Monatshefte für Chemie 122, 1097 – 1108 (1991)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Static and Dynamic Stereochemistry of 1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl)

Karl Schlögl[1, *, **], **Zhi Li**[1], and **Christoph Kratky**[2]

[1] Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria
[2] Institut für Physikalische Chemie, Universität Graz, A-8010 Graz, Austria

Summary. The title compound **2** was prepared either by highpressure reaction of 1,1′-bianthryl with ethylene or by coupling of 1-bromo-9,10-dihydro-9,10-ethanoanthracene (**4**). Both syntheses afforded a mixture of diastereoisomers (meso **2 a** and racemate **2 b**) in a ratio of 1.5 : 1 and 2.3 : 1, respectively. Configurational assignment was possible both from the ^{1}H- and ^{13}C-NMR spectra and by coupling of laevorotatory **4** (accessibly by enantioselective chromatography on triacetyl cellulose in ethanol) to laevorotatory **2 b**. (+)-**4** was tranformed into the dextrorotatory carboxylic acid (+)-**5** of known configuration (9 *R*) thus establishing the configuration of (+)-**4** as (9 *R*) too and hence the centrochirality in (−)-**2 b** as (9 *S*)(9′ *S*). The racemic form **2 b** is a conformational (appr. 1.8 : 1) mixture of two rotamers.

The rotational barrier was established as $\Delta G^{\#} = 92 - 95\,\mathrm{kJ\,mol^{-1}}$ (depending on the temperature) both by ^{1}H-NMR and CD kinetics (based on equilibration of the separated optically active rotamers of *racem.* **2**). For the latter preferred conformations were assumed allowing the assignment of the axial chirality: e.g. (−)-(9 *S*)$(R)_a$(9′*S*) for the main rotamer of (−)-**2 b** [and (−)(9 *S*)$(S)_a$(9′*S*) for the underpopulated one].

All assumptions were confirmed by X-ray crystal structure analyses of **2 a** and the main rotamer of **2 b** with torsional angles around the 1,1′-bonds of −111.1 and −121.2°, respectively.

Keywords. Circular dichroism; Chemical and chiroptical correlation; Enantioselective chromatography; Torsional isomers and barriers; X-ray crystal structures.

Statische und dynamische Stereochemie von 1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl)

Zusammenfassung. Die Titelverbindung **2** wurde durch Hochdruckreaktion von 1,1′-Bianthryl mit Ethylen oder durch Kupplung von 1-Brom-9,10-dihydro-9,10-ethano-anthracen (**4**) als Mischung der Diastereomeren (Mesoform **2 a** und Racemat **2 b**) im Verhältnis von 1.5 : 1 bzw. 2.3 : 1 erhalten. Die konfigurative Zuordnung erfolgte sowohl aus den ^{1}H- und ^{13}C-NMR-Spektren als auch durch Kupplung von linksdrehendem **4** zu (−)-**2 b**. Optisch aktives **4** war durch enantioselektive Chromatographie an Triacetylcellulose in Ethanol optisch rein zugänglich. Seine Konfiguration wurde durch Umwandlung in die entsprechende Carbonsäure **5** (bekannter Chiralität) als (+)(9*R*) [bzw. (−)(9*S*)] bestimmt. Damit war auch die Zentrochiralität im erwähnten Kupplungsprodukt (−)-(**2 b**) als (9*S*)(9′*S*) festgelegt. Das Racemat **2 b** ist eine Mischung von Rotameren im Verhältnis von 1.8 : 1.

** Dedicated to Prof. K. L. Komarek (Vienna) with cordial wishes on the occasion of the 65th anniversary of his birthday

Die Rotationsbarriere wurde (in Abhängigkeit von der Temperatur) als $\Delta G^{\#} = 92 - 95\,\mathrm{kJ\,mol^{-1}}$ sowohl durch ^{1}H-NMR- als auch CD-Kinetik (basierend auf der Äquilibrierung der getrennten optisch aktiven Rotameren von *racem.* **2**) ermittelt. Für die letzteren können aufgrund der Annahme bevorzugter Konformationen auch die Symbole für die Axialchiralität vorgeschlagen werden. Für (−)-**2b**: $(9S)(R)_a(9'S)$ für das überpopulierte bzw. (−)-$(9S)(S)_a(9'S)$ für das unterpopulierte Rotamer.

Diese Annahmen wurden durch Röntgenstrukturanalysen von **2a** und des Hauptrotamers von **2b** (mit Torsionswinkeln von −111.1 bzw. −121.2°) bestätigt.

Introduction

Insertion of a second stereogenic unit into axialchiral structures (i.e. torsional stereoisomers with a rotational barrier higher than appr. 95 kJ/mol) leads to compounds with interesting static and dynamic stereochemical features.

In previous papers we have described tricarbonylchromium complexes of disubstituted biphenyls [1], 2,2′-bi-annulenyls [2] and 1,1′-biferrocenyls [3] which combine the elements of axial (torsional) and planar chirality [4]. Preferred configurations and conformations, chiroptical properties and absolute chiralities of these novel chiral compounds were investigated in some detail – based on the fact that two stereogenic units within one molecule give rise to two principal stereoisomers, namely *racemic* and *meso* forms, each of which can consist of pairs of enantiomeric conformers. With a sufficiently high rotational barrier the *meso* form might be resolvable into enantiomers.

9,10-Dihydro-9,10-ethano-anthracenes (cf. **4**) resemble topologically in some respect bridged annulenes (e. g. 1,6-methano[10]annulenes) [2] since both have a bridged aromatic perimeter. Suitable substitution decreases the symmetry sufficiently to give chiral structures with C_1 or C_2-symmetry and can thus be obtained optically active, preferably by enantioselective chromatography [5]. Whereas the latter can be classified as planarchiral [4], in the former the carbon atoms 9 and 10 are chiral centers. Several optically active ethano-anthracenes have been prepared and their absolute chirality established [6].

