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Syntheses and Absolute Stereochemistry of Chiral 9,10-Dihydro-9,10-ethanoanthracenes and their Tricarbonylchromium Complexes

Z. Li[‡], **A. Werner**, and **K. Schlögl***

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Summary. Several chiral mono- and disubstituted 9,10-dihydro-9,10-ethanoanthracenes have been prepared from the corresponding anthracenes. Most of them were separated into enantiomers by chromatography on cellulose triacetate (*CTA*) and their absolute chiralities established by chiroptical comparison (via their CD spectra) with key compounds of known configuration. From the laevorotatory 1,5-dibromo derivative **16** the dextrorotatory dideuterio hydrocarbon (+)(9*S*, 10*S*)-**20** was obtained.

Complexation of 2,6-dimethyl 9,10-dihydro-9,10-ethanoanthracene (+)-**25**, obtained by enantioselective chromatography on *CTA* [with its chirality (9*R*,10*R*) deduced from optical comparison with the 2-monomethyl derivative of known configuration], with $Cr(CO)_6$ afforded two mono tricarbonylchromium complexes [*endo*(+)-**26** and *exo*(+)-**27**] as well as the bis-*exo*,*endo*-complex (+)-**28**. Configurational assignments (*exo*, *endo*) are based on the absorption patterns of the bridge protons in the ^{1}H-NMR spectra.

Keywords. (+)-1,5-Dideuterio-9,10-dihydro-9,10-ethanoanthracene; Enantioselective chromatography on *CTA*; Circular dichroism; Configurational correlation; Tricarbonylchromium complexes.

Synthesen und absolute Stereochemie von chiralen 9,10-Dihydro-9,10-ethanoanthracenen und ihren Tricarbonylchrom-Komplexen

Zusammenfassung. Mehrere chirale mono- und disubstituierte 9,10-Dihydro-9,10-ethanonanthracene wurden aus den entsprechenden Anthracenen durch Diels-Alder-Reaktion mit Ethylen dargestellt und die meisten davon durch Chromatographie an Cellulose-triacetat (*CTA*) präparativ in die Enantiomeren getrennt. Chiroptischer Vergleich (über die CD-Spektren) mit Schlüsselverbindungen bekannter Konfiguration ermöglichte die Festlegung ihrer absoluten Chiralitäten. Aus dem linksdrehenden 1,5-Dibromderivat **16** erhielt man den rechtsdrehenden 1,5-dideuterierten Kohlenwasserstoff (+)-(9*S*,10*S*)-**20**.

Komplexierung von rechtsdrehendem 2,6-Dimethyl-9,10-dihydro-9,10-ethanoanthracen (+)-**25** (erhalten durch enantioselektive Chromatographie an *CTA*) der absoluten Chiralität (9*R*,10*R*), welche durch optischen Vergleich mit dem 2-Monomethylderivat bekannter Konfiguration festgelegt wurde,

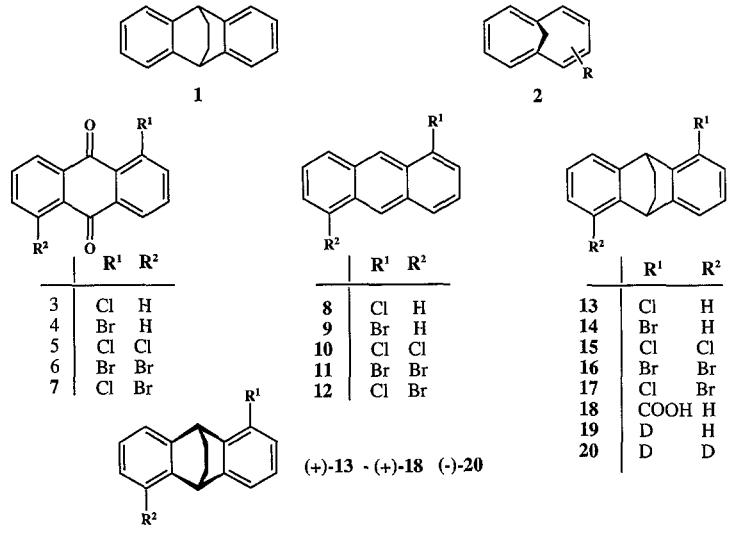
[‡] On leave from Research Institute of Chemical Processing and Utilization of Forest Products, Nanking, P.R. China.

mit $Cr(CO)_6$ lieferte zwei Mono-tricarbonylchrom-Komplexe [*endo*(+)-**26** und *exo*(+)-**27**] neben dem Bis-*exo*,*endo*-Komplex (+)-**28**. Die konfigurative Zuordnung (*exo*, *endo*) war aufgrund der Absorptionen der Brücken-H-Atome in den ^{1}H-NMR-Spektren möglich.

Introduction

9,10-Dihydro-9,10-ethanoanthracene (dibenzo[2.2.2]octadiene, **1**) and various substitution products thereof are conveniently available by Diels-Alder reactions of anthracene or appropriate derivatives (e.g. with ethylene or other dienophiles) [1]. The C_{2v} symmetry of the parent compound **1** is decreased by mono- or (symmetrical) 1,5- or 2,6-disubstitution to C_1 or C_2, giving rise to chiral structures.

Extensive investigations in the field of planarchiral structures [2] caused us to resume studies on chiral derivatives of **1**. Such compounds resemble topologically in some respect planarchiral structures, as for instance bridged [10] and [14] annulenes (e.g. **2**) [3]; both have aromatic perimeters bridged by a C-1 or C-2 unit. Whereas **2**, however, have to be classified as planarchiral [2, 3], substituted ethanoanthracenes (derivatives of **1**) are centrochiral with C-9 and C-10, respectively, as chiral centers. Racemic mixtures can be separated into enantiomers either by classical means, e.g. by crystallization of diastereomeric salts [4, 5] or by enantioselective chromatography on a chiral stationary phase, e.g. crystalline cellulose triacetate (*CTA*). Since absolute chiralities of optically active key compounds (1-carboxylic acid **18** and 1,5-dichloro derivative **15**) are known [4, 6], the absolute stereochemistry of new derivatives of **1** can easily be established either by chiroptical comparison or by chemical transformation.



Recently we have described the static and dynamic stereochemistry of 1,1′-bi(9,10-dihydro-9,10-ethano-anthryl) [7]. We now report on the syntheses, optical resolution and chiroptical properties of new chiral derivatives of **1**, especially of the 1-deuterio and 1,5-dideuterio-9,10-dihydro-9,10-ethanoanthracene which represent *chiral aromatic hydrocarbons* with a chirality due to substitution of hydrogen by

deuterium. In addition some tricarbonylchromium complexes of chiral ethanoanthracenes are described which might be of some interest with regard to a possible intramolecular migration of the $Cr(CO)_3$ group. (cf. also Ref. [8]).

