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Stereochemistry of Planarchiral Compounds, Part XIII [1]: Crystal Structure of Meso-10,10′-dibromo-2,2′-bi-(1,6-methano-[10]-annulenyl)

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Summary. Crystallization of the mesoform of the title compound **1** from benzene-pentane in the presence of 5% of $(+)(R)_p(S)_a(R)_p$-**1** afforded crystals, the structure of which was determined in the achiral spacegroup $P2_1/a - C^5_{2h}$. The configuration $(R)_p(S)_p$ was confirmed, the torsional angle τ around the 2,2′-bond is 68.6° and 72.1° (C3-C2-C2′-C3′ and C1-C2-C2′-C1′, resp.). The twist of the "best planes" through the perimeter carbonatoms 3, 4, 5 and 7, 8, 9 (3′, 4′, etc., resp.) is 26.0° and 19.8°. The colours of the crystals of the stereoisomers of **1** depend on the torsional angles and thereby on the conjugation of the π-systems. Meso, monoclinic (70.3°): light yellow; racemate, opt. inactive (56.2°): yellow; enantiomer of the racemate (34.4°): orange (average τ-values).

Keywords. Crystal structure analysis; Axial and planar chirality; Torsional isomers; Meso-10,10′-dibromo-2,2′-bi-(1,6-methano-[10]-annulenyl).

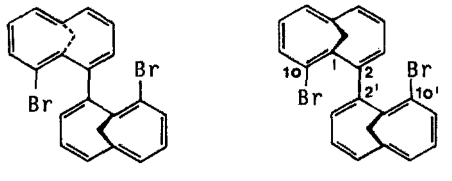
Stereochemie planarchiraler Verbindungen, 13. Mitt.: Die Kristallstruktur von Meso-10,10′-dibrom-2,2′-bi-(1,6-methano-[10]-annulenyl)

Zusammenfassung. Kristallisation der Meso-Form der Titelverbindung **1** aus Benzol-Pentan in Gegenwart von 5% $(+)(R)_p(S)_a(R)_p$-**1** lieferte Kristalle, deren Struktur in der achiralen Raumgruppe $P2_1/a - C^5_{2h}$ bestimmt werden konnte: Die Konfiguration $(R)_p(S)_p$ wurde bestätigt, der Torsionswinkel τ um die 2,2′-Bindung beträgt 68.6 bzw. 72.1° (C3-C2-C2′-C3′ bzw. C1-C2-C2′-C1′). Die Verkippung der „besten Ebenen", definiert durch die Perimeter-C-Atome 3, 4, 5 und 7, 8, 9 (bzw. 3′, 4′, etc.) beträgt 26.0 bzw. 19.8°. Die Farben der Kristalle der Stereoisomere von **1** hängen von den Torsionswinkeln τ und damit von der Konjugation der π-Systeme ab: Meso, monoklin (70.3°): hellgelb; Racemat, opt. inaktiv (56.2°): gelb: Enantiomer des Racemates (34.4°): orange (gemittelte Werte).

Introduction

2,2′-Bi-(1,6-methano-[10]-annulenyl)s combine elements of both planar and axial chirality within one molecule. The two possible combinations of planar chiralities $(R)_p$ and $(S)_p$ result in a racemic and a mesoform: $(R)_p(R)_p/(S)_p(S)_p$ and $(R)_p(S)_p$, respectively. The additional element of axial chirality gives rise to the interesting dynamic stereochemistry of these compounds which has been studied in some detail

[1], [2]. For the racemic form of 10,10′-dibromo-2,2′-bi-(1,6-methano-[10]-annulenyl) (**1**) two diastereomers: $(R)_p(R)_a(R)_p$ and $(R)_p(S)_a(R)_p$ and their enantiomers: $(S)_p(S)_a(S)_p$ and $(S)_p(R)_a(S)_p$ result[1].