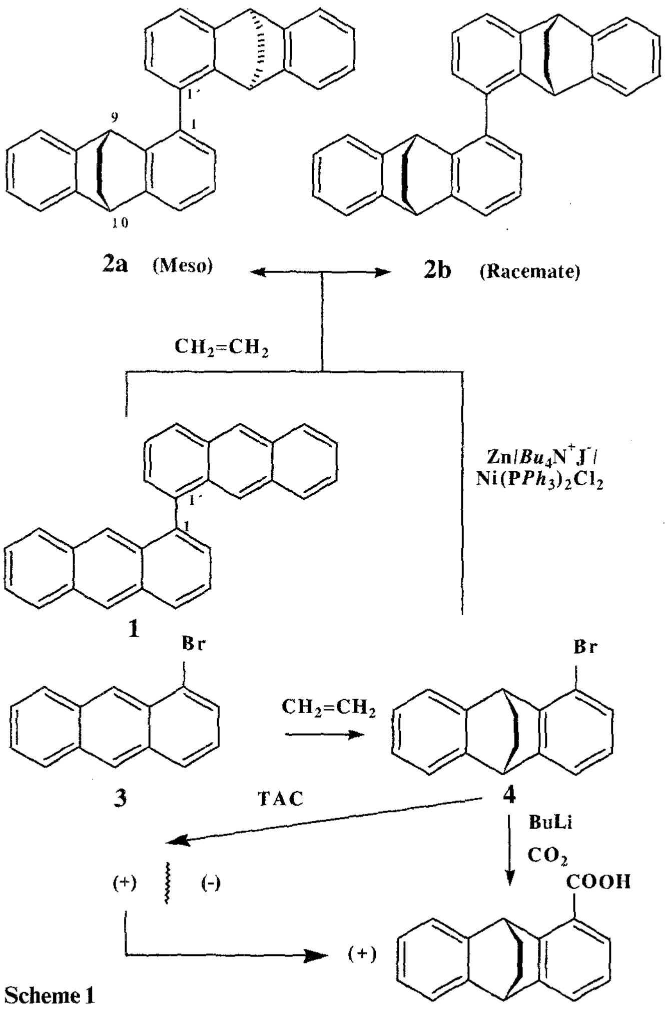
We have now prepared 1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl) (**2**) separated it into its stereoisomeric forms (*meso*- and *racemic* form, **2a** and **2b**, resp.), and investigated the static and dynamic stereochemistry of these torsional isomeric biaryls.

Results and Discussion

Syntheses and Separation of Stereoisomers of **2**

For the synthesis of the desired biaryl **2** two possibilities seemed feasible: 1. Reaction of 1,1′-bianthranyl (**1**) with ethylene under pressure at elevated temperature and pressure (as employed for the preparation of 9,10-dihydro-9,10-ethano-anthracene [7]); or 2. Coupling of 1-bromo-9,10-dihydro-9,10-ethano-anthracene (**4**). In both cases a mixture of stereoisomers **2a** and **2b** could be expected.

1,1′-Bianthryl (**1**) is accessible from 1,1′-bi-anthrachinonyl [8] by reduction with Zn in ammonia [9]. Subsequent treatment with ethylene in toluene (at 180°C and 90 bar for 100 h) gave the crude diastereomeric mixture of **2** (**a** and **b**) in excellent yield. On the other hand 1-bromoanthracene (**3**) [10] and ethylene afforded the 9,10-dihydro-9,10-ethano derivative **4** in 88% yield. The latter could be coupled with a mixture of Zn, tetrabutylammonium iodide and $Ni(PPh_3)_2Cl_2$ [11] to give the diastereomeric mixture of **2** in 23% yield. This method, although less efficient than the reaction of **1** with ethylene, is important for the preparation of optically active **2b** from optically active **4** (*vide infra*).



Scheme 1

It should be mentioned that attempts to couple 1-chloro-9,10-dihydro-9,10-ethano-anthracene, accessible from 1-chloro-anthracene [12], to the dimer **2** failed.

According to HPLC analyses the synthesis of **2** from bianthryl **1** gave a mixture of *meso*:*racem* (**a**:**b**) = 1.5 : 1, whereas coupling of **4** yielded a ratio **a**:**b** of 2.3 : 1. Preparative separation of this mixture of diastereomers proved to be rather difficult: Chromatography on silica gel or alumina in most solvents was unefficient. In *n*-hexane/CH_2Cl_2 a separation of *meso*-**2** (**2a**) together with one rotamer (**2b'**) of the *racemate* from the second (main) rotamer (**2b**) was possible. Crystallization of the mixture from toluene afforded pure **2a** (m. p. 230 – 232°C). Cooling of the toluene solution of a product mixture (insoluble in ligroin-ethyl acetate) to 0°C (see Ex-

