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Short Communication

Chiral Crystals of "*meso*"-1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl). Chiroptical Properties, Absolute Chirality and Rotational Barrier

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Summary. Chiral crystals of "*meso*"-1,1′-bi(9,10-dihydro-9,10-ethano-anthryl) (**1a**) were obtained optically active by crystallization from chloroform/hexane by the vapor diffusion method (orthorhombic space group $P2_12_12_1$). The chiroptical properties of **1a** were recorded in dichloromethane at 0 and 10 °C, resp. ($[\alpha]_D = -90°$). Its absolute chirality is assigned as $(-)(R)_a$ from chiroptical comparison (CD) both with the main rotamer (**1b**) and the underpopulated one (**1c**) of the *racemic* form of known chirality. The rotational barrier of **1a** was established as $\Delta G^{\neq}_{301} = 94.3\,\text{kJ mol}^{-1}$ by CD-kinetics as well as by kinetics of racemization.

Keywords. Vapour diffusion method; Circular dichroism; Configurational correlation.

Chirale Kristalle von „*meso*"-1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl). Chiroptische Eigenschaften, absolute Chiralität und Rotationsbarriere (Kurze Mitt.)

Zusammenfassung. Optisch aktive Kristalle von „*meso*"-1,1′-Bi(9,10-dihydro-9,10-ethano-anthryl) (**1a**) wurden aus Chloroform/Hexan mit Hilfe der Dampfdiffusionsmethode erhalten (orthorhombische Raumgruppe $P2_12_12_1$). Die chiroptischen Eigenschaften von **1a** wurden in CH_2Cl_2 bei 0° und 10 °C gemessen: $[\alpha]_D = -90°$. Die absolute Chiralität $(-)(R)_a$ konnte mit hoher Wahrscheinlichkeit durch chiroptischen Vergleich (über die CD-Spektren) sowohl mit dem Hauptrotamer (**1b**) als auch dem unterpopulierten Rotamer (**1c**) der Racemform jeweils gesicherter Konfiguration zugeordnet werden. Die Rotationsbarriere $\Delta G^{\neq}_{301}$ von **1a** wurde durch CD- und Racemisierungs-Kinetik als $94.3\,\text{kJ mol}^{-1}$ ermittelt.

Introduction

Axialchiral (torsional isomeric) biaryls containing an additional stereogenic unit within the aryl moieties can give rise to two main distereomers (meso and racemic

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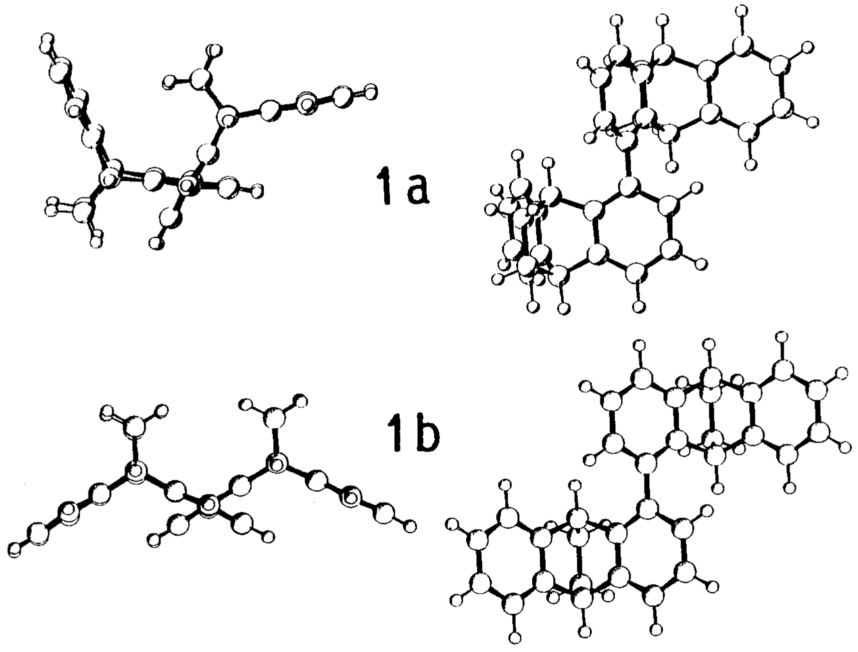

Fig. 1. X-ray crystal structures of 1,1′-bi(9,10-dihydro-9,10-ethano-anthryl); meso (**1a**) and main rotamer of the racemate (**1b**) [4]

form). Within each, enantiomers and/or torsionalisomeric rotamers are possible – their accessibility depending on the height of the rotational (torsional) barrier.

