Monatshefte für Chemie 120, 453—462 (1989)

Monatshefte für Chemie
Chemical Monthly

Stereochemistry of Planarchiral Compounds, Part XII [1]: Absolute Chiralities and X-ray Crystal Structures of 2,2′-Bi(1,6-methano[10]annulenyl)s

Axel Meyer[1], **Karl Schlögl**[1,*,**], **Walter Keller**[2], 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 absolute chirality of the dextrorotatory main rotamer of 10,10′-dibromo-2,2′-bi(1,6-methano[10]annulenyl) (**1 b**), obtained by low temperature chromatography or by crystallisation of the (+)-enantiomer of **1 b**, was established by observation of anomalous X-ray diffraction as (+)-$(R)_p(R)_a(R)_p$-**1 b**. This result was confirmed by reduction of (+)-**1 b** to a dextrorotatory 2,2′-bi(1,6-methano[10]annulenyl) (**1 a**), which in turn was accessible by coupling of (−)-2-Bromo-1,6-methano[10]annulene (**3**) of known chirality $(S)_p$ and, moreover, by enantioselective chromatography of **1 a** on triacetyl cellulose in ethanol. This correlation determines also the chirality of (+)-**1 a** as $(S)_p(S)_p$.

According to the X-ray analyses the main rotamer of (+)-**1 b** and the meso-form (**2 b**) adopt crystal structures in which the bromine atoms come close to the CH_2-bridges. The torsional angles around the 2,2′-bonds vary between 33°, 53° and 65° for (+)-**1 b**, racem. **1 b** and the mesoform **2 b**, respectively.

Keywords: Bijvoet method, Chemical and chiroptical correlation; Circular dichroism; Enantioselective chromatography; 10,10′-Dibromo-2,2′-bi(1,6-methano[10]annulenyl); Torsional isomers.

Stereochemie planarchiraler Verbindungen, 12. Mitt. [1]: Absolute Chiralität und Röntgenkristallstrukturen von 2,2′-Bi(1,6-methano[10]annulenyl)en

Zusammenfassung. Die absolute Chiralität des rechtsdrehenden (als Hauptmenge im Gemisch vorliegenden) Rotamers von 10,10′-Dibrom-2,2′-bi(1,6-methano[10]annulenyl) (**1 b**) (erhältlich durch Tieftemperatur-Chromatographie oder Kristallisation des (+)-Enantiomers von **1 b**) wurde durch Röntgenstrukturanalyse (Bijvoet-Methode) als (+)-$(R)_p(R)_a(R)_p$ ermittelt. Dieses Ergebnis konnte durch Reduktion von (+)-**1 b** bestätigt werden: Sie führte zu einem rechtsdrehenden 2,2′-Bi(1,6-methano[10]annulenyl) (**1 a**), das seinerseits durch Kupplung von (−)-2-Brom-1,6-methano[10]annulen (**3**) bekannter Chiralität $(S)_p$ erhalten wurde (und auch durch enantioselektive Chromatographie von **1 a** an Triacetylcellulose in Ethanol zugänglich ist). Diese Korrelation legt auch die Chiralität des (+)-Enantiomers von racem. **1 a** als $(S)_p(S)_p$ fest.

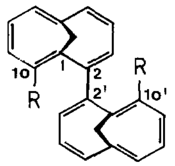
Nach den Röntgenstrukturanalysen des (Haupt)-Rotationsisomers von (+)-**1 b** und der Mesoform (**2 b**) liegen im Kristall Konformere vor, in denen die Bromatome den CH_2-Brücken nahekommen. Die Torsionswinkel um die 2,2′-Bindung variieren von 33° über 53° bis 65° für (+)-**1 b**, racem. **1 b** und meso **2 b**.

** Dedicated to Prof. Dr. G. Snatzke (Bochum) with cordial wishes on the occasion of the 60th anniversary of his birthday

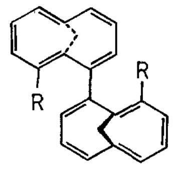
Introduction

2,2′-Bi(1,6-methano[10]annulenyl)s of the general structures **1**/**2** – accessible by coupling of the corresponding 2-bromo-1,6-methano[10]annulenes (**3**) [1] – exhibit interesting stereochemical features, as they combine two elements of chirality within one molecule: both torsional (axial) chirality (around the 2,2′-bond) and planar (annulene) chirality. Consequently two main diastereomers are feasible: a racemate and a mesoform, both being mixtures of rotamers [1].