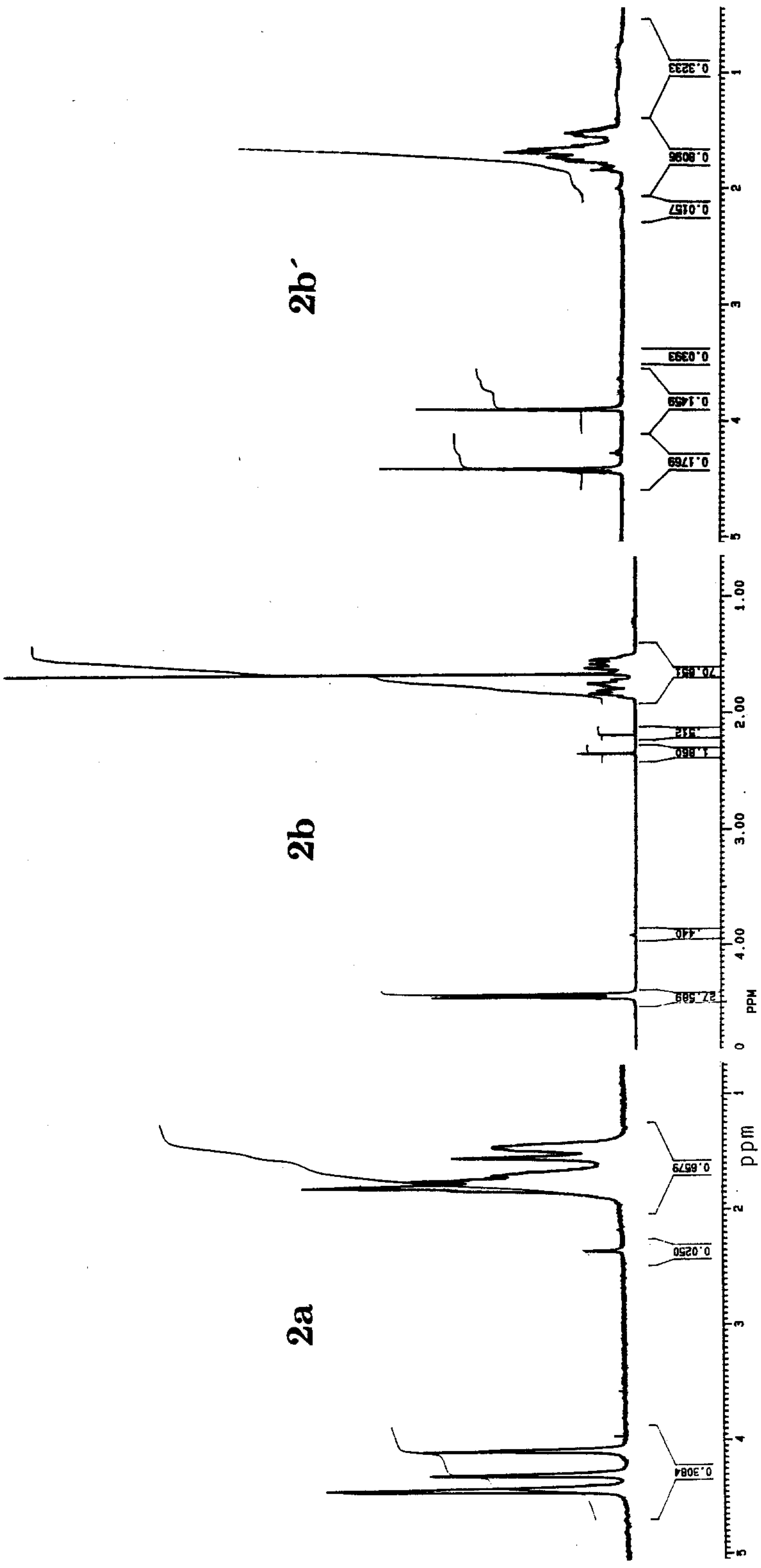


Fig. 1. 400 MHz ^{1}H-NMR spectra of *meso* and two rotamers of *racem.* 1,1′-bi(9,10-dihydro-9,10-ethanoanthryl) (**2a** and **2b**) in CDCl$_3$ (only the significant region of the bridge protons is shown)

perimental) gave the main rotamer **2b** (m.p 297 – 299°C). At room temperature a fast equilibration of the two rotamers (**2b** and **2b′**) takes place; the underpopulated torsional isomer **b′** could be isolated by preparative TLC on silica gel in hexane/CH_2Cl_2 (where it is less strongly adsorbed) and eluation at −20°C with CH_2Cl_2.

The configurational assigments followed both from the synthesis of laevorotatory **2b** from the optically active bromoderivative (−)-**4** [this coupling has to give (*one* enantiomer) of the *racemate* **2b**] and from the ^{1}H- and ^{13}C-NMR spectra: In the former the bridgehead protons in **2a** and **2b** showed significantly different resonances (see Fig. 1), whereas in the latter the expected number of lines compatible with C_1-symmetry (32 for **2a**, in solution) and C_2-symmetry (16 pairs for **2b**) could be found. From the proton spectrum the ratio of the torsional isomers of **2b** : **2b′** was deduced as 1.8 : 1 (at 20°C),1.7 : 1 (at 30°C) and 1.6 : 1 (at 50°C). The same ratio was found in the ^{13}C-NMR spectra, where each pair of lines occurs in the intensity of 1.7 : 1 (at 30°C).

Rotational Barriers and Absolute Stereochemistry

According to the results described for the separation, the *racemate* **2b** is a conformational mixture of two rotamers, each of them consisting of a *racemic* mixture of enantiomers [in close analogy to the 2,2′-bi(1,6-methano[10]annulenyls] [cf. 2]. 1,1′-Bianthryl (**1**) as several other bianthryls can be obtained in optically active form with considerable optical stability [13]. Thus its rotational (racemization) barrier has to amount to at least 100 kJ mol^{-1}.

Meso-**2** shows no significant change in its ^{1}H-NMR spectrum between −20 and +90°C. On the other hand a torsional barrier between the two rotamers of

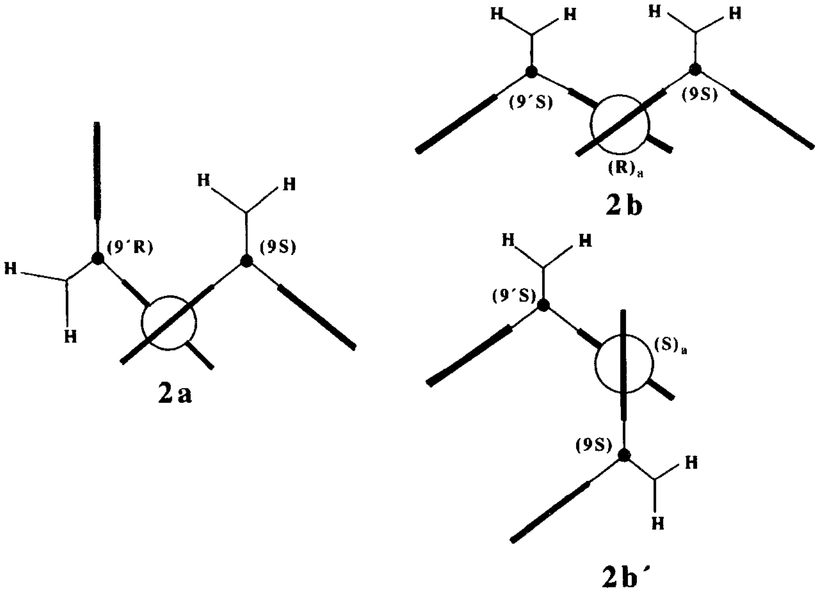


Fig. 2. *Meso*-and two rotamers of *racem.* 1,1′-bi-(9,10-dihydro-9,10-ethanoanthryl) [**2a** and (−)-**2b**, the latter obtained by coupling of the (−)(9*S*)-1-bromo derivative **4**]: **b** = main, **b′** = underpopulated rotamer (schematic representation)

the *racemate* **2b** exists. It could be established both from ^{1}H-NMR-kinetics (by equilibration of **2b** to **2b′** in chloroform, *vide supra*) and by CD-kinetics for optically active **2b′** to **2b** (*vide infra*) as follows:

^{1}H-NMR: $\Delta G^{\#}_{313}$ and $\Delta G^{\#}_{323}$, respectively = 95.4 and 95.1 kJ mol^{-1}.

CD: $\Delta G^{\#}_{293}$ and $\Delta G^{\#}_{303}$, respectively = 92.6 and 93.4 (±0.1) kJ mol^{-1} ($\Delta G^0 = 1.3$ kJ).