Results and Discussion

Deuterated ethanoanthracenes

Our first aim in pursuing these studies has been the preparation and chiroptical studies of mono- and di-deuterio-derivatives of **1** (**19** and **20**, resp.), especially in context with our recent synthesis of optically active, 2,7-dideuterio-1,6-methano-[10]annulene [9], a chiral aromatic hydrocarbon. **19** and **20** were accessible from the corresponding optically active mono- and dibromo- derivatives **14** and **16**. The chloro derivatives **13** and **17** were prepared in optically active form, too. As the absolute chirality of **15** had been established previously [as (+)(9*R*,10*R*)] [6] the assignment of absolute chiralities to all optically active chloro and bromoderivatives **13–17** was possible by chiroptical (CD) comparison. In the same way the absolute chiralities of the deuterio ethanoanthracenes **19**, **20** were deduced.

The chloro and bromo anthracenes **8–12**, required for the preparation of the corresponding halogenated ethanoanthracenes, are accessible from the halogenated anthrachinones **3–7** by reduction (either with Zn in ammonia, e.g. for **3** to **8**, or with $NaBH_4$ and subsequent treatment with KI/NaH_2PO_2 in methanol). Treatment of the anthracenes **8–12** with ethylene in toluene (at 180 °C and about 100 bar) gave the corresponding ethanoanthracenes **13–17** in excellent yields. 1,5-Dibromo anthrachinone **6** can be obtained from the dichloro derivative **5** by refluxing with a mixture of KBr, $CuCl_2$ and H_3PO_4 in nitrobenzene for 90 h. A shorter reaction time (40 h) furnished a mixture of **6** with the 1-chloro-5-bromo derivative **7**, which was converted into the mixture of the corresponding halogenated anthracenes **11** and **12** and subsequently into the mixture of ethano derivatives **16** and **17**. These chiral compounds were separated into their enantiomers by enantioselective chromatography on cellulose triacetate. In the same chromatographic system the separation of the mixed chloro-bromo ethanoanthracene **17** from the dibromo-derivative **16** was possible, although the selectivity is far lower than the enantioselectivity. Likewise all other halogenated ethanoanthracenes **13–16** could easily be separated into enantiomers by chromatography on *CTA*. For the optical resolution of **14** and its configurational correlation with the carboxylic acid **18** of known absolute chirality [4] see Ref. [7].

All halogenated optically active ethanoanthracenes **13–17** exhibit similar CD-spectra with negative effects between 210 and 215 nm and positive effects at 267 and 276 nm indicative for (*S*) centrochirality (see Fig. 1); therefore optical comparison of (+)-**13**, (+)-**16** and (+)-**17** with (+)-**15** [of established configuration (9*R*,10*R*)] [6] and (+)-**14** [of established configuration (9*R*)] [7] allowed the configurational assignment (+)(9*R*) and (−)(9*S*) for **13**, (+)(9*R*,10*R*) and (−)(9*S*,10*S*) for **16** and **17**.

Treatment of the bromo derivatives (−)-**14** and (−)-**16** with *Bu*-Li in dry ether and subsequent quenching with D_2O furnished the corresponding deuterio compounds **19** and (+)-**20** in yields of 87 and 79%. The degree of deuteration for **19** was determined by NMR- and mass spectroscopy as 72% and the degree of

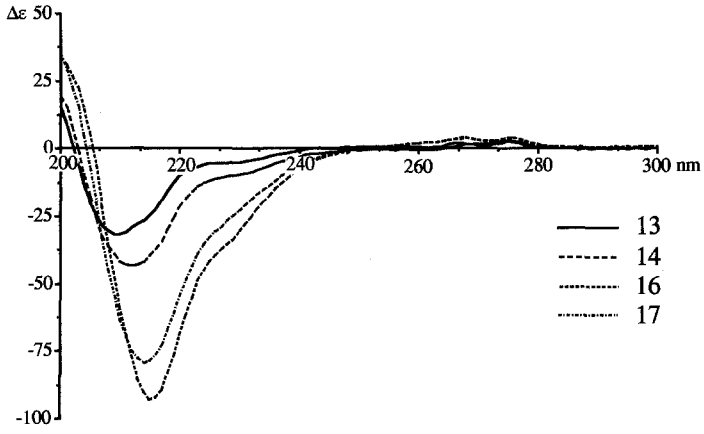


Fig. 1. CD spectra of laevorotatory enantiomers of **13**, **14**, **16**, and **17** (in isooctane)

dideuteration for **20** as 86% by mass spectroscopy. Whereas hardly any significant chiroptical phenomena could be observed for **19**, the dideuterated compound **20** obtained from (−)-**16** is dextrorotatory ($[\alpha]_D^{20} = +1.6°$ in $CHCl_3$) and exhibits a pronounced CD-spectrum (see Fig. 2) with a negative effect at 263 nm and positive effect at 267 and 272 nm. The absolute configuration for **20** is deduced as (+)(9*S*,10*S*) and (−)(9*R*,10*R*), respectively, from (−)-(9*S*,10*S*)-**16**.

Chromatographic Separations

Resolution of enantiomers was achieved by enantioselective chromatography on swollen microcrystalline cellulose triacetate. The chromatographic system used was a preparative HPLC with a column 63 × 690 mm filled with 1000 g of *CTA* Merck 15–25 μm using a pump with a low deadvolume. In cases of poor separation the system was used in cyclic mode i.e. the eluate from the column was fed on the column again. This was repeated till complete separation was achieved [cf. 10, 11]. The progress of enantioseparation was monitored by UV and a polarimeter with a flow cell. Optically purity of only partially resolved peaks was deduced on line from the plot of absorbance A versus optical rotation α [11, 12].

Preparative enantioseparation of the monochloro derivative **13** was performed with 1.7 g of the racemate. Baseline separation was achieved with two cycles showing an enantioselectivity coefficient $\alpha = 1.42$ and eluting the leavorotatory isomer (9*S*,10*S*) first with $[\alpha]_D^{20} = -125°$, the second peak gave an $[\alpha]_D^{20}$ of $+126°$.

Resolution of the racemic bromo-derivative **14** was achieved with a 1.1 g sample in two cycles and $\alpha = 1.50$ also eluting the laevorotatory isomer first.