Representative examples of such stereoisomers are tricarbonylchromium complexes of biphenyls [1], 1,1′-bi-ferrocenyls [2], 2,2′-bi-annulenyls [3] or the recently described 1,1′-bi-(9,10-dihydro-9,10-ethano-anthryls) (**1**) [4]. Enantiomers of the racemic form exist as an appr. 1.8:1 conformational mixture of two rotamers (**1b** and **1c**) with a torsional barrier $\Delta G^{\neq}$ of 92–95 kJ mol^{-1} (at 293 and 323 K, resp.). Laevorotatory enantiomers of **1b** and **1c** were accessible by coupling of (−)-1-bromo-9,10-dihydro-9,10-ethano-anthracene of known absolute configuration (−)(9*S*). The mesoform **1a** shows no significant change of its ^{1}H nmr spectrum between − 20 and + 90 °C. Both the obviously rather low rotational barrier and especially the low solubility prohibited an optical resolution by enantioselective chromatography.

Fig. 1 depicts the X-ray crystal structures of the mesoform **1a** and of the main rotamer **1b** of the racemate.

Results and Discussion

Absolute Stereochemistry

The pure mesoform **1a** was obtained by chromatography of the mixture of stereoisomers of **1** on silica gel in *n*-hexane/CH_2Cl_2 [4]. Subsequent crystallization from *n*-hexane/chloroform by the vapour diffusion method yielded crystals in the orthorhombic (chiral) spacegroup $P2_12_12_1$, as established from the X-ray structure analysis (Fig. 1).

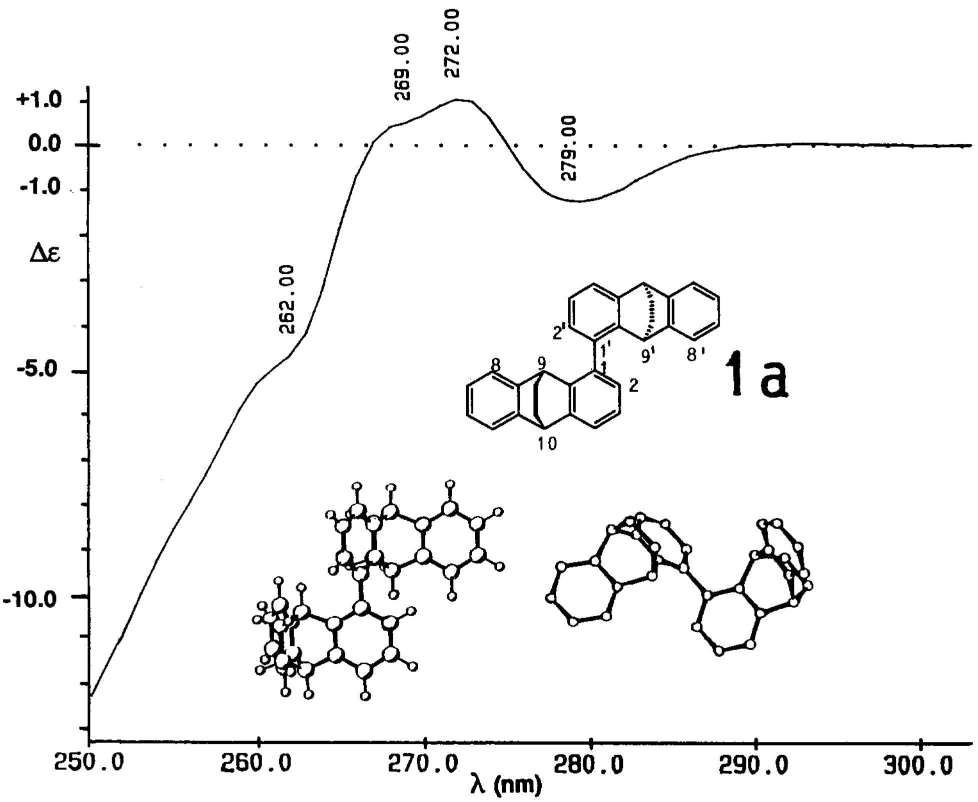

Fig. 2. CD-spectrum of (−)-**1a** in CH_2Cl_2 (recorded on a Dichrograph Mark 6; Jobin-Yvon)

An individual crystal of **1a** was dissolved in CH_2Cl_2 at 0 °C (owing to the low solubility in other solvents) and its circular dichroism spectrum immediately recorded at 10 °C (see Fig. 2). $[\alpha]_D$ (at 0 °C) = − 90 ± 10° (CH_2Cl_2, $c = 0.0075$, as determined by UV-spectroscopy).