In contrast, e.g. to bi(methano-annulenyls) [2, 14] the *racemic* form **2b** of the bi(ethanoanthracene) could not be resolved by enantioselective chromatography on triacetyl cellulose – mainly because of solubility problems. Optically active **2b** could however be obtained by coupling of the enantiomers of the bromo derivative **4** which in turn were easily accessible by chromatography on triacetyl cellulose in ethanol: $[\alpha]_D$ +140 and −143°, respectively (in ethanol). Baseline separation established optical purity. Coupling of (−)-**4** [in analogy to the racemic form (vide supra)] afforded a laevorotatory mixture of the two rotamers of **2b** in a ratio of appr. of 1.7:1 (according to NMR spectroscopy): $[\alpha]_D = -159°$. This result not only confirmed the configurational assignment of the *racemic* form **2b** (only the *racamate* can be formed from enantiomerically pure **4**), but established the absolute chirality of the biaryl **2b** too – at least for the chiral centers 9 and 9′. (+)-**4** was then transformed by lithiation and subsequent carboxylation into the *dextro*rotatory carboxylic acid (+)-**5**, the configuration of which had previously been established

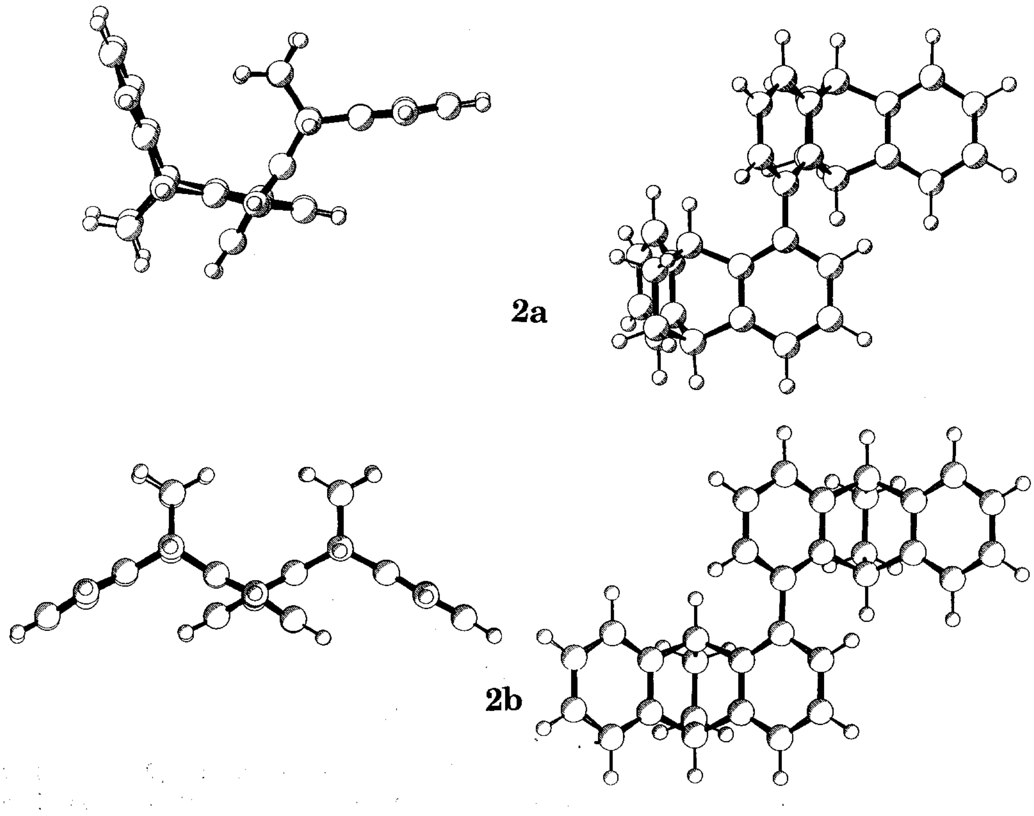


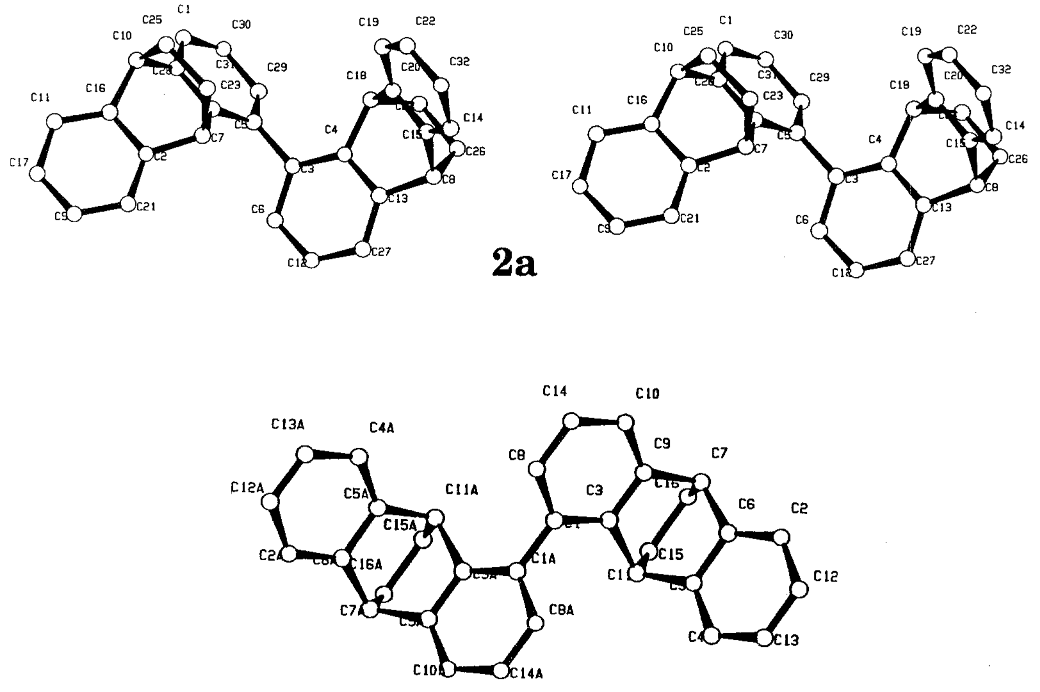
Fig. 3. "Pluto"-drawings of the mesoform **2a** and of the *main* rotamer **2b**

as (9*R*) by kinetic resolution [6 b]. The schematic formulae in Fig. 2 depict the two possible rotamers for (−)-**2 b**.