Meso **1** *Racemate*

In the case of the mesoform, only two enantiomeric forms are feasible: $(R)_p(R)_a(S)_p$ and $(R)_p(S)_a(S)_p$ which cannot be separated at room temperature due to the low rotational barrier around the 2,2′-bond in solution: 58 kJ/mol, as determined by dynamic ^{1}H-nmr spectroscopy in $CDCl_3$ [2]. Probably because of twinning, we had difficulties in evaluating the crystal structure of this mesoform [1].

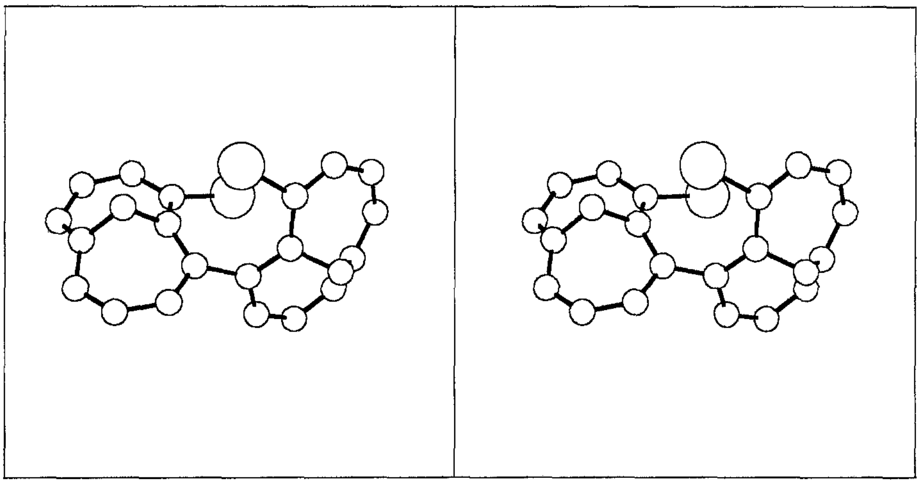


Fig. 1. Stereoscopic presentation of meso-10,10′-dibromo-2,2′-bi-(1,6-methano-[10]-annulenyl)

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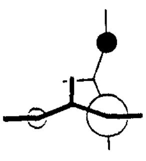
[1] In Ref. [1] the stereochemical descriptor for the dextrorotatory enantiomer of the racemic form of **1** was erroneously given as $(+)$-$(R)_p(R)_a(R)_p$. It should read however as $(+)$-$(R)_p(S)_a(R)_p$, since a clockwise rotation around the 2,2′-bond (torsional angle C3-C2-C2′-C3′ = − 33°) results in a counterclockwise arrangement of the "ligands" according to the CIP rules [3] and therefore has to be described by the descriptor $(S)_a$