The static and dynamic stereochemistry of the 10,10′-dibromo derivative **1b** has been studied in some detail [1], thereby revealing rotational barriers of 85 and 88 kJ mol^{-1} for the two racemic forms and 58 kJ mol^{-1} for meso-**2b**. (For the parent compounds **1a** and **2a** barriers of 63 and $\leqslant$ 45 kJ mol^{-1} had been found [2]).

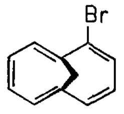


1 *(Racemate)**



2 *(Meso)**

a: R = H **b**: R = Br



(−)(*S*)-**3**

1b was separated into its enantiomers by enantioselective chromatography on triacetyl cellulose (*TAC*) [3] ($[\alpha]_D^{20}$ in ethanol + and − 525°) [1]. According to the relatively high barrier to rotation these enantiomers being equilibrium mixtures of rotational isomers were separable into their rotamers (in a ratio of 3.6 to 1) by chromatography on silicagel at 0°C. Their chiroptical properties were determined at − 10°C. All results were supported by (dynamic) ^{1}H- and ^{13}C-NMR spectroscopy [1].

We now report on the absolute stereochemistry of the rotamers of the dibromo derivative **1b**, determined by direct anomalous X-ray diffraction (Bijvoet method) as well as by chemical correlation with (−)-2-bromo-1,6-methano[10]annulene (**3**) of known absolute configuration $(S)_p$ [4]. Via this correlation the absolute chirality of the (optically active) parent bi-annulenyl **1a** was established as well. X-ray crystal structure analyses revealed significant differences in the torsional angles around the respective 2,2′-bonds of the racemic and the optically active rotamer of **1b** and the mesoform **2b**, together with rather unexpected conformations in the crystals.

---

* Only one enantiomer and rotamer, respectively, is shown

Results and Discussion

X-Ray Crystal Structures

1 b and **2 b** are rather flexible molecules as they can rotate around the 2,2'-bond; their solutions are mixtures of different conformers. As we were able to isolate and crystallize some of the pure rotamers [1], it was interesting to study the conformations they adopt in the solid state. Especially the determination of the absolute stereochemistry of one enantiomer of **1 b** promised to be valuable for our studies.

In the case of **1 b**, we obtained crystals of the main rotamer of the racemic mixture as well as of the pure enantiomers, whereas the meso-form, not being separable into enantiomers, crystallized as a "racemate" only [1].

Crystal structures were determined for optically active $(+)$-$(R)_p(R)_a(R)_p$-**1 b** and the racemate. The structure of the meso-form **2 b** was determined as well, but due to difficulties (twinning) the result is unreliable, and we refrain from reporting atomic coordinates.

Figures 1 and 2 a show the crystal structures of the racemic and the main rotamer of $(+)$-**1 b**.