This structural assumption was confirmed by X-ray crystal analysis both of the main rotamer of **2 b** and the *meso*-form **2 a** (see Figs. 3 and 4) with torsional angles around the 1,1′-bond of −111.1° for **2 a** (C 14-C 1-C 17-C 30. Fig. 4) and −121.2° for **2 b** (C 14-C 1-C 1A-C 14A; Fig.4). Accordingly, the chirality (9*S*)(*R*)$_a$(9′*S*) can be assigned to the *laevo*rotatory main rotamer (where the subscript a stands for axial chirality) and the chirality (9*S*)(*S*)$_a$(9′*S*) to the underpopulated (obviously the more sterically hindered, see Fig. 2) *laevo*rotatory rotamer **2 b′** and *vice versa* for *dextro*rotatory **2 b**.

The bi-ethanoanthryls **2** represent axialchiral biaryls. With considerably caution a chiroptical comparison with a 2,2′-disubstituted biphenyl might be feasible: For (−)-2,2′-dimethylbiphenyl the configuration (*R*)$_a$ had been established [15]. This is in accordance with the axial chirality deduced for the main rotamer **2 b** (cf. Fig. 2).

Both optically active rotamers were separated by preparative TLC; only for the main rotamer the amount obtained was sufficient for the determination of the specific rotation: $[\alpha]_D = -234°$ (CH_2Cl_2). For both rotamers, however, the circular dichroism could be measured (at 0°C, see Fig. 5). Because of the low solubility of the bi-ethanoanthryls **2**, methylene chloride had to be used as solvent and therefore the CD could only be recorded until appr. 240 nm (Fig. 5). At the present obviously no significant conclusion as to the absolute chirality can be drawn from these spectra. (Cf. Ref. [6] for the CD spectra of chiral *mono*nuclear 9,10-dihydro-9,10-



2a

2b

Fig. 4. X-ray crystal structures of **2 a** (*meso*) and **2 b** (*racemate*, main rotamer)

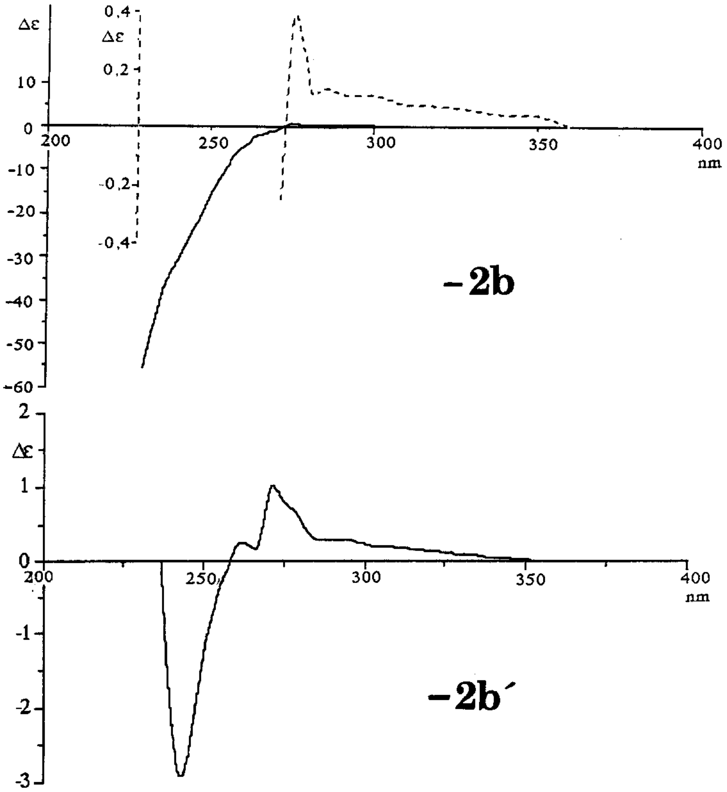


Fig. 5. CD spectra of *laevo*rotatory rotamers of **2b**: **b** = main, **b′** = underpopulated (in methylene chloride)

ethano-anthracenes). As mentioned above, from the corresponding CD-kinetics the rotational barrier between the two conformers was deduced (appr. 93 kJ mol^{-1}) – in accordance with the values from dynamic NMR-spectroscopy.

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. HPLC: HP 1090-M (Hewlett-Packard) with a diode-array detector. MS: Varian MAT CH-7. Optical rotations: Perkin-Elmer 241 polarimeter. CD: Dichrograph Mark III (Jobin Yvon). NMR (in $CDCl_3$): Bruker WM-250 and AM-400 WB spectrometer in FT mode using Aspect-2000 (250 MHz) and -3000 computers (400 MHz).

1,1′-Bianthryl (**1**)

A well ground mixture of 5.26 g of 1,1′-Bi-anthrachinonyl (12.7 mmol) [8] and 42.21 g of Zn powder (640 mmol) was refluxed with 420 ml of aqueous ammonia (25%) for 3 h. After 1 h the deep red solution had became colourless. After cooling the mixtur of Zn powder and **1** was separated by filtration, washed with water, dried and reextracted with ethyl acetate (400 ml). The residue (after evaporation) was extracted with 100 ml of boiling toluene and 200 ml of hot chloroform. The crude residue was purified by chromatography on a short column of silica gel (25 × 200 mm) in ligroin. Crystallisation from toluene gave 0.642 g (14%) of bianthryl **1**.

M.p. 290 – 295°C. (Lit. [9] 321 – 322°.) $C_{28}H_{18}$ (354.4). MS (*m/e*): 354 (100%, *M*), 350 (19%, *M*-4), 177 (5.3%, *M*/2). ^{1}H-NMR: $\delta = 7.28$ (m, 2H, $J = 8.0$, 6.8, 1.2 Hz, H-7, H-7′), 7.42 (m, 2H, $J = 8.0$, 6.8, 1.2 Hz, H-6, H-6′), 7.54 (dd, 2H, $J = 6.8$, 1.2 Hz, H-2, H-2′), 7.60 (d, 2H, $J = 8.0$ Hz, H-8, H-8′), 7.63 (t, 2H, $J = 8.0$, 6.8 Hz, H-3, H-3′), 8.01 (s, 2H, H-9, H-9′), 8.02 (d, 2H, $J = 8.0$ Hz, H-4, H-4′), 8.17 (d, 2H, $J = 8.0$ Hz, H-5, H-5′), 8.56 ppm (s, 2H, H-10, H-10′).