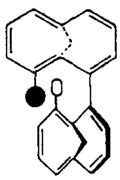


Table 1. Atomic coordinates and dislocation parameters (e.s.d.'s in parentheses) for meso-10,10′-dibromo-2,2′-bi-(1,6-methano-[10]-annulenyl) (monoclinic modification). ATF = $\exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*)$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.17687 (4)	0.82747 (8)	0.65725 (4)	0.0595 (4)	0.0627 (4)	0.0743 (5)	0.0164 (3)	0.0135 (3)	0.0024 (4)
Br2	− 0.13363 (4)	0.74643 (8)	1.17967 (4)	0.0709 (4)	0.0571 (4)	0.0704 (4)	− 0.0167 (4)	− 0.0025 (3)	0.0027 (4)
C1	0.0248 (4)	1.0732 (7)	0.6366 (4)	0.0585 (35)	0.0415 (36)	0.0580 (42)	− 0.0005 (28)	− 0.0079 (30)	− 0.0097 (32)
C2	− 0.0276 (4)	1.0489 (7)	0.7114 (4)	0.0446 (30)	0.0609 (39)	0.0506 (38)	0.0041 (30)	− 0.0030 (27)	− 0.0016 (33)
C3	− 0.1020 (4)	1.1587 (9)	0.7285 (4)	0.0490 (33)	0.0671 (47)	0.0568 (40)	0.0135 (34)	0.0017 (29)	0.0081 (37)
C4	− 0.1115 (5)	1.3247 (11)	0.7065 (5)	0.0762 (47)	0.0848 (54)	0.0799 (53)	0.0343 (44)	0.0010 (40)	− 0.0104 (49)
C5	− 0.0515 (6)	1.4157 (9)	0.6572 (5)	0.1111 (57)	0.0520 (46)	0.0746 (55)	0.0286 (43)	− 0.0022 (44)	0.0042 (41)
C6	0.0065 (5)	1.3434 (8)	0.5983 (4)	0.0886 (48)	0.0522 (43)	0.0518 (42)	0.0089 (39)	− 0.0057 (37)	0.0026 (37)
C7	0.0966 (6)	1.3994 (8)	0.5735 (5)	0.1153 (61)	0.0455 (42)	0.0942 (59)	− 0.0049 (45)	0.0053 (48)	0.0104 (41)
C8	0.1712 (5)	1.2977 (9)	0.5522 (5)	0.0959 (53)	0.0739 (57)	0.0924 (56)	0.0014 (42)	0.0194 (44)	0.0172 (45)
C9	0.1822 (4)	1.1279 (8)	0.5729 (4)	0.0602 (39)	0.0692 (49)	0.0660 (47)	0.0028 (35)	0.0210 (34)	− 0.0047 (38)
C10	0.1227 (4)	1.0320 (7)	0.6178 (4)	0.0462 (32)	0.0504 (37)	0.0498 (38)	0.0067 (28)	0.0003 (27)	− 0.0093 (32)
C11	− 0.0206 (4)	1.1781 (9)	0.5685 (4)	0.0615 (35)	0.0694 (46)	0.0529 (41)	0.0066 (34)	− 0.0093 (30)	− 0.0026 (37)
C1′	0.0741 (3)	0.9144 (7)	0.8323 (3)	0.0357 (29)	0.0454 (34)	0.0494 (35)	0.0038 (25)	0.0112 (25)	0.0060 (29)
C2′	− 0.0076 (3)	0.9161 (7)	0.7750 (4)	0.0399 (30)	0.0476 (35)	0.0562 (38)	− 0.0053 (28)	0.0093 (28)	− 0.0038 (31)
C3′	− 0.0785 (4)	0.7964 (8)	0.7807 (4)	0.0497 (34)	0.0632 (47)	0.0772 (47)	− 0.0025 (32)	− 0.0038 (31)	− 0.0103 (40)
C4′	− 0.0969 (4)	0.6917 (8)	0.8519 (5)	0.0499 (35)	0.0597 (43)	0.1292 (63)	− 0.0173 (32)	0.0359 (39)	− 0.0109 (46)
C5′	− 0.0500 (5)	0.6747 (8)	0.9278 (5)	0.0749 (45)	0.0546 (41)	0.0863 (53)	− 0.0058 (37)	0.0180 (39)	0.0107 (42)
C6′	0.0433 (4)	0.7335 (8)	0.9419 (4)	0.0701 (43)	0.0466 (38)	0.0560 (41)	0.0165 (33)	0.0051 (34)	0.0055 (36)
C7′	0.0822 (5)	0.7953 (10)	1.0154 (6)	0.0760 (50)	0.0731 (60)	0.0769 (60)	0.0271 (42)	0.0234 (47)	0.0189 (49)
C8′	0.1545 (5)	0.9194 (11)	1.0165 (5)	0.0729 (49)	0.0876 (61)	0.0613 (54)	0.0273 (44)	− 0.0057 (43)	0.0076 (51)
C9′	0.1762 (4)	1.0264 (9)	0.9514 (4)	0.0433 (34)	0.0632 (45)	0.0631 (48)	0.0039 (34)	− 0.0094 (32)	0.0016 (41)
C10′	0.1287 (3)	1.0404 (7)	0.8719 (4)	0.0359 (29)	0.0456 (34)	0.0641 (42)	− 0.0017 (26)	0.0065 (28)	− 0.0017 (32)
C11′	0.1038 (4)	0.7495 (7)	0.8653 (4)	0.0595 (33)	0.0425 (31)	0.0633 (38)	0.0083 (32)	0.0094 (29)	− 0.0038 (36)