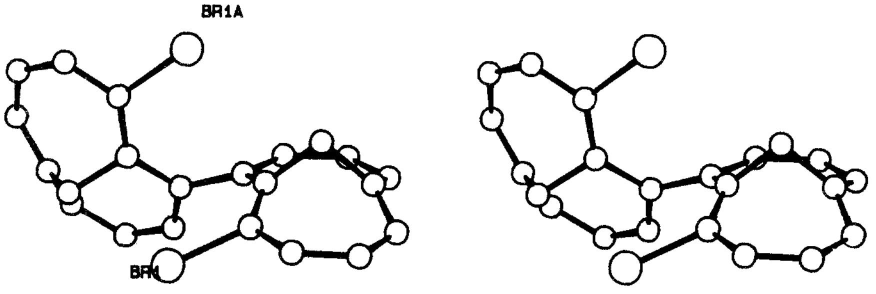


Fig. 1. X-ray crystal structure of the main rotamer of (racemic) **1 b**

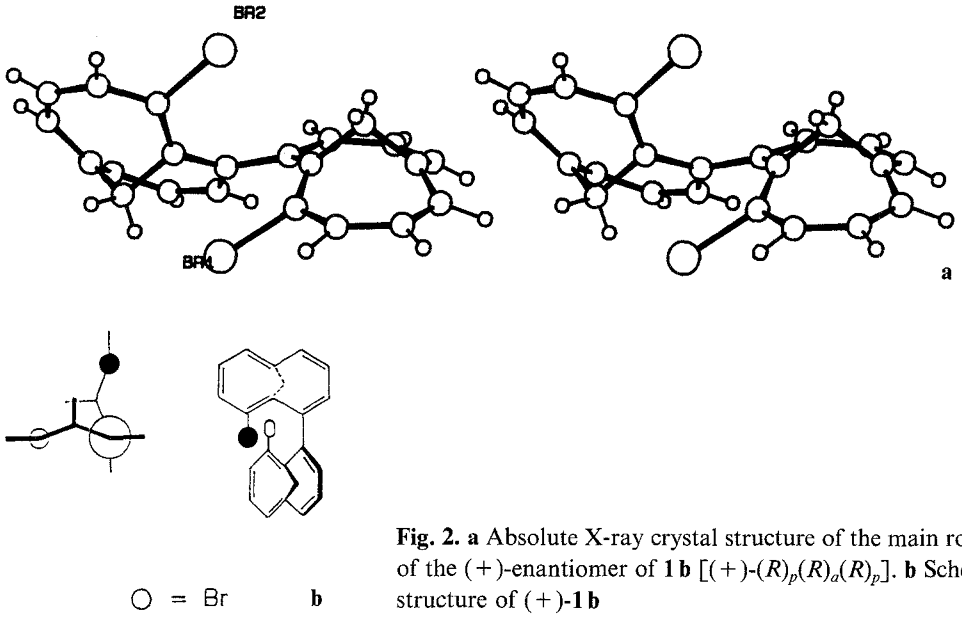


Fig. 2. a Absolute X-ray crystal structure of the main rotamer of the $(+)$-enantiomer of **1 b** [$(+)$-$(R)_p(R)_a(R)_p$]. **b** Schematic structure of $(+)$-**1 b**

Table 1. Torsional angles (°) and short intramolecular distances [Å] for the bi-annulenyls **1b** and **2b**

	C1-C2-C2'-C1'	C3-C2-C2'-C3'	Br1-C11'	Br1-C1'	Br-C2'	Br-Br
(+)-**1b**	36.0 (9)	32.8 (9)	3.35/3.49	3.11/3.34	3.34/3.34	4.40
racem.-**1b**	59.8 (1.3)	52.6 (1.3)	3.52	3.30	3.22	4.70
meso-**2b**	72 (6)	65 (5)				(4.5)

According to Fig. 2a, (+)-**1b** has the absolute chirality (+)-$(R)_p(R)_a(R)_p$ (where the subscripts *p* and *a* stand for planar [= annulene] and axial [= torsional] chirality, resp., cf. Ref. [5]). Fig. 2b depicts this conformation schematically (cf. Ref. [1]).

As the relative configuration is the same in both structures, conformational differences can only be due to differences in the packing forces. The torsion angle C3-C2-C2'-C3' (cf. Table 1) appears to be sensitive to these differences. Still, the overall conformation does not change appreciably, which is evident from the non-bonded intramolecular distances shown in Table 1.

In the case of **2b**, the corresponding torsional angle amounts to 65°, the Br-Br' distance is 4.5 Å (see Table 1 and Fig. 3), although these values are rather uncertain due to problems with twinning of the crystals (see experimental part).

Whereas the significant differences in the rotational barriers between meso-**2b** and racemic **1b** (30 kJ mol^{-1}) may be due to different modes of interaction of the bromines and the hydrogenes during rotation (cf. [1]), an explanation for the conformational preferences would require further studies, especially by varying the substituents in positions 10 and 10' of structure **1** and **2**, respectively.

So far we have been unsuccessful to obtain crystals of the underpopulated rotamer of **1b** suitable for an X-ray crystal analysis, but from the results presented it follows that the enantiomers of the underpopulated rotamers of **1b** have the chiralities $(S)_p(R)_a(S)_p$ and $(R)_p(S)_a(R)_p$, respectively, as schematically depicted in Fig. 4.