In the separation of 830 mg of the mixture of racemic **16** and **17** the enantiomers of the mixed haloderivatives were separated in one pass over the column with an enantioselectivity coefficient $\alpha = 1.69$. Both laevorotatory dihalogenated compounds were eluted first in one peak. Crystalline *CTA* is a suitable stationary phase for separations of aromatic geometric isomers, too. Therefore we tried to separate the dibromo ethanoanthracene **16** from bromo–chloro ethanoanthracene **17** on the

same chromatographic system. The separation of the optically active derivatives **16** and **17** required 14 cycles with a separation coefficient of $\alpha = 1.05$.

450 mg of pure racemic **16** in 80 ml of ethanol was separated in one cycle with an enantioselectivity coefficient of $\alpha = 1.74$. First eluted (−)(9*S*,10*S*)-**16** showed an $[\alpha]_D^{20}$ of −243°. Evaporation of the second peak furnished (+)(9*R*,10*R*)-**16** with $[\alpha]_D^{20} = 248°$.

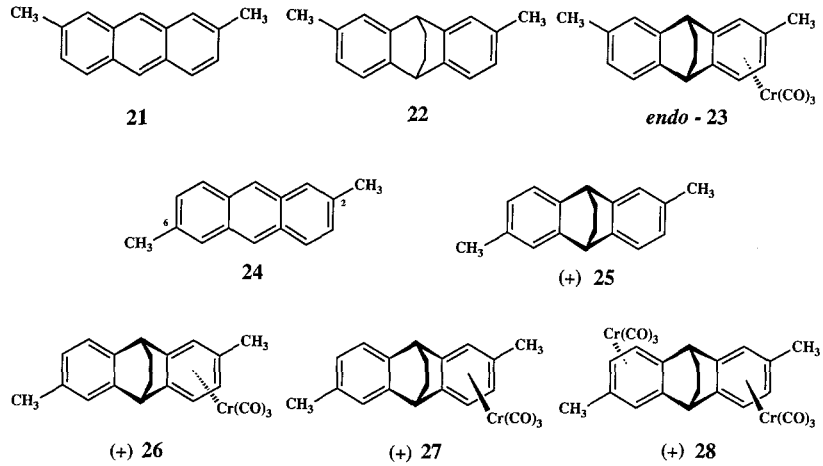
250 mg of 2,6-dimethyl 9,10-dihydro-9, 10-ethanoanthraceme **25** were separated in one run with an enantioselectivity coefficient $\alpha = 2.65$. First eluted (−)(9*S*,10*S*)-enantiomer gave $[\alpha]_D^{20} = -100°$. The second peak gave the other enantiomer with $[\alpha]_D^{20} = +103°$ [13].

Dimethyl-ethanoanthracene Tricarbonylchromium Complexes

Reaction of $Cr(CO)_6$ with 2,7-dimethyl-9,10-dihydro-9,10-ethanoanthracene (**22**) accessible from the corresponding anthracene **21** [14] gave a mixture of *exo* and *endo* complexes. The pure *endo*-complex **23** and traces of *exo*-complex were obtained by chromatography on silica (in ligroin/ethyl acetate 95:5). Its *endo*-configuration was established by ^{1}H-NMR spectroscopy.

Treatment of the isomeric 2,6-dimethyl ethanoanthracene **24** with ethylene afforded the chiral ethanoanthracene **25**, which was separated into its enantiomers by chromatography on *CTA*. The dextrorotatory (+)-**25**, less strongly adsorbed, exhibited an $[\alpha]_D^{20}$ of +103° (ethanol). Its absolute chirality (9*R*, 10*R*) was deduced from chiroptical comparison with 2-methyl-9,10-dihydro-9,10-ethanoanthracene of established configuration (+)-(9*R*) [4].

From (+)-**25** the three dextrorotatory tricarbonylchromium complexes [monocomplexes (+)-**26** and (+)-**27**, and the bis-complex (+)-**28**] were accessible. The ratio of these complexes can be governed by the stochiometry of the $Cr(CO)_6$ used for complexation: an 1.6 fold excess of the ethanoanthracene gives exclusively the monocomplexes. With an 1.7 fold excess of $Cr(CO)_6$ on the other hand all three complexes can be obtained and separated by medium pressure chromatography on silica. Elution followed the sequence **27** (*exo*), **26** (*endo*) in hexane/ethylacetate 95:5; **28** (bis-*exo,endo*) was then eluted by hexane/ethylacetate 1:1. It should be noted,



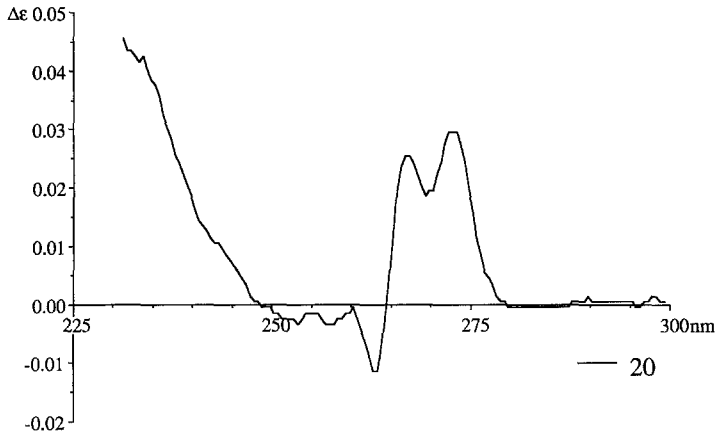


Fig. 2. CD spectrum of dextrorotatory **20** (in isooctane)

that in a recent preparation of racemic 2,6-dimethyl-ethanoanthracene-$Cr(CO)_3$ complexes [8] the *exo* complex **27** could not be isolated.

Configurational assignments – *exo* and *endo* – were possible from the ^{1}H-NMR spectra (vide infra), the stereochemical notations for the C_2-symmetrical hydrocarbon in the complexes with regard to the centrochirality follow from the chirality of the dextrorotatory ligand **25**, the metallocene $[(R,S)_m]$ chirality [cf. 15] can then be deduced from the known relative (*exo*, *endo*) position of the tricabonylchromium moiety: (+)-**26** (*endo*): $(S)_m(9R,10S)$; (+)-**27** (*exo*): $(R)_m(9R,10S)$; (+)-**28** (bis-*exo*, *endo*):$(R)_m(S)_m(9R, 10R)$. Optical rotations ($[\alpha]_D^{20}$ in ethanol): dextro-rotatory complexes **26** + 28°; **27** + 40°; **28** + 10°. For the circular dichroism spectra vide infra.

^{1}H-*NMR Spectra*

All ^{1}H-NMR spectra were recorded in $CDCl_3$ at 400 MHz (δ-values in ppm). The configurational assignments (*exo*, *endo*) were easily possible from the absorption patterns of the four bridge-protons.