1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl) (**2a**, **b**)

(a) *From 1,1′-bianthryl*: A solution of 1.0 g (2.8 mmol) of **1** in 40 ml of toluene was heated with stirring to 180°C in an atmosphere of ethylene (90 bar) for 107 h. After cooling and evaporating the solvent in vacuo the residue (1.3 g) according to HPLC consisted of a mixture of approx. 10% of starting material **1** and the desired **2** (as a mixture of *meso* and *racemic* **2**, **a** and **b** in a ratio of 1.5 : 1). TLC; *Rf*-values in *n*-hexane-CH_2Cl_2 (80 : 20): 0.42 (**2a** and 1.rotamer of **2b**); 0.37 (2.rotamer of **2b**). This mixture (1.3 g) was extracted twice with ligroin/ethyl acetate (95 : 5) (400 and 300 ml, resp.). The solution was evaporated and the residue subjected to chromatography on silica gel (Si-60) in the abovementioned solvent. Unreacted **1** was separated and 0.605 g of **2** (53%) was obtained as a stereoisomeric mixture. Three crystallizations from toluene afforded the pure (HPLC!) *meso* form (**2a**) M.p. 230 – 232°C. $C_{32}H_{26}$ (410.6). MS: 410 (29.7%, *M*), 382 (100%, *M*-C_2H_4), 355 (19.6%, *M*-C_4H_8), 352 (32.7%, *M*-2 C_2H_5), 177 (25%, *M*-C_4H_8/2). ^{1}H-NMR (here and subsequently only the relevant resonances of the protons at C-9 and C-10 are given, see also Fig. 1 for the bridge protons): $\delta = 4.083$ (t, 1H, $J = 2.7$ Hz, H-9), 4.290 (t, 1H, $J = 2.0$ Hz, H-9′), 4.411 (t, 1H, $J = 2.7$ Hz, H-10), 4.428 ppm (t, 1H, $J =$ 2.0 Hz, H-10′). ^{13}C-NMR: $\delta = 44.565$, 44.519 (C-10, C-10′), 40.662, 40.515 ppm (C-9, C-9′).

The product insoluble in ligroin-ethyl acetate (0.548 g, *vide supra*) is also a mixture of stereoisomers, in which one rotamer of the *racemate* dominates; it could be purified by cooling a toluene solution to 0°C: Yield 0.2 g, m. p. 297 – 299°C. According to its ^{1}H-NMR spectrum (cf. Fig. 1) this product is the pure (TLC!) main rotamer **2b**. $C_{32}H_{26}$ (410.6). MS: 410 (30.1%, *M*), 382 (100%, *M*-C_2H_4), 354 (41.5%, *M*-C_4H_8), 352 (83%, *M*-2 C_2H_5), 177 (17.6%, *M*-C_4H_8/2). ^{1}H-NMR (at −20°C): 4.419 (t, 2H, $J = 2.5$ Hz, H-9, H9′), 4.443 ppm (t, 2H, $J = 2.5$ Hz, H-10, H-10′). See also Fig. 1.

Isolation of the pure underpopulated rotamer of *racem.* **2** (**b′**) was possible by preparative TLC (on Si-60) in hexane-CH_2Cl_2 (85 : 15) (where it is less strongly adsorbed) at 0°C and elution with CH_2Cl_2 at −20°C. In solution (at room temperature) a fast equilibration with the main rotamer occurs. No crystals could be obtained. ^{1}H-NMR (at −20°C): 3.903 (t, 2H, $J = 2.5$ Hz, H-9, H-9′), 4.418 (t, 2H, $J = 2.5$ Hz, H-10, H10′). Cf. Fig. 1. ^{13}C-NMR (equilibrium mixture): 44.558, 44.526 (C-10, C-10′), 40.653, 40.544 (C-9, C-9′). Dynamic NMR spectroscopy using the bridge protons (Fig. 1) as monitor protons lead to the torsional barrier (see Discussion).

(b) *From 1-bromo-9,10-dihydro-9,10-ethano-anthracene* (**4**)

4 was prepared by treating 2.55 g (9.9 mmol) of 1-bromo anthracene (**3**) [10] in toluene (80 ml) with ethylene under pressure (75 bar) at 180°C for 44 h. Isolation of the product was performed by evaporating the solution and chromatography on a silica gel column (25 × 200 mm) in ligroin. Crystallization of the product obtained from ligroin (20 ml) afforded 2.49 g (88%) of **4**; m. p. 112 – 114°C. $C_{16}H_{13}Br$ (285.2). MS: 286/284 (20.4/21.4%, *M*), 258/256 (97/100%, *M*-C_2H_4), 177 (45.4%, *M*-C_2H_4-Br). ^{1}H-NMR: 1.699 (s, 4H, H-11, H-12), 4.325 (s, 1H, H-10), 4.811 (s, 1H, H-9), 6.933 (t, 1H, $J = 7.8$ Hz, H-3), 7.094 – 7.139 (m, 2H, H-6, H-7), 7.182 (d, 1H, $J = 7.8$ Hz, H-4), 7.285 (dd, 1H, $J = 7.8$ and 1 Hz, H-2), 7.249 – 7.327 (m, 2H, H-5, H-8). ^{13}C-NMR: 146.195 (C-9a), 143.357 (C-4a), 142.805 (C-10a), 142.732 (C-8a), 129.088 (C-2), 126.888 (C-3), 125.876, 125.785 (C-6, C-7), 123.726, 123.264 (C-5, C-8), 122.437 (C-4), 119.136 (C-1), 44.535, 42.969 (C-9, C-10), 26.219, 25.595 (C-11, C-12).

For the coupling of **4**, into a mixture of Zn (100 mg), Ni(P*Ph*$_3$)$_2$Cl$_2$ (34 mg) and tetrabutylammonium iodide (162 mg) (previously dried for 1 h in high vacuum at room temp.) 10 ml of dry *THF* were injected under Ar. After the original green colour of the solution had turned into red-brown, a solution of **4** (89 mg, 0.31 mmol) in dry *THF* (7 ml) was added dropwise and after 30 min the mixture was warmed to 50°C and kept for 16 h. Dilution with ligroin (20 ml), filtration and chromatography over a column of silica gel, repeated chromatography of the residue in ligroin (50 ml) (column: 25 × 200 mm) and elution with ethyl acetate afforded a mixture of 15 mg (23%) of **2 a** and **2 b** in a ratio of 2.3 : 1 (HPLC!). Separation of this mixture was achieved as described for the synthesis of **2** from 1,1′-bianthryl. The stereoisomers were identical in every respect (TLC, HPLC, ^{1}H-NMR) with those described sub (a).

