthrenequinone (17)

The reaction of 1.00g (3.06 mmol) of (±)-5 with Na/Me_3SiCl in toluene was performed as described in ref.4. Repeated column chromatography on SiO_2 ($CHCl_3$, R_f = 0.34, and petroleum ether 40/60/ ethyl acetate, 4:1, R_f = 0.60) afforded 0.39g (1.51 mmol) of orange crystals. Yield 49%; m.p. 136-138°C.

IR (KBr): ν'_{CH}, 3080, 2980, 2940, 2880; ν'_{CO}, 1680; $\nu'_{C=C}$, 1580 cm^{-1}.- ^1H NMR ($CDCl_3$/TMS) δ: 1.04 (6H, t, CH_3); 2.60-2.83 (4H, m, CH_2); 7.42 (2H, t, H-2/7, 3J = 7.1 Hz); 7.62 (2H, d, H-3/6, ^3J = 7.1 Hz); 7.81 (2H, d, H-1/8, ^3J = 7.1 Hz). ---- UV (MeOH) λ_{max} (lgϵ): 333 (3.43); 270 (3.76); 248 (4.28); 210 nm (4.49).

Anal. for $C_{18}H_{16}O_2 * 0.2\ H_2O$: Calc. C, 80.16%; H, 6.15%. Found C, 79.92%; H, 5.87%.

LC on (+)-poly(trityl methacrylate)/SiO_2 (MeOH, - 20°C) k' : 0.3, $(-)_{436}-[-]_{290}$-17; 0.5, $(+)_{436}$ - $[+]_{290}$-17. These conditions served for obtaining the on-line CD spectrum in Table 2.

(±)-3,4,5,6-Tetramethyl-9,10-phenanthrenequinone (18)[4]

$(+)_{546}$-3,4,5,6-Tetramethyl-9,10-phenanthrenequinone (18)[4]

$(-)_{546}$-3,4,5,6-Tetramethyl-9,10-phenanthrenequinone (18)[4]

From semipreparative LC on triacetylcellulose (EtOH/H_2O, 96:4) a sample was obtained exactly as described in ref. 4 but without an additional ^1H NMR peak. $[\alpha]^{22}_{546}$ = -843 ± 95 (0.03g/100ml MeCN).

By a modified acyloin condensation[11] another sample was obtained for chemical correlation (Scheme 2) in the following way: 0.10g (0.31 mmol) of $(-)_{365}$-**6** (P_o = 45%) were dissolved in 10ml of N_2-saturated abs. benzene. This solution was dropped to a suspension of 0.25g of Na/K and 0.22g (2.76 mmol) of Me_3SiCl in 10ml of abs. benzene under N_2. Additional stirring at room temperature for 3d in the absence of light. Work-up and purification as described in ref.4 afforded 0.02g (0.09 mmol) of yellow crystals. Yield 31%; m.p. 187-191°C. P = 12% (LC on triacetylcellulose, EtOH/H_2O, 96:4, and comparison of [α] with the one obtained above after semipreparative LC on triacetylcellulose).

(±)-1,3,4,5,6,8-Hexamethyl-9,10-phenanthrenequinone (20)[4]

$(-)_{546}$-1,3,4,5,6,8-Hexamethyl-9,10-phenanthrenequinone (20)[4]

(±)-Octamethyl-9,10-phenanthrenequinone (21)[4]

$(+)_{546}$-Octamethyl-9,10-phenanthrenequinone (21)[4]

(±)-Octachloro-9,10-phenanthrenequinone (22)[43]
Yield 61% (ref.[43] 55%); m.p. 301-303°C (ref.[43] 312-315°C).

$(+)_{546}$-Octochloro-9,10-phenanthrenequinone (22)[44]
From semipreparative LC on triacetylcellulose (EtOH/H_2O, 96:4) upon injection in toluene as solvent, exclusion of light and cooling of the eluate to 0°C until evaporation in order to avoid formation of the corresponding ethyl hemiacetal. k' = 0.8 (+) at 365 nm. M.p. 280-300°C. P = 65% (LC[2,28] on triacetylcellulose (EtOH/H_2O, 96:4)).

$[\alpha]^{22}_{365}$ = +320 ± 70; $[\alpha]^{22}_{546}$ = +500 ± 50 (MeCN; calculated for P_o = 100%).

(±)-2,4-Di-tert.butyl-5,6,7-trimethoxy-9,10-phenanthrenequinone (23)
A solution of 0.16g (0.35 mmol) of (±)-**14** in 15ml (230 mmol) of DMSO and 6ml (66 mmol) of acetic anhydride was stirred for 5h in the dark at 20°C. 25ml of H_2O were added and the mixture was extracted with $CHCl_3$ (3 x 50 ml). The organic layer was dried with Na_2SO_4 and the solvent evaporated. (Column chromatography on SiO_2 (petroleum ether 40/60/ ethyl acetate, 3:1) afforded 0.06g (0.14 mmol) of orange crystals. Yield 40%; m.p. 56-59°C.