In the parent compound 9,10-dihydro-9,10-ethanoanthracene (**1**) these appear at 1.66 (triplet) (the bridgehead protons H-9 and H-10 as singlet at 4.38). Very similar absorptions can be found in the dimethylderivatives [e.g. **25**: 1.69 (s) and 4.22(s)]. The $Cr(CO)_3$ group in *exo*-position to the bridge (such as in **27** or **28**) lies in the neighbourhood of two bridge protons which therefore are shifted downfield, whereas in the *endo*-complexes (**23**, **26**) no deshielding occurs and all four bridge protons absorb at higher field:

27 (*exo*): two multiplets (1 H each) from 2.03–2.13 and 2.20–2.31 and one (2 H) from 1.59–1.74.

26 (*endo*): 1.61–1.77 (m, 4 H). Similarly the *endo*-complex **23** absorbs at 1.59–1.80 (m, 4 H).

28 (*exo-endo*): two multiplets (1 H each) 2.07–2.20 and 2.23–2.36, one (2 H) from 1.56–1.77.

The H-9 and H-10 protons of all complexes are shifted slightly highfield (to about 3.9) as compared to the ligands.

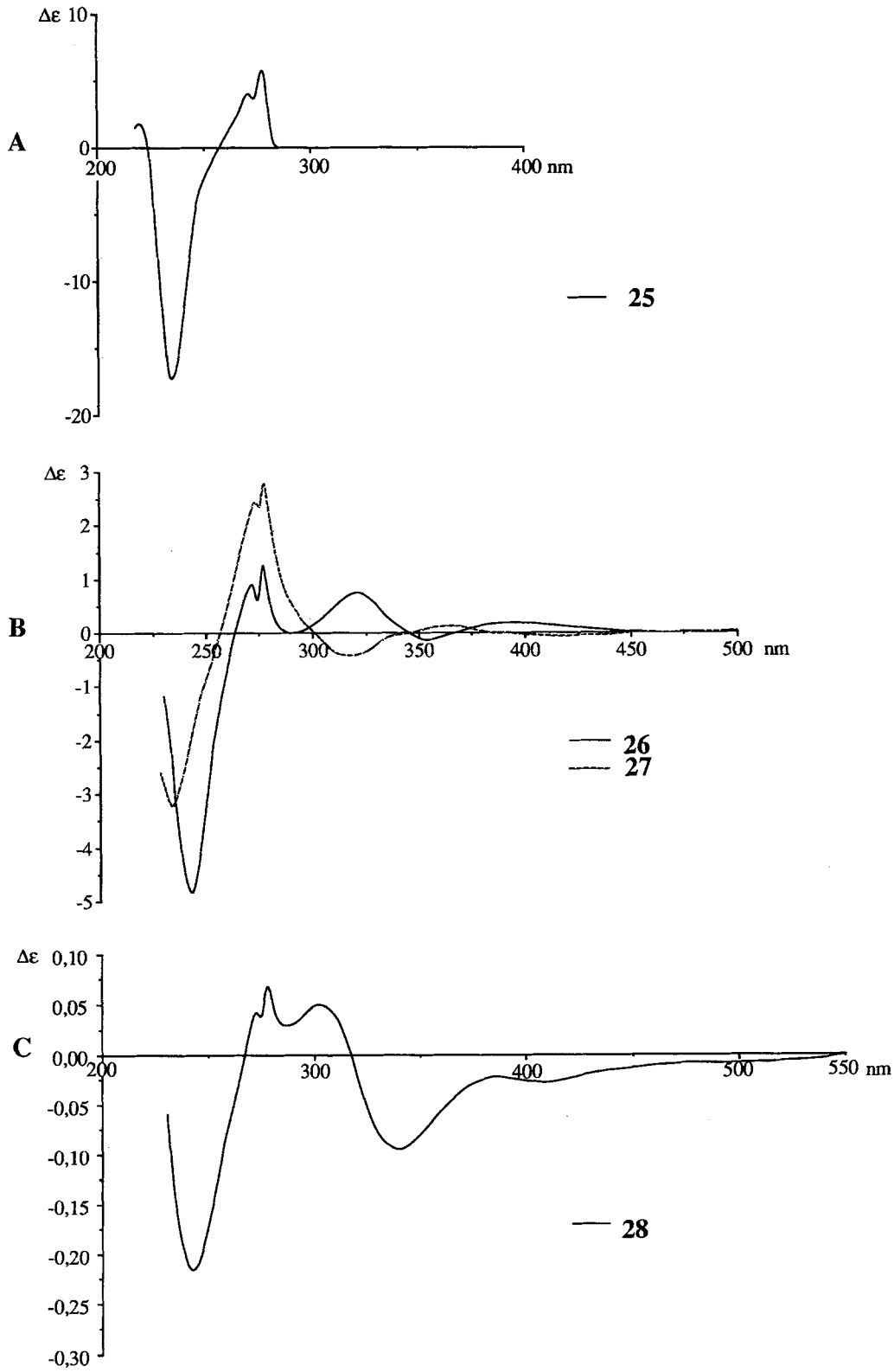


Fig. 3. **A** CD spectrum of dextrorotatory **25** (in ethanol); **B** CD spectra of dextrorotatory **26** and **27** in (ethanol); **C** CD spectrum of dextrorotatory **28** (in ethanol)

The ^{13}C-NMR spectra recorded at 100 MHz (cf. experimental part) are in full agreement with the assignments given.

Circular Dichroism

In the CD-spectrum of (+)-**25** there are positive effects at 220, 270 and 277 nm and a negative effect at 234 nm, which show the (9*R*, 10*R*)-centrochirality (see Fig. 3). For (+)-**26** (*endo*) there exist additional negative effects at 317 and 410 nm and a positive effect at 365 nm due to $(S)_m$-metallocene chirality. In contrast, (+)-**27** (*exo*) has positive effects at 320 and 395 nm and a negative effect at 355 nm corresponding to $(R)_m$-metallocene chirality. As a result of the combination of $(S)_m$ and $(R)_m$-metallocene chiralities (+)-**28** (*exo-endo*) shows a complex CD-spectrum with several effects between 280 and 550 nm.