(+)- and (−)-1-Bromo-9,10-dihydro-9,10-ethano-anthracene (**4**)

Enantioselective chromatography of racem. **4** (1.12 g) on microcrystalline triacetyl cellulose (Merck, 63 × 690 mm column) in ethanol at 40°C in the recycling mode [5] gave enantiomerically pure **4** after 2 runs ($\alpha = 1.42$, $k'_1 = 1.19$, $k'_2 = 1.69$; UV detection at 254 nm); the *laevo*rotatory enantiomer was eluted first: (−)-**4**, m.p. 149−150°C (ethanol); $[\alpha]_D = -143°$ ($c = 0.084$ in ethanol). (+)-**4**, m.p. 150−151°C; $[\alpha]_D = +140°$. For the ^{1}H-NMR spectra see racem. **4**. The absolute configurations (+)(9*R*) and (−)(9*S*), resp., follow from the transformation into the optically active carboxylic acid **5**.

(+)(9R)-9,10-Dihydro-9,10-ethano-anthracene-1-carboxylic acid (**5**) *from (+)*-**4**

A solution of 0.20 ml of *n*-Butyl Li (in hexane) was added dropwise to a solution of (+)-**4** (48 mg) in 8 ml of dry ether at −78°C. After 30 min and warming to roomtemp. the solution was poured onto 3 g of crushed dry ice. Addition of water (after 10 min), separation of the organic layer and extraction with HCl (10%) and extraction of the aqueous layer with ether, extraction of the combined ether solutions with saturated aqueous $NaHCO_3$, acidification of this extract and extraction with ether gave, after drying ($MgSO_4$) and evaporation, 14 mg (33%) of the carboxylic acid **5**. $C_{17}H_{14}O_2$ (250.3). M.p. 199−201°C (Lit. [6 b]: 200−201°C). $[\alpha]_D = +197°$ (ethanol). Lit. [6 b]: +185°.

(−)(9S,9′S)-1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl) [(−)-**2 b**]

Coupling of (−)-**4** (610 mg) as described for the racemate (vide supra) gave 79 mg (18%) of laevorotatory **2 b** as a mixture of the two rotamers. No *meso* product (**2 a**) could be detected. (−)-**2 b** was identical in every respect (HPLC, TLC, UV, MS and ^{1}H-NMR spectra) with the racemate described above. $[\alpha]_D = -159°$ (equilibrium mixture in CH_2Cl_2 at 20°C). Preparative TLC as described for racemic **2 b** afforded both (*laevo*rotatory) rotamers; main conformer: $[\alpha]_D = -234°$ ($c = 0.11$ in CH_2Cl_2). For the CD-spectra see Fig. 5. UV (in CH_2Cl_2), **2 a** and **2 b**: $\lambda_{max} = 272$ and 263 nm ($\varepsilon \sim 2300 - 4200$).

Crystal Structure Analysis of **2 a**

Diffraction data were collected at a temperature of 298 K on a modified STOE diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Unit cell parameters were obtained by a least squares refinement against the setting angles of 58 reflections with $9° < 2\vartheta < 24°$. Crystals are orthorhombic, space group $P2_12_12_1$, with 4 formula units $C_{32}H_{26}$ (formula weight 410.6) in the unit cell: $a = 8.151(3)$ Å, $b = 11.633(4)$ Å, $c = 23.373(10)$ Å, $V = 2216(1)$ Å^3, $d_{calc} = 1.23$ g/cm^3.

Intensity data (ω/ϑ-scan, $\Delta/\omega = 1.2°$) were collected for one octant of reciprocal space ($0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 27$, $5.5° \leqslant 2\vartheta \leqslant 50°$), yielding 2 479 observed, 2 228 unique (assuming Friedel's law) and 1 102 significant [$F_{obs} > 5\sigma(F)$] structure factors. Lp correction and an empirical absorption correction were applied to the data. Three standard reflections were periodically remeasured; they showed r.m.s. intensity fluctuations of 1.3, 1.1 and 0.6%, respectively.

Table 1. Atomic coordinates ($\times 10^4$) and displacement coefficients ($\times 10^4$, U values in Å^2) for **2a** (Table 1a) and **2b** (1b). E.s.d.'s in parentheses. The isotropic temperature factor has the form $T = \exp[-8\pi^2 U \sin^2\Theta/\lambda^2]$

Table 1a

Atom	x/a	y/b	z/c	U_{iso}
C(1)	-67(8)	-2837(5)	5849(3)	374(16)
C(2)	-292(9)	-3085(6)	5268(3)	492(18)
C(3)	-1213(9)	-4053(6)	5107(3)	557(19)
C(4)	-1930(8)	-4760(6)	5514(3)	516(19)
C(5)	-1724(7)	-4505(5)	6088(2)	379(15)
C(6)	-2477(9)	-5156(6)	6573(3)	459(17)
C(7)	-3376(7)	-4296(5)	6951(2)	399(15)
C(8)	-4992(8)	-4355(6)	7127(3)	493(18)
C(9)	-5610(9)	-3496(6)	7476(3)	593(20)
C(10)	-4639(9)	-2598(6)	7644(3)	583(21)
C(11)	-3016(8)	-2519(6)	7474(3)	474(18)
C(12)	-2380(8)	-3380(5)	7122(3)	396(15)
C(13)	-650(8)	-3452(5)	6898(2)	411(16)
C(14)	-765(8)	-3564(5)	6262(3)	388(15)
C(15)	85(8)	-4603(5)	7127(3)	510(18)
C(16)	-1020(8)	-5618(6)	6941(3)	495(18)
C(17)	831(8)	-1774(5)	6022(3)	368(15)
C(18)	2332(8)	-1841(6)	6315(3)	464(18)
C(19)	3161(8)	-858(5)	6494(3)	475(17)
C(20)	2512(9)	213(6)	6378(3)	476(17)
C(21)	1047(8)	322(5)	6082(3)	400(16)
C(22)	162(9)	1406(6)	5939(3)	487(18)
C(23)	-298(8)	1399(5)	5311(3)	399(16)
C(24)	0(9)	2275(6)	4916(3)	510(18)
C(25)	-563(8)	2130(6)	4361(3)	574(20)
C(26)	-1447(9)	1178(6)	4206(3)	543(20)
C(27)	-1769(8)	299(6)	4601(3)	519(19)
C(28)	-1176(8)	417(5)	5153(3)	407(16)
C(29)	-1445(8)	-415(6)	5640(3)	456(17)
C(30)	213(8)	-672(5)	5910(2)	397(16)
C(31)	-2428(9)	266(6)	6099(3)	562(19)
C(32)	-1513(9)	1392(6)	6266(3)	540(19)