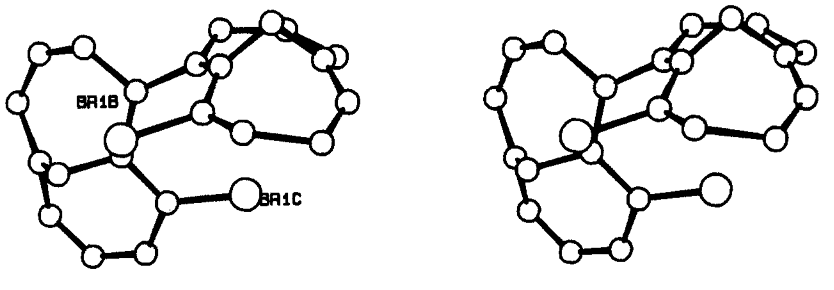


Fig. 3. Preliminary X-ray structure of meso-**2b**

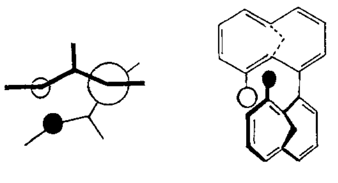
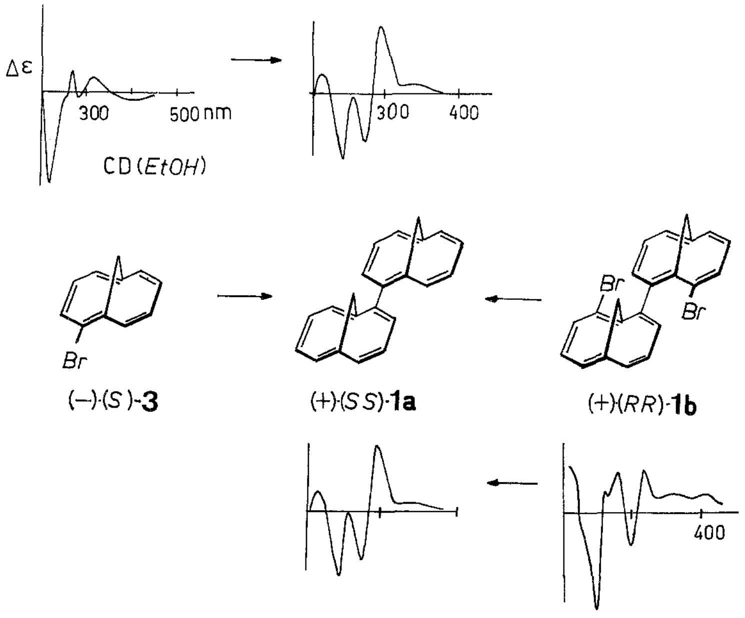


Fig. 4. Schematic representation of the absolute structure of the underpopulated rotamer of (+)-**1b**: $(R)_p(S)_a(R)_p$



Scheme 1

Chemical Correlation – Chirality of 2,2′-Bi(1,6-methano[10]annulenyl) (**1 a**)

The absolute configurations of optically active 2- and 2,7-substituted 1,6-methano[10]annulenes as well as their chiroptical properties are known [4].

It therefore seemed worthwhile to correlate the chiralities of these "mononuclear" annulenes with those of the bi-annulenyls **1** by an unambiguous chemical transformation. The key compound for such a correlation was the (optically active) parent biannulenyl **1 a**. This was accessible by coupling of (−)-(*S*)-2-bromo-1,6-methano[10]annulene (**3**) on one hand and by reductive debromination of (+)-$(R)_p(R)_a(R)_p$-**1 b** (with Zn/HCl in *THF*) on the other. Both reactions furnished a dextrorotatory 2,2′-bi(1,6-methano[10]annulenyl) (**1 a**) identical in every respect (HPLC, ^{1}H-NMR and CD) (see Scheme 1). This correlation not only confirms the results on the chiralities of the mono- and binuclear annulenes (cf. Ref. [4]), but also establishes the absolute chirality of the parent biannulenyl **1 a** as (+)-$(S)_p(S)_p$[1].

The enantiomers of **1 a** also were obtained by chromatography of the racemate (accessible by coupling of racem. **3**) on triacetylcellulose in ethanol[2]; due to the low rotational barrier (63 kJ mol^{-1} [2]) these enantiomers are obviously an (inseparable) equilibrium mixture of rotamers.

Acknowledgements

Support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (under projects P-5137, P 5840, and P 5767) is gratefully acknowledged. A. Meyer is indepted to Hoechst Austria AG for financial support. We are grateful to Prof. E. Vogel and U. Lerch (Köln) for supplying us with 2-

---

[1] The change in the stereochemical notation for the annulene (= planar) chirality from **1 b** to **1 a** [$(R)_p$ to $(S)_p$] is due to substitution of Br by H

[2] So far only an analytical separation of racemic. **1 a** (on CHIRALPAK® or CHIRACEL®) had been described [2]

bromo-1,6-methano[10]annulene and for experimental advice, to Dr. W. Weissensteiner for helpful discussions, to Dr. A. Werner and Dr. M. Widhalm for help with chromatographic problems, to Dr. W. Silhan for recording NMR spectra and to Mr. H. Bieler and Dr. A. Nikiforov (all Vienna University) for the mass spectra.