Experimental Part

Melting points were determined on a Kofler microscope and are uncorrected. Medium pressure liquid chromatography (MPLC) was performed on Merck LiChroprep Si-60 (25–40 μm) on columns (32 × 600 mm) with an FMI pump and an ISCO UA-5 UV detector. Microcrystalline CTA (Merck, 15–25 μm) was used for enantioselective chromatography (column: 63 × 690 mm, UV detector). Optical rotations: Perkin-Elmer 241 polarimeter. CD: Dichrograph Mark 6 (Jobin Yvon). MS: Varian MAT CH-7. NMR (in $CDCl_3$): Bruker WM-250 and AM-400WB spectrometer in FT mode using Aspect-2000 (250 MHz) and -3000 computers (400 MHz). UV: Perkin-Elmer, Lambda 7 UV-VIS spectrophotometer. IR: Perkin Elmer 1740 Infrared Fourier Transform Spectrometer.

(+)- and (−)-1-Chloro-9,10-dihydro-9,10-ethanoanthracene (**13**)

1-Chloro-anthracene (**8**) was prepared from 1 -chloroanthrachinone (**3**) and Zn in ammonia [16], m.p. 77.5–79 °C (lit. 79 °C). 5.70 g (26.8 mmol) of **8** were dissolved in 90 ml of toluene and treated with ethylene under pressure (118 bar) at 180 °C for 43 h. Purification of the product was performed by chromatography on a silica gel column (25 × 200 mm) in ligroin. Subsequent crystallization of the product obtained from *n*-heptane (40 ml) afforded 4.43 g (69%) of **13**; m.p. 109–110 °C. $C_{16}H_{13}Cl$ (240.7). MS: 242/240 (4.8/14.5%, *M*), 214/212 (32.3/100%, $M-C_2H_4$). ^{1}H-NMR: δ 1.70 (s. 4 H, H-11, H-12), 4.34 (s, 1 H, 10), 4.84 (s, 1 H, H-9), 7.00 (dd, 1 H, J = 7.0 and 8.0 Hz, H-3), 7.08–7.16 (m, 3 H, H-2, H-6, H-7), 7.16 (d, 1 H, J = 7.0 Hz, H-4), 7.23–7.34 (m, 2 H, H-5, H-8). ^{13}C-NMR: δ 25.63, 26.24, (Cl2, C11), 40.25, 44.30, (C9, C10), 121.77 (C4), 123.30, 123.72, (C5, C8), 125.77, 125.85, (C6, C7), 126.01 (C2), 126.46 (C3), 129.19 (C1), 140.88, 142.74, (C8a, C10a), 143.39 (C9a), 146.15 (C4a). UV (in isooctane) λ, (ε): 208 (37700), 257 (740), 263 (970), 271 (970).

Enantioselective chromatography of racem. **13** (1.701 g) on *CTA* (Merck, 63 × 690 mm column) in ethanol at 40 °C in the recycling mode gave enantiomerically pure **13** after 2 runs (α = 1.42, K'_1 = 0.85, K'_1 = 1.21; UV detection at 254 mm); the laevorotatory enantiomer was eluted first: (−)(9*S*)-**13**, m.p. 144.5–146.5 °C, $[\alpha]_D^{20} = -125°$ (c = 0.3025 in ethanol). (+)(9*R*)-**13**, m.p. 143–145 °C, $[\alpha]_D^{20} = +126°$ (c = 0.4675 in ethanol). CD of (−)(9*S*)-**13**, [$\lambda(\Delta\varepsilon)$, in isooctane]: 210 nm (−32.40), 255 (−0.003), 260(+0.18), 262 (+0.09), 268 (+1.61), 270 (+1.39), 275 (+2.63).

(+)- and (−)-1,5-Dibromo-9,10-dihydro-9,10-ethanoanthracene (**16**)

A mixture of 1,5-dichloro-anthrachinone **5**, KBr, $CuCl_2$ and H_3PO_4 (85%) in nitrobenzene was refluxed at 195–205 °C for 92 h. The precipitate was filtered off and washed with water, ether and acetone. Twice crystallization of the crude product from toluene afforded pure yellow crystals **6**, m.p. 303.5–304.5 °C

(lit. 293 °C) [17]. **6** was treated with $NaBH_4$ and subsequently with KI/NaH_2PO_2 to give 1,5-dibromo-anthracene **11**, m.p. 207–208 °C (lit. 209 °C) [18].

1.80 g (5.4 mmol) of **11** were dissolved in 80 ml of toluene and then treated with ethylene (82 bar, 180 °C) for 67 h. Chromatography on silica in ligroin and subsequent crystallization from ligroin (20 ml) gave 1.49 g (76%) of **16**, m.p. 131.5–134.5 °C. $C_{16}H_{12}Br_2$ 364.1). MS: 366/364/362 (7.0/17.7/10.9%, *M*), 338/336/334 (52.1/100/54.3%, $M-C_2H_4$), 257/255 (9.4/10.3%, $M-C_2H_4-Br$), 176 (62.5%, $M-C_2H_4-2Br$). ^{1}H-NMR: δ 1.70 (s, 4 H, H-11, H-12), 4.82 (s, 2 H, H-9, H-10), 6.08 (dd, 2 H, $J = 7.4$ and 8.0 Hz, H-3, H-7), 7.25 (d, 2 H, $J = 7.4$ Hz, H-4, H-8), 7.32 (dd, 2 H, $J = 8.0$ and 1.0 Hz, H-2, H-6). ^{13}C-NMR: δ 25.36 (C11, C12), 43.68 (C9, C10), 119.21 (C1, C5), 123.06 (C4, C8), 127.33 (C3, C7), 129.61 (C2, C6), 142.59 (C4a, C8a), 145.28 (C9a, C10a). UV (in isooctane) λ (ε): 214 (39120), 258 (596), 264 (673), 268 (692), 275 (592).

450 mg of racem. **16** were resolved into its enantiomers by enantioselective chromatography on *CTA* (Merck, 63 × 690 mm column) in ethanol at 40 °C ($\alpha = 1.74$, $K'_1 = 0.70$, $K'_1 = 1.22$; UV detection at 254 nm); the laevorotatory enantiomer was eluted first: (−)(9*S*,10*S*)-**16**, m.p. 125–126 °C, $[\alpha]_D^{20} = -243°$ ($c = 0.114$ in ethanol). (+)(9*R*,10*R*)-**16**, m.p. 124–125.5 °C, $[\alpha]_D^{20} = +248°$ ($c = 0.1315$ in ethanol). CD of (−)(9*S*,10*S*)-**16**, [$\lambda(\Delta\varepsilon)$, in iso-octane]: 215 nm (−92.70), 267 (+3.92), 272 (+2.66), 276 (+4.16).