^1H NMR ($CDCl_3$/TMS) δ: 1.28, 1.36 (18H, 2s, 2 CMe_3); 3.30, 3.96, 4.01 (9H, 3s, OMe); 7.27 (1H, s, H-8); 7.84 (1H, d, H-1, ^4J = 2.3 Hz); 7.91 (1H, d, H-3, ^4J = 2.3 Hz).- UV ($CHCl_3$) λ_{max} (lgε): 276 (3.93); 355 nm (3.20).—MS (70 eV, T_E = 120°C) m/z (%): 410 (37) [M^+]; 382 (100) [M^+-CO]; 367 (80) [M^+-CO - CH_3]; 353 (56) [M^+- C_4H_9]; 337 (15) [M^+- CO - CH_3 - CH_2O]; 325 (15) [M^+ - C_4H_9 - CO].

LC on triacetylcellulose (EtOH/H_2O, 96:4, 22°C) k' : 0.3 for both enantiomers, $(+)_{436}$- $[-]_{320}$- 23 eluting first. These conditions served for obtaining the on-line CD spectrum in Table 2.

(±)-5,8-Dimethylbenzo[c]-9,10-phenanthrenequinone (24)

A solution of 0.31g (1.2 mmol) of (±) - 12 in 25ml acetic acid was treated with 0.56g (3.2 mmol) of iodic acid in 5 ml of H_2O. After refluxing for 2.5h 100ml of H_2O were added. The mixture was extracted with CH_2Cl_2 (2 x 100ml) and the organic layer washed with H_2O (2 x 100ml), 10% Na_2CO_3 solution (2 x 100ml), sat. $Na_2S_2O_3$ solution (100ml) and H_2O (2 x 100ml). Drying over $MgSO_4$ and evaporating the solvent gave a deep-red, viscous oil. Repeated column chromatography on SiO_2 (CH_2Cl_2 / cyclohexane, 4:1, and cyclohexane/ benzene, 1:2) resulted in 0.02 g (0.06 mmol) of orange crystals. Yield 5%; m.p. 149-152°C.

^1H NMR ($CDCl_3$/TMS) δ: 2.03 (3H, s, Me-5); 2.66 (3H, s, Me-8); 7.53 (1H, m, H-12 or H-13); 7.64 (1H, s, H-12 or H-13); 7.81 (1H, m, H-11); 7.89 (1H, m, H-14); 7.90, 7.98 (2H, AB, H-7/8, J_{AB} = 8.4 Hz).- UV ($CHCl_3$) $_{max}$ (lgε): 239 (4.70); 285 (4.75); 350 nm (4.06).

LC on triacetylcellulose (EtOH/H_2O, 96:4, 22°C) k' : 1.2, $(-)_{546}$- $[-]_{290}$ - 24; the enantiomer eluted second is base-line separated but not easily detected. These conditions served for obtaining the on-line CD spectrum in Table 2. It was calibrated[30] (c = 0.093 mmol/l) and resulted in the following data of λ_{max} ($\Delta\varepsilon_{max}$ in l $mol^{-1}cm^{-1}$): 270 (-3.9); 320 (+1.6); 370 (-0.4); 400 (-0.6); 475 nm (-1.0).

(±)-5,7-Di-tert.butyl-1-methylbenzo[c]-9,10-phenanthrenequinone (25)

A solution of 0.087g (0.35 mmol) of (±)-15 in 7 ml (111 mmol) of DMSO and 3 ml (33 mmmol) of acetic anhydride was stirred for 3d in the dark at 20°C. 10 ml of H_2O were added to the red solution which was extracted with $CHCl_3$. The organic layer was dried with Na_2SO_4 and the solvent evaporated. Dry-column chromatography on SiO_2 ($CHCl_3$, R_f = 0.47) resulted in 0.018 g (0.047 mmol) of deep-red crystals. Yield 27%; m.p. 82-85°C.

^{1}H NMR ($CDCl_3$/TMS) δ: 0.98 (9H, s, CMe_3-5); 1.41 (9H, s, CMe_3-7); 2.77 (3H, s, Me-1); 7.29-7.94 (7H, m, arene H). ------ UV (EtOH) λ_{max} (lg ϵ): 310 (3.79); 240 (4.32); 210 (4.48). -----MS (70 eV, T_E = 153°C) m/z (%): 384 (19) [M^+]; 356 (69) [M^+- CO]; 341 (100) [M^+ - CO - CH_3]; 328 (89) [M^+ - 2 CO].

LC on triacetylcellulose ($EtOH/H_2O$, 96:4, 22°C) k' : 0.3 for both enantiomers, $(+)_{546}$-$[+]_{290}$- **25** eluting first. These conditions served for obtaining the on-line CD spectrum in Table 2.

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