Experimental

Crystal Structure Analysis

Measurements were carried out on a modified STOE-4-cycle diffractometer (Eulerian cradle geometry) with Mo-Kα-radiation ($\lambda = 0.7169$ Å, graphite monochromator); the racemic forms were measured at low temperature using a NONIUS low temperature apparatus and an EUROTHERM temperature controller.

Densities were measured by the flotation method (CsCl/H_2O), calculated densities for $C_{22}H_{16}Br_2$. Programs used: SHELXS [7], SHELX [8], PLUTO [9], PLATON [10] and DIFABS [11].

(+)-$(R)_p(R)_a(R)_p$-10,10'-Dibromo-2,2'-bi(1,6-methano[10]annulenyl) (**1 b**)

Orange crystals were obtained from $CHCl_3$/*n*-Pentan by the vapour diffusion method. A specimen of approx. 0.2 × 0.2 × 0.15 mm was mounted in viscous oil [6] and shock-cooled to 101(1)K. Cell constants were determined by a least-squares fit to the setting angles of 86 reflexions in the range $9 \leqslant 2\theta \leqslant 20°$: Space group $P2_12_12_1$, $a = 9.674(2)$, $b = 12.440(4)$, $c = 13.855(2)$ Å; $V = 1\,667.4$ Å^3, $z = 4$. $\rho_{calc} = 1.753$ g/cm^3 (101 K), $\rho_{exp} = 1.708$ g/cm^3 (293 K (2)), $F(000) = 872$. Data were collected for Friedel-equivalent quadrants ($-11 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 16$ and $-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 0$, $-16 \leqslant l \leqslant 0$); scan technique: ω-scan, $\Delta\omega = 1.2°$, giving 2939 unique reflexions [2648 with $F \geqslant 3\sigma(F)$]; empirical absorption correction [11] ($\mu = 48.1$ cm^{-1}); Lp-correction.

Solution with Patterson methods [7], anisotropic refinement of the bromine and isotropic refinement of all remaining atoms (including hydrogen) yielded a weighted residual $R_w = 0.038$ [$1/\sigma^2(F)$-weights]. Highest peak in the last Δ F-Fourier synthesis: 1.5 e Å^{-3}; atomic coordinates and equivalents isotropic temperature coefficients are listed in Table 2.

The absolute configuration was determined by determining the intensities of 40 Bijvoet reflexions (at $2\theta, \omega, X, \Phi$ and $-2\theta, -\omega, X, \Phi$) expected to show large differences due to anomalous dispersion. They were selected from structure factor calculation for both enantiomeric forms [7]. The signs of 38 of these differences favoured the (+)-$(R)_p(R)_a(R)_p$ enantiomer, whereas for two reflexions the differences were not significant.

Moreover, refinement of (−)-$(S)_p(S)_a(S)_p$-**1 b** (by inversion of all coordinates) yielded a significantly higher residual of $R_w = 0.0422$ (vs. 0.038).

Racem.-10,10'-Dibromo-2,2'-bi(1,6-methano[10]annulenyl) (**1 b**)

Dark yellow crystals were obtained by vapour-diffusion from benzene/*n*-Pentane. A specimen of 0.25 × 0.2 × 0.15 mm was mounted and cooled as described above [$T = 98(1)$ K]. Cell constants were determined by the refinement of 17 reflexions ($10 \leqslant 2\theta \leqslant 15°$). Space group Pbcn, $a = 7.465(3)$, $b = 13.709(6)$, $c = 16.606(16)$ Å, $V = 1\,699.3$ Å^3, $z = 4$; $\rho_{calc} = 1.650$ g/cm^3 (98 K), $\rho_{exp} = 1.686$ g/cm^3 (293(2) K), $F(000) = 872$. Data collection for one octant ($0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 19$, $0 \leqslant l \leqslant 23$); scan technique: ω-scan, $\Delta\omega = 1.2°$, 2421 unique reflexions [1011 with $F \geqslant 4\sigma(F)$], empirical absorption correction [11] ($\mu = 47.2$ cm^{-1}), Lp-correction.