(−)-1-Chloro-5-bromo-9,10-dihydro-9,10-ethanoanthracene (**17**)

1-Chloro-5-bromo-anthrachinone **7** was prepared in the same way as **6**. A short reaction time (40 h) gave a mixture of **7** and **6**. The ratio of **7**:**6** is 1:1 (from analysis of ^{1}H-NMR spectrum), m.p. 290–292 °C. The mixture was reduced to the correspondent anthracene (**12**:**11** = 1:1 from ^{1}H-NMR by using the procedure for **11**. m.p. 200–201 °C. Subsequent treatment with ethylene in the same way as for **16** afforded a mixture of 1-chloro-5-bromo-9,10-dihydro-9,10-ethanoanthracene (**17**) and 1,5-dibromo-9,10-dihydro-ethanoanthracene (**16**) in 1:1 (from ^{1}H-NMR analysis).

830 mg of the obtained mixture were dissolved in 80 ml of ethanol, then separated by chromatography on *CTA* (Merck, 63 × 690 mm column) in ethanol at 40 °C using the recycling technique, ($\alpha_1 = 1.69$, $K'_1 = 0.84$, $K'_2 = 1.42$, $\alpha_2 = 1.05$, $K'_3 = 0.78$, $K'_4 = 0.82$; UV detection at 254 nm); After the first run, the dextrorotatory enantiomers of **16** and **17** were eluted together, but the chromatography of the laevorotatory enantiomers continued. After the 14 cycles, the lavevorotatory enantiomer of **17** was eluted first: (−)(9*S*,10*S*)-**17**, m.p. 115–116.5 °C, $[\alpha]_D^{20} = -223°$ ($c = 0.169$ in ethanol). $C_{16}H_{12}ClBr$ (319.6). MS: 320/318 (14.2/13.4%, *M*), 294/292/290 (24.2/100/75.5%, $M-C_2H_4$), 211 (12.3%, $M-C_2H_4-Br$), 176 (44.1%, $M-C_2H_4-Br-Cl$). ^{1}H-NMR: δ 1.70 (d, 4 H, $J = 1.4$, H-11, H-12), 4.82 (s, 1 H), 4.85 (s, 1 H), H-9, H-10), 6.98 (dd, 1 H, $J = 8.0$ and 1.4 Hz, H-7), 7.04 (dd, 1 H, $J = 8.0$ and 7.4 Hz, H-3), 7.15 (dd, 1 H, $J = 8.0$ and 1.4 Hz, H-2), 7.22 (d, 1 H, $J = 7.4$ Hz, H-4), 7.25 (d, 1 H, $J = 7.4$ Hz, H-8), 7.32 (dd, 1 H, $J = 8.0$ and 1.2 Hz, H-6). ^{13}C-NMR: δ 25.19, 25.22, (C12, C11), 40.81 (C9), 43.26 (C10), 119.08 (C5), 122.23 (C4), 122.89 (C8), 126.35 (C2), 126.74 (C3), 127.15 (C7), 129.18 (C1), 129.42 (C6), 140.48 (C8a), 142.44 (C4a), 145.07, 145.12, (C9a, C10a). UV (in isooctane) λ, (ε): 212 (39710), 258 (480), 265 (563), 267 (566), 276 (447). CD [$\lambda(\Delta\varepsilon)$, in isooctane]: 214 nm (−78.40), 268 (+3.56), 272 (+2.52), 276 (+3.37).

1-Deuterio-9,10-dihydro-9,10-ethanoanthracene (**19**)

To a solution of 114 mg (0.40 mmol) of (−)(9*S*)-1-bromo-9,10-dihydro-9,10-ethanoanthracene **14** in 16 ml of abs. ether 0.41 ml (1.6 *N* in hexane, 0.66 mmol) of *n-Bu*Li was added at 0 °C under argon atmosphere. After the mixture had been stired at room temperature for 1 h, 1 ml (50 mmol) of D_2O ($\geqslant 99.96\%$) was injected very slowly into the solution. The ether layer was separated, dried over $MgSO_4$, filtered and evaporated. The resulting product was purified by chromatography on silica in ligroin. Yield 67 mg (87%) of **19**, m.p. 137–139 °C. The degree of deuteration: 72% (determined by MS and ^{1}H-NMR). ^{1}H-NMR: δ 1.66 (t, 4 H, H-11, H-12), 4.38 (s, 2 H, H-9, H-10), 7.03–7.11

(m, 4H, H-2, H-3, H-6, H-7), 7.25–7.32 (m, 3H, H-4, H-5, H-8). ^{13}C-NMR: δ 26.66 (C11, C12), 43.99 (C9), 44.05 (C10), 123.24 (C4, C5, C8), 125.39 (C2), 125.50 (C3, C6, C7), 143.7 (C9a), 143.8 (C4a, C10a, C8a). UV (in isooctane) λ, (ε): 204 (35320), 252 (579), 259 (845), 265 (1359), 272 (1676). No significant chiroptical phenomena could be observed.

(+)(9S,10S)-1,5-Dideuterio-9,10-dihydro-9,10-ethanoanthracene (**20**)

1.5 ml (1.6 *N* in hexane, 2.40 mmol) of *n-Bu*Li were injected into a solution of 224 mg (0.62 mmol) of (−)(9*S*,10*S*)-1,5-dibromo-9,10-dihydro-9,10-ethanoanthracene **16** in 50 ml of abs. ether unter argon atmosphere at 0 °C. The mixture was then stirred at room temperature. After 2 h and 3.5 h twice 1.0 ml (1.6 *N* in hexane, 1.6 mmol) of *n-Bu*Li was added to the solution. After the mixture had been stired for additional 1 h, 3 ml (150 mmol) of D_2O ($\geqslant$99.96%) was added very slowly. Then the ether layer was separated, dried over $MgSO_4$, filtered and evaporated. Subsequent chromatography on silica in ligroin afforded 102 mg (79%) of dextrorotatory **20**, its absolute configuration is (+)(9*S*,10*S*), m.p. 138.5–143 °C, degree of di-deuteration: 86% (determined by MS), $[\alpha]_D^{20} = +1.6°$ ($c = 1.021$ in $CHCl_3$). ^{1}H-NMR: δ 1.66 (t, 4H, H-11, H-12), 4.38 (s, 2H, H-9, H-10), 7.03–7.11 (d, 4H, H-2, H-3, H-5, H-6), 7.24–7.33 (m, 2H, H-4, H-8). ^{13}C-NMR: δ26.66 (C11, C12), 44.00 (C9, C10), 123.0 (C1, C5), 123.23 (C4, C8), 125.39 (C2, C6), 125.49 (C3, C7), 143.73 (C9a, C10a), 143.81 (C4a, C8a). UV (in isooctane)λ, (ε): 204 (36230), 252 (580), 259 (863), 265 (1381), 272 (1696). CD [λ ($\Delta\varepsilon$), in iso-octane]: 263 (−0.016), 267 (+0.027), 270 (+0.013), 273 (+0.031).