The absolute chirality of (−)-**1a** could be assigned with high probability as $(R)_a$ by chiroptical (CD) comparison with **1b** and **1c** of established configuration: (−)(9*S*)$(R)_a$(9′*S*) and (−)(9*S*)$(S)_a$(9′*S*), resp. [4]: (−)-**1a** exhibits positive Cotton effects at 269 and 272 nm (Δε + 0.52 and + 1.04, resp.) and negative effects at 262 (shoulder) and 279 nm (Δε − 4.71 and − 1.30, resp.) (Fig. 2). (−)-**1b**, on the other hand with the torsional chirality $(R)_a$ shows a negative effect at 262 nm, too, whereas (−)$(S)_a$-**1c** has positive effects at 262 and 279 nm (shoulder) opposite to those of (−)-**1a** [4]. Moreover, the Δε-values of (−)-**1b** between 250 and 260 nm are more negative than

Table 1. Torsional angles (°) for **1a** and **1b**

Angle	C9C1C1′C9′	C9C1C1′C2′	C2C1C1′C9′	C2C1C1′C2
meso-**1a**	− 110.1	68.9	65.4	− 115.6
racem. **1b**	− 121.7	60.0	60.0	− 118.3

those of (−)-**1c** [with the opposite axial chirality $(S)_a$]. Consequently, negative $\Delta\varepsilon$-values in this region seem to be indicative of $(R)_a$ axial chirality.

This configurational assignment for the "meso" form **1a** [$(-)(R)_a$] is also supported by chiroptical comparison with biphenyls, such as $(R)_a$-6,6′-dibromo-2,2′-dimethyl-biphenyl with signs of the Cotton effects (from longer to shorter wavelengths) comparable to those of (−)-**1a** [5].

Dynamic Stereochemistry

The rotational barrier of **1a** was determined from following the racemization of the laevorotatory enantiomer in CH_2Cl_2 both by CD spectroscopy and by kinetics of its optical rotation. As monitors the Cotton effect at 262 nm (CD) and the optical rotation at 365 nm were chosen. Both methods gave the same result, namely a torsional barrier of $\Delta G^{\neq}$ of 94.3 kJ mol^{-1} (at 301 K).

The two rotational isomers **1b** and **1c** are diastereomers, and hence there exists a ΔG^0 of 1.3 kJ mol^{-1} with rotational barriers $\Delta G^{\neq}$ of 94.7 and 93.4 kJ, resp. at 303 K [4]. For the two *enantiomers* of the mesoform **1a** ΔG^0 has to be zero.

A full (360°) torsion around the 1-1′-bond in **1** (*meso*-**1a**, racemates **1b** and **1c**) encounters three significant steric barriers, namely between positions 2 and 9′ (and 2′ and 9, resp.), as well as positions 8 and 8′ and 9 and 9′ (see Fig. 2 for the numbering). The overall torsional barrier will be determined by the least severe interaction, i.e. between positions 2 and 9′ (2′ and 9).

The torsional angles around the 1-1′-bond in **1a** and racem. **1b** (as established from X-ray data [4]) are presented in Table 1. The differences are not significant, the benzene rings involved are almost planar in both cases.

Whereas the rotational barrier of the mesoform of 10,10′-dibromo-2,2′-bi-(1,6-methano[10]annulenyl) is appr. 30 kJ mol^1 lower than that of the racemate [3], the rotational barriers of the three stereoisomers of 1,1′-bi(9,10-dihydro-9,10-ethano-anthryl) (**1a**, **b**, and **c**) are almost identical (94.3, 94.7 and 93.4 kJ). In the bridged biannulenyls the tenmembered perimeter is puckered (like a W-shape) and hence during rotation of the racemate the significant 3-10′ (and 3′-10) interactions take place at the same time, whereas in the mesoform these positions can pass each other successively, which decreases the barrier considerably [3]. From the above-mentioned results (see also Table 1) it follows that in the case of 1,1′-bianthryls C1, C2 and C9 (and C1′, C2′ and C9′, resp.) are nearly in the same plane both in the mesoform and in the racemate. Therefore the significant 2-9′ and 2′-9 interactions take place simultaneously; consequently, the torsional barriers for both forms are practically equal.

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