Solution with Patterson methods and refinement as described above, $R_w = 0.0615$ [$1/\sigma^2(F)$-weights]. Highest peak in last ΔF-Fourier synthesis: 1.7 e Å^{-3}. Atomic coordinates and equivalents isotropic temperature parameters are listed in Table 3.

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent temperature parameters ($Å^2 \times 10^4$) for $(+)$-$(R)_p(R)_a(R)_p$-**1b**

	x/a	y/b	z/c	U(iso)
BR1	1991 (1)	6547 (1)	6271 (1)	190 (4)
BR2	711 (1)	5117 (1)	9036 (1)	156 (3)
C1	-333 (6)	5205 (6)	6863 (4)	116 (15)
C2	304 (7)	4157 (5)	6802 (5)	108 (16)
C3	-528 (7)	3274 (6)	6610 (5)	142 (17)
C4	-1902 (8)	3232 (6)	6188 (5)	202 (17)
C5	-2747 (8)	4065 (6)	5956 (6)	185 (18)
C6	-2576 (7)	5098 (6)	6313 (4)	183 (16)
C7	-2924 (8)	6056 (5)	5868 (5)	189 (17)
C8	-2160 (8)	7003 (6)	6011 (5)	206 (18)
C9	-791 (7)	7087 (6)	6322 (5)	168 (16)
C10	105 (7)	6228 (5)	6550 (5)	130 (17)
C11	-1777 (8)	5205 (7)	7214 (5)	180 (18)
C1′	2693 (7)	4558 (5)	7540 (4)	111 (16)
C2′	1817 (7)	3957 (5)	6894 (5)	115 (16)
C3′	2403 (7)	3152 (6)	6342 (5)	162 (19)
C4′	3669 (7)	2586 (6)	6422 (6)	196 (19)
C5′	4724 (8)	2753 (6)	7078 (5)	166 (18)
C6′	4819 (7)	3728 (6)	7610 (5)	151 (17)
C7′	5378 (7)	3861 (6)	8530 (5)	167 (17)
C8′	4883 (8)	4644 (6)	9145 (5)	188 (19)
C9′	3592 (7)	5138 (6)	9128 (5)	170 (16)
C10′	2508 (7)	4943 (7)	8490 (4)	150 (14)
C11′	4117 (8)	4677 (6)	7181 (5)	145 (17)
H3	-34 (56)	2544 (45)	6704 (39)	7 (164)
H4	-2038 (81)	2536 (60)	6028 (57)	549 (241)
H5	-3347 (75)	4043 (59)	5501 (49)	391 (259)
H7	-3754 (59)	6063 (46)	5401 (37)	42 (169)
H8	-2549 (55)	7674 (45)	5776 (38)	22 (164)
H9	-138 (62)	7788 (52)	6315 (48)	263 (198)
H11	-2011 (68)	4726 (50)	7460 (38)	79 (177)
H12	-1815 (61)	5971 (46)	7572 (35)	40 (158)
H3′	1826 (60)	2863 (46)	5905 (41)	103 (170)
H4′	3745 (55)	1941 (45)	6055 (42)	93 (169)
H5′	5399 (63)	2175 (50)	7270 (42)	138 (185)
H7′	6029 (50)	3273 (41)	8758 (39)	3 (149)
H8′	5409 (61)	4881 (58)	9652 (41)	257 (187)
H9′	3301 (72)	5504 (58)	9621 (47)	410 (243)
H12′	4153 (63)	4709 (56)	6549 (47)	312 (207)
H11′	4676 (55)	5311 (46)	7370 (35)	1 (157)

Meso-10,10′-Dibromo-2,2′-bi(1,6-methano[10]annulenyl) (**2b**)

Crystals were obtained by the vapour diffusion method or by cooling hot saturated solutions from several different solvents. They showed two distinct sets of diffraction patterns depending on the solvent used. Cell constants for specimen crystallized from dioxane and for those from CH_3CN were determined from diffractometer measurements and presession photographs.