2,7-Dimethyl-9,10-dihydro-9,10-ethanoanthracene (**22**)

2,7-Dimethylanthracene **21** was synthesized by the method of Morgan et al. [14]. Diels-Alder reaction with ethylene in toluene at 180 °C and 127 bar for 30 h afforded crude **22**, which was purified by chromatography on *CTA* (Merck, 63 × 690 mm column) in ethanol at 40 °C in 2 runs, m.p. 104–108 °C. $C_{18}H_{18}$ (234.3). MS: 234 (20.1%, M), 206 (100%, $M-C_2H_4$). ^{1}H-NMR: δ 1.58 (s, 4H, H-11, H-12), 2.19 (s, 6H, $2CH_3$), 4.19 (s, 1H), 4.23 (S, 1H), (H9, H10), 6.87 (dd, 2H, $J = 7.8$ and 1.0 Hz, H-3, H-6), 7.06 (s, 2H, H-1, H-8), 7.11 (d, 2H, $J = 7.8$ Hz, H-4, H-5).

2,7-Dimethyl-9,10-dihydro-9,10-ethanoanthracene endo-tricarbonylchromium (**23**)

200 mg (0.86 mmol) of **22** and 100 mg (0.45 mmol) of hexacarbonylchromium were added to 30 ml of di-*n*-butyl ether/*THF* (11:1). After 3 cycles of "freeze-pump-thaw" degassing the mixture was refluxed for 48 h under argon atmosphere. The cooled solution was filtered over Celite, the solvent and excess hexacarbonylchromium removed in vacuo. Subsequent middle pressure liquid chromatograpy (MPLC) on silica in ligroin/ethylacetate (95:5) gave the pure *endo*-tricarbonylchromium complex **23** (traces of *exo*-tricarbonylchromium complex were not isolated), m.p. 156–156 °C (dec.). $C_{21}H_{18}O_3Cr$ (370.4). MS: 370 (10.3%, *M*), 314 (8.4%, *M*–2CO), 286 (100%, *M*–3CO), 258 (13.8%, *M*–3CO–C_2H_4), 206 (17.3%, *M*–C_2H_4–$Cr(CO)_3$), 52 (87%, Cr). ^{1}H-NMR: δ 1.59–1.80 (m, 4H, H-11, H-12), 2.12 (s, 3H, CH_3 on C2), 2.32 (s, 3H, CH_3 on C7), 3.90–3.99 (m, 2H, H-9, H-10), 4.94 (dd, 1H, $J =$ 6.2 and 1.2 Hz, H-3), 5.42 (s, 1H, H-1), 5.59 (d, 1H, $J = 6.2$ Hz, H-4), 6.97 (d, 1H, $J = 7.8$ Hz, H-6), 7.06 (s, 1H, H-8), 7.07 (d, 1H, $J =$ 7.8 Hz, H-5). IR (KBr): ν(CO), 1950 (s), 1883 (s), 1874 (s), 1862 (s).

(+)- and (−)-2,6-Dimethyl-9,10-dihydro-9,10-ethanoanthracene (**25**)

2,6-Dimethyl-anthracene **24** was prepared by the method of Morgan et al. [14]. 1.08 g (5.2 mmol) of **24** in 80 ml of toluene were treated with ethylene at 180 °C and 140 bar for 40 h. The cooled mixture was filtered and purified by chromatography on silica in ligroin/ethylacetate (95:5). Crystallization from ethanol, filtration and evaporation of the filtrate afforded 460 mg (36%) of pure **25**. m.p. 68–70 °C. $C_{18}H_{18}$(234.3). MS: 234 (17.3%, M), 206 (100%, M–C_2H_2). ^{1}H-NMR: δ 1.69 (s, 4H,

H-11, H-12), 2.28 (s, 6 H, $2CH_3$), 4.26(s, 2 H, H-9, H-10), 6.88 (d, 2 H, $J = 7.8$ Hz, H-3, H-7), 7.07 (s, 2 H, H-1, H-5), 7.12(d, 2 H, $J = 7.8$ Hz, H-4, H-8). ^{13}C-NMR: δ 21.20 ($2CH_3$), 26.88 (C11, C12), 43.67 (C9, C10), 122.97 (C4, C8), 124.05 (C1, C5), 125.85 (C3, C7), 134.93 (C2, C6), 140.96 (C4a, C8a), 144.14 (C9a, C10a). UV (in ethanol) λ, (ε): 262 (2017), 270 (2891), 277 (3748).

Enantioselective chromatography of racem.-**25** (250 mg) on CTA (Merck, 63 × 690 mm) in ethanol at 40 °C gave enantiomerically pure **25** in 1 run ($\alpha = 2.65$, $K'_1 = 0.48$, $K'_2 = 1.27$; UV detection at 280 nm). The laevorotatory enantiomer was eluted first: (−)(9*S*,10*S*)-**25**, m.p. 83–85 °C, $[\alpha]_D^{20} = -100.2°$ ($c = 0.500$ in ethanol). (+) (9*R*,10*R*)-**25**, m.p. 98–100 °C, $[\alpha]_D^{20} = +102.6°$ ($c = 0.4825$ in ethanol). CD of (+) (9*R*,10*R*)-**25**, [λ ($\Delta\varepsilon$), in ethanol]: 220 nm (+1.81), 234 (−17.23), 270 (+4.03), 274 (+3.70), 277 (+5.80).

(+)-2,6-Dimethyl-9,10-dihydro-9,10-ethanoanthracene endo-tricarbonylchromium (**26**), *(+)-exo-tricarbonylchromium* (**27**), *and (+)-endo-exo-bis(tricarbonylchromium)* (**28**)

The mixture of (+)(9*R*,20*R*)-**25** and hexacarbonylchromium in 60 ml of di-*n*-butyl ether/*THF* (5:1) was refluxed under argon atmosphere after 3 cycles of "freeze-pump-thaw" degassing. The cooled solution was filtered over Celite and the filtrate evaporated. Pure (+)-*endo*-tricarbonylchromium **26** and (+)-*exo*-tricarbonylchromium **27** were isolated at first by MPLC on silica gel (column 32 × 600 mm) in ligroin/ethyl acetate (95:5), and then the pure (+)-*endo-exo*-bis(tricarbonylchromium) **28** was eluted by a solvent mixture of 50:50 hexane/ethyl acetate.