Table 1b

Atom	x/a	y/b	z/c	U_{iso}
C(1)	5509(5)	254(0)	4826(4)	343(15)
C(2)	6508(5)	-812(17)	5303(4)	417(17)
C(3)	7479(6)	-847(16)	4997(4)	414(17)
C(4)	7485(5)	186(18)	4213(4)	392(16)
C(5)	6526(5)	1202(17)	3732(4)	347(15)
C(6)	6398(6)	2349(16)	2865(4)	400(18)
C(7)	5408(5)	1254(15)	2251(4)	326(14)
C(8)	5388(5)	178(20)	1468(4)	424(18)
C(9)	4399(6)	-831(18)	997(4)	516(20)
C(10)	3425(6)	-739(18)	1303(4)	487(18)
C(11)	3435(5)	347(14)	2085(4)	403(18)
C(12)	4422(5)	1309(17)	2562(4)	344(15)
C(13)	4579(5)	2466(15)	3431(4)	344(16)
C(14)	5551(5)	1235(18)	4038(4)	322(14)
C(15)	4993(6)	4950(18)	3322(5)	476(18)
C(16)	6071(6)	4873(17)	2972(4)	499(19)

The structure was solved with direct methods and refined with least-squares. In order to maintain a reasonable observation-to-parameter ratio, only isotropic atomic displacement parameters (a.d.p.'s) were refined for the carbon atoms. Hydrogen atoms were included at calculated positions, and their (isotropic) a.d.p. was allowed to refine. $R = 0.047$ (unit weights) for 155 parameters and 1 102 observations. A final difference electron density map showed features up to 0.17 e/Å^3. Atomic coordinates are listed in Table 1a, computer programs are summarized in Ref. [16].

Crystal Structure Analysis of **2b**

Experimental conditions as above: Unit cell parameters from 14 reflections with $9° < 2\vartheta < 15°$; monoclinic space group I2, $Z = 2$ (same formula as above), $a = 12.17(4)$ Å, $b = 5.82(1)$ Å, $c = 16.00(4)$ Å, $\beta = 103.56(21)°$, $V = 1\,102(1)$ Å^3, $d_{calc} = 1.24$ g/cm^3.

Intensity data (ω-scan, $\Delta\omega = 1.2°$) for two octants ($-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 7$, $0 \leqslant l \leqslant 21$, $5.5° \leqslant 2\vartheta \leqslant 56°$), 1 506 observed, 1 458 unique and 667 significant [$F_{obs} > 5\sigma(F)$] structure factors. R.m.s. intensity fluctuations of the standard reflections: 1.3, 2.1 and 1.4%, respectively.

Refinement conditions as above: $R = 0.053$ (unit weights) for 77 parameters and 667 observations. Highest feature in final difference electron density map: 0.17e/Å^3. Atomic coordinates in Table 1b.

Acknowledgements

Support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (projects P-6537 and P-5840) is gratefully acknowledged. Zhi Li is indepted to the Government of the Peoples Republic of China and to the "Österr. Akademiker-Austausch-Dienst" for grants. We are very grateful to Dr. A. Werner for chromatographic separations, to Mag. H. P. Kählig for recording the NMR spectra (including NMR kinetics), to Mr. H. Bieler (all Vienna) for the mass spectra and to Mr. Mohamed Abdou (Graz) for his valuable help in the crystal structure analyses.

References

[1] Schlögl K. (1986) J. Organometal. Chem. **300**: 219; Schlögl K., Werner A., Widhalm M. (1986) Monatsh. Chem. **117**: 1423
[2] Meyer A., Schlögl K., Keller W., Kratky Ch. (1989) Monatsh. Chem. **120**: 453
[3] Krajnik P., Kratky Ch., Schlögl K., Widhalm M. (1990) Monatsh. Chem. **121**: 945
[4] Schlögl K. (1984) Planarchiral Structure. In: Topics Curr. Chem. **125**: 27
[5] Schlögl K., Widhalm M. (1982) Chem. Ber. **115**: 3042; (1984) Monatsh. Chem. **115**: 1113; Werner A. (1989) Kontakte (Merck, Darmstadt) **1989** (3): 50
[6] a) Hagishita S., Kuriyama K. (1972) Tetrahedron **28**: 1435; b) Paul J., Schlögl K. (1973) Monatsh. Chem. **104**: 274; c) Tatemitsu H., Ogura F., Nakagawa M. (1973) Bull. Chem. Soc. Japan **46**: 915; d) Brienne M. J., Jacques J. (1973) Bull. Soc. Chim. France **1973**: 190; (1974) Bull. Soc. Chim. France **1974**: 2647
[7] Paul J., Schlögl K. (1973) Monatsh. Chem. **104**: 263
[8] Ullmann F., Minajeff W. (1912) Ber. Dtsch. Chem. Ges. **45**: 687
[9] A wrong structure had been proposed in the original paper: Scholl R., Mansfeld J. (1910) Ber. Dtsch. Chem. Ges. **43**: 1734; cf. also: Bell F., Waring D. H. (1949) J. Chem. Soc. **1949**: 267
[10] Netka J., Crump St. L., Rickborn B. (1986) J. Org. Chem. **51**: 1189
[11] Cf. Iyoda M., Sato K., Oda M. (1985) Tetrahedron Lett. **26**: 3829 for the coupling of bromo-1,6-methano[10]annulene
[12] Camenzind R., Rickbon B. (1986) J. Org. Chem. **51**: 1914
[13] Bell F., Waring D. H. (1949) J. Chem. Soc. **1949**: 1579
[14] Meyer A., Schlögl K., Lerch U., Vogel E. (1988) Chem. Ber. **121**: 917
[15] Klyne W., Buckingham J. (eds.) (1978) Atlas of Stereochemistry, Vol. 1, 2nd Ed. Chapman & Hall, London, p. 219
[16] (a) Sheldrick G. M. (1986) SHELXS-86, A Computer Program for Crystal Structure Solution. Univ. of Göttingen, BRD; (b) Sheldrick G. M. (1976) SHELX-76, A Computer Program for Crystal Structure Determination. Univ. of Cambridge, England; (c) DIFABS: Walker N., Stuart D. (1983) Acta Crystallogr. **AT 39**: 158; (d) Motherwell, S.: Program PLUTO. University of Cambridge, England

Received June 21, 1991. Accepted July 8, 1991