Crystals obtained from dioxane showed an orthorhombic Laue symmetry [$a = 45.19(3)$, $b = 6.840(4)$, $c = 21.72(2)$ Å] with non-crystallographic extinctions (reflexions *hkl* observed only if

Table 3. Fractional atomic coordinates (× 10^4) and equivalent temperature parameters (Å^2 × 10^4) for racem.-**1 b**

	x/a	y/b	z/c	U(iso)
BR1	2517 (2)	1649 (1)	1652 (1)	165 (4)
C1	-1009 (12)	786 (8)	1623 (7)	87 (20)
C2	-751 (12)	6 (8)	2210 (6)	73 (20)
C3	-1880 (13)	-802 (10)	2208 (6)	149 (22)
C4	-3038 (13)	-1170 (8)	1596 (7)	205 (25)
C5	-3339 (13)	-765 (8)	836 (6)	148 (22)
C6	-2925 (12)	215 (7)	631 (6)	125 (24)
C7	-2296 (16)	535 (6)	-116 (6)	123 (22)
C8	-1152 (15)	1345 (8)	-184 (7)	181 (25)
C9	-39 (15)	1733 (8)	426 (6)	133 (22)
C10	193 (13)	1364 (7)	1207 (6)	55 (20)
C11	-2914 (12)	890 (9)	1332 (6)	126 (22)
H3	-830(383)	-1092(144)	2768(253)	2084(1675)
H4	-3716(124)	-1966 (63)	1737 (56)	235 (270)
H5	-4156(153)	-1109 (85)	392 (76)	694 (469)
H7	-2830(163)	65(100)	-602 (64)	731 (448)
H8	-673(125)	1836 (67)	-760 (58)	128 (298)
H9	436(115)	2210 (60)	340 (51)	96 (262)
H11	-3368(151)	1522 (85)	1187 (72)	398 (419)
H12	-4066(132)	568 (72)	1765 (60)	189 (350)

$l = 2n + 1$ and $h = 2n$), strongly indicating twinning. Crystals from CH_3CN also exhibit orthorhombic Laue symmetry with cell constants $a = 22.761$ (2), $b = 6.899$ (6) and $c = 21.88$ (2) Å, space group P 2_1cn, $z = 8$, $\rho_{calc} = 1.702$ g/cm^3 [$T = 298$ (2) K]. Data collection of a complete quadrant to a 2θ value of 50° yielded 5 254 unique reflexions [2 377 with $F \geqslant 4\sigma(F)$], ω scan technique, $\Delta\omega = 1.0°$ Lp-correction and empirical absorption correction were applied.

The structure was solved by location of the four bromine atoms in the Patterson map, but during refinement some of the annulene-C's remained unobservable: they were included in the refinement at calculated positions. Their structural parameters turned out to be quite stable as the least-squares procedure conveyed. Nevertheless, the temperature parameters of corresponding atoms of the two "independent" molecules are highly negatively correlated. Moreover, the two molecules are approximately correlated by a non-crystallographic two-fold screw axis.

For these reasons and because of large uncertainties of positional parameters (resulting in large differences of chemically equivalent bond lengths and angles) no atomic coordinates are given; only the torsion angles are used for comparison with the racemic forms (see Table 1).

Chemical Correlation

For the preparation of the racemic biannulenyls see Refs. [1] and [2]. Medium pressure liquid chromatography (MPLC) was performed on Merck LiChroprep Si-60 (25–40 μm) in *n*-hexane-*THF* (0.6%, distilled over $LiAlH_4$) on columns (52 × 400 mm) with a FMI pump (at 2.0–2.8 bar, 20–25 ml/min) and an ISCO UA-5 UV-detector. HPLC: Hewlett-Packard HP 1090-M (on reversed phase KG in various solvents and at various temperatures, e.g. methanol-water, 4 : 1, at 40°C) with a diode-array detector. MS: Varian MAT CH-7. Optical rotations: Perkin-Elmer 241 polarimeter. CD: Dichrograph Mark III (Jobin-Yvon). All NMR spectra were recorded on a Bruker WM-250 spectrometer (in $CDCl_3$ or CD_2Cl_2) in FT-mode using an Aspect-2000 computer. UV spectra were measured on a Perkin-Elmer Lambda-7 spectrometer (in ethanol or *n*-hexane).

(−)-(S)-2-Bromo-1,6-methano[10]annulene (**3**)

450 mg of racem. **3** were resolved into its enantiomers on triacetylcellulose (column: 63 × 660 mm) in ethanol at 40°C by the recycling technique [3], using an UV-detector at 280 nm. After 4 cycles the enantiomeric purity was higher than 98% ($[\alpha]_D^{20} - 52°$ for the less adsorbed enantiomer). A positive Cotton effect at 330 nm indicates (*S*)-chirality [4].