Ratio of (+)-**25**/$Cr(CO)_6$	Reaction time	Yield (+)-**26**	(+)-**27**	(+)-**28**
1.6:1	49 h	14%	6%	0
1:1.7	25 h	22%	20%	21%

(+)$(S)_m$(9*R*,10*S*)-**26**: m.p. 191–193 °C, $[\alpha]_D^{20} = +28°$ ($c = 0.095$ in ethanol). $C_{12}H_{18})_3Cr$ (370.4). MS: 370 (12.2%, *M*), 314 (7.5%, *M*–2CO), 286 (100%, *M*–3CO), 206 (17.5%, *M*–C_2H_4–$Cr(CO)_3$), 52 (68.7%, Cr). ^{1}H-NMR: δ 1.61–1.77 (m, 4 H, H-11, H-12), 2.12 (s, 3 H, CH_3 on C2), 2.32 (s, 3 H, CH_3 on C6), 3.91 (s, 1 H), 3.97 (s, 1 H), (H-9, H-10), 4.95 (dd, 1 H, $J = 6.2$ and 1.6 Hz, H-3), 5.43 (s, 1 H, H-1), 5.59 (d, 1 H, $J = 6.2$ Hz, H-4), 6.97 (dd, 1 H, $J = 7.2$ and 1.0 Hz, H-7), 7.01 (s, 1 H, H-5), 7.11 (d, 1 H, = 7.2 Hz, H-8). ^{13}C-NMR: δ 20.46, 21.34, ($2CH_3$), 26.86, 27.00, (C11, C12), 41.54, 41.63, (C9, C10), 91.05, 91.88, 91.99, (C3, C1, C4), 105.9 (C2), 113.0 (C4a), 116.2 (C9a), 122.73 (C8), 123.25 (C5), 126.43 (C7), 135.73 (C6), 138.4 (C8a), 142.08 (C10a). IR (KBr): ν(CO), 1956 (s), 1883 (s), 1849 (s), 1818(m). UV (in ethanol) λ, (ε): 319 (7700). CD [$\lambda(\Delta\varepsilon)$, in ethanol]: 235 nm (−3.10), 272 (+2.41), 274 (+2.37), 276 (+2.69), 317 (−0.46), 365 (+0.14), 410 (−0.07).

(+)$(R)_m$(9*R*,10*S*)-**27**: m.p. 56–58 °C, $[\alpha]_D^{20} \sim \rightarrow 40°$ ($c = 0.075$ in ethanol). $C_{21}H_{18}O_3Cr$ (370.4). MS: 370. (8.6%, *M*), 314 (10.8%, *M*–2CO), 286 (85.1%, *M*–3CO), 258 (14.9%, *M*–CO–C_2H_4), 206 (37.0%, *M*–C_2H_4–$Cr(CO)_3$), 52 (100%, Cr). ^{1}H-NMR: δ 1.59–1.74 (m, 2 H), 2.03–2.13 (m, 1 H), 2.20–2.31 (m, 1 H), (H-11, H-12), 2.09 (s, 3 H, CH_3 on C2), 2.28 (s, 3 H, CH_3 on C6), 3.95 (s, 1 H), 4.00 (s, 1 H), (H-9, H-10), 4.96 (d, 1 H, $J = 6.2$ Hz, H-3), 5.38 (s, 1 H, H-1), 5.54 (d, 1 H, $J = 6.2$ Hz; H-4), 7.01 (d, 1 H, $J = 7.2$ Hz, H-7), 7.04 (s, 1 H, H-5), 7.10 (d, 1 H, $J = 7.2$ Hz, H-8). ^{13}C-NMR: δ 20.39, 21.18, ($2CH_3$), 28.86, 29.39, (C11, C12), 42.03, 42.22, (C9, C10), 91.29, 91.80, (C3, C1, C4), 106.16 (C2), 119.36 (C4a), 122.13 (C9a), 123.25, 124.61, 126.77, (C8, C5, C7), 136.16 (C6), 139.97 (C8a), 142.57 (C10a). (C10a). IR (KBr): ν(CO), 1953 (s), 1865 (s). UV (in ethanol) λ, (ε): 320 (8440), 277 (5800), 268 (6440). CD [λ ($\Delta\varepsilon$), in ethanol]: 242 nm (−4.67), 271 (+0.89), 274 (+0.63), 277 (+1.23), 288 (−0.01), 320 (+0.77), 355 (−0.11), 395 (+0.19).

(+) $(S)_m(R)_m(9R,10R)$-**28**: $[\alpha]_D^{20} = +10.0°$ ($c = 0.24$ in ethanol). $C_{24}H_{18}O_6Cr_2$ (506.4). MS: 506 (11.1%, *M*), 422 (22.6%, *M*–3CO), 370 (5.6%, *M*–$Cr(CO)_3$), 366 (13.1%, *M*–5CO), 338 (9.9%, *M*–6CO), 286 (100%, *M*–$Cr(CO)_3$–3CO), 258 (13.7%, *M*–$Cr(CO)_3$–3CO–C_2H_4), 234 (12.8%, *M*–$2Cr(CO)_3$), 206 (70.1%, *M*–$2Cr(CO)_3$–C_2H_4), 52 (82.4%, Cr). ^{1}H-NMR: δ 1.56–1.77 (m, 2H), 207–2.20 (m, 1H), 2.23–2.36 (m, 1H), (H-11, H-12), 2.11 (s, 3H), 2.15 (s, 3H), ($2CH_3$), 3.76 (s, 2H, H-9, H-10), 4.96 (dd, 1H, $J = 6.2$ and 1.6 Hz, H-7), 5.09 (dd, 1H, $J = 6.2$ and 1.6 Hz, H-3), 5.50 (s, 1H, H-1), 5.52 (s, 1H. H-5), 5.53 (d, 1H, $J = 6.2$ Hz, H-4), 5.61 (d, 1H, $J = 6.2$ Hz, H-8). ^{13}C-NMR: δ 20.35, 20.43, ($2CH_3$), 28.74, 29.32, (C11, C12), 40.03, 40.16, (C9, C10), 91.25, 91.60, 91.64, 91.73, (C4, C8, C1, C5), 92.39, 92.52, (C3, C7), 106.25, 106.97, (C6, C2), 110.7 (C8a), 112.0 (C10a), 115.9 (C4a), 118.6 (C9a). IR (KBr): ν(CO), 1954(s), 1893 (s), 1870 (s). UV (in ethanol) λ, (ε): 323 (1790). CD [$\lambda(\Delta\varepsilon)$, in ethanol]: 242 nm (+0.216), 272 (−0.042), 274 (−0.038), 277 (−0.069), 285 (−0.029), 300 (−0.050), 340 (+0.096), 385 (+0.021), 410 (+0.028).

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