2,2′-Bi(1,6-methano[10]annulenyl) (**1a** *and* **2a**)

To a solution of vacuum-dried Zn (578 mg), $Ni[P(C_6H_5)_3]_2Cl_2$ (289 mg) and tetrabutyl ammoniumiodide (1.63 g) in 12 ml of dry *THF* after 15 min under Ar, 977 mg (3.46 mmol) of racem. **3** in dry *THF* (5 ml) were added dropwise; after 30 min at room temperature the mixture was warmed for 90 min to 50°C. 20 ml of *n*-hexane were then added, the mixture filtered from some precipitate and the solution poured over a short column of silica gel. TLC (in *n*-hexane) showed two main products; no starting material (**3**) was present. They were identified by their UV-spectra (cf. Ref. [2]) as meso-**2a** ($R_F = 0.2$) and racemic-**1a** ($R_F = 0.3$). **1a**; MS (*m*/e): 282 (*M*, 31%), 265 (18.7%), 252 (17.7%), 141 (16.2%), 86 (43.7%), 84 (67.4%), 49 (100%). UV (ethanol): nm (ε): 357 (15200), 272 (43000), 246 (55000). **2a**; UV (*n*-Hexane): 318 (11400), 256 (58700).

By the same procedure 75 mg of (−)-**3** were coupled to give only one (dextrorotatory) product identical (TLC, UV, MS) with racemic **1a**. Optical rotation: $[\alpha]_D^{20} = +710° \pm 70°$ [ethanol, $c = 0.012$ (UV!)]; CD (in ethanol): nm (Δε): 340 (+6), 292 (+51), 269 (−37), 236 (−49), [208 (+15?)] (see also Scheme 1).

Debromination of (+)-10,10′-Dibromo-2,2′-bi(1,6-methano[10]annulenyl) (**1b**): *(+)-2,2′-Bi(1,6-methano[10]annulenyl)* (**1a**)

Attempts to reduce (debrominate) **1b** with *n-Bu*-Li at −78°C in dry *THF* and subsequent treatment with water gave – even after 20 sec – a rather complex mixture, which contained (according to TLC) only traces of the desired product **1a**.

Stirring of **1b** with Zn-powder and a few drops of conc. HCl in a solution of *THF* at room temperature for 2 h, however, yielded practically pure **1a**, identified by UV, MS, TLC and its strong fluorescence at 366 nm. From (+)-**1b** dextrorotatory **1a** was obtained with a CD-spectrum (in ethanol) identical to that of the product obtained by coupling of (−)-**3** (vide supra) (see also Scheme 1).

(+)- and (−)-**1a** were also obtained from racemic **1a** (oil) by chromatography on *TAC* in ethanol in one run at 40°C, were the laevorotatory enantiomer is eluted first (1.81 and 3.53 V_0 resp.), with the same CD spectrum (in ethanol) of the (+)-enantiomer as the product obtained by reduction of (+)-**1b** or by coupling of (−)-**3** as described above (see also Scheme 1).

References

[1] Part 11: Meyer A., Schlögl K., Lerch U., Vogel E. (1988) Chem. Ber. **121**: 971

[2] Iyoda M., Sato K., Oda M. (1985) Tetrahedron Lett. **26**: 3829

[3] Schlögl K., Widhalm M., Schwamborn M. (1983) Monatsh. Chem. **114**: 605

[4] Scharf J., Schlögl K., Widhalm M., Lex J., Tückmantel W., Vogel E., Pertlik F. (1986) Monatsh. Chem. **117**: 255

[5] Schlögl K. (1984) Planarchiral Molecular Structures. Springer, Berlin Heidelberg New York Tokyo (Topics in Current Chemistry, Vol. 125, p. 27); Jones P. G. (1984) Acta Cryst. **A 40**: 663

[6] Hope H., Nichols B. G. (1981) Acta Cryst. **A 37**: 158

[7] Sheldrick G. M. (1986) SHELXS-86, a computer program for crystal structure solution. Univ. of Göttingen

[8] Sheldrick G. M. (1976) SHELX-76, a computer program for crystal structure determination. Univ. of Cambridge

[9] Motherwell S. (1976) PLUTO, a program for plotting molecular and crystal structures. Cambridge Crystallographic Data Centre, Cambridge

[10] Spek A. L. (1982) In: Sayre D. (ed.) Computational Crystallography. Clarendon Press, Oxford, p. 528

[11] Walker S. (1983) Acta Cryst. **A 39**: 158

Received November 11, 1988. Accepted December 2, 1988