Table 1 (continued)

Atom	x/a	y/b	z/c	U_{iso}	Atom	x/a	y/b	z/c	U_{iso}
H3	− 0.145 (2)	1.133 (5)	0.766 (2)	0.025 (11)	H3′	− 0.118 (3)	0.797 (5)	0.742 (3)	0.037 (12)
H4	− 0.150 (4)	1.381 (7)	0.735 (4)	0.090 (19)	H4′	− 0.140 (3)	0.651 (5)	0.849 (3)	0.036 (12)
H5	− 0.041 (4)	1.534 (6)	0.669 (3)	0.081 (17)	H5′	− 0.080 (3)	0.614 (7)	0.980 (4)	0.063 (17)
H7	0.108 (3)	1.498 (5)	0.572 (3)	0.038 (12)	H7′	0.059 (4)	0.769 (7)	1.067 (4)	0.060 (19)
H8	0.232 (5)	1.343 (9)	0.517 (5)	0.146 (29)	H8′	0.179 (4)	0.935 (7)	1.070 (4)	0.057 (19)
H9	0.232 (3)	1.081 (6)	0.548 (3)	0.069 (16)	H9′	0.218 (3)	1.111 (6)	0.965 (3)	0.050 (17)
H11a	0.001 (3)	1.160 (6)	0.496 (3)	0.057 (14)	H11′a	0.087 (2)	0.668 (4)	0.828 (2)	0.009 (9)
H11b	− 0.082 (3)	1.165 (5)	0.568 (3)	0.034 (12)	H11′b	0.184 (3)	0.740 (6)	0.888 (3)	0.050 (13)

Results and Discussion

We now attempted to "freeze out" enantiomerisation in the solid state and to obtain a different modification of optical active crystals by crystallizing meso-**1** from optical active solvents [4]. Whereas crystallisation from α-pinene yielded the same orthorhombic crystals as described in Ref. [1], we obtained a different monoclinic modification from a saturated benzene/pentane solution containing 5% of the optically active enantiomer of $(+)(R)_p(S)_a(R)_p$ (weight-% referring to meso-form) after inducing crystallisation by seeding with a small specimen of this stereoisomer. Unfortunately, even the crystals obtained thereby belonged to an achiral space group ($P2_1/a$); however, the crystal structure was determined by standard

Table 2. (a) Bond lengths (in Å): e.s.d. < 0.08 for C−H, < 0.02 for C−C, (b) bond angles (in °): e.s.d. < 1.1°

(a)	Br1	C10	1.914	Br1′	C10′	1.907	C1	C2	1.418
	C1	C10	1.436	C1	C11	1.482	C2	C3	1.396
	C2	C2′	1.486	C3	C4	1.397	C3	H3	0.875
	C4	C5	1.373	C4	H4	0.844	C5	C6	1.379
	C5	H5	0.987	C6	C7	1.396	C6	C11	1.465
	C7	C8	1.373	C7	H7	0.819	C8	C9	1.424
	C8	H8	1.099	C9	C10	1.352	C9	H9	0.891
	C11	H11a	1.195	C11	H11b	0.859	C1′	C2′	1.409
	C1′	C10′	1.399	C1′	C11′	1.487	C2′	C3′	1.386
	C3′	C4′	1.434	C3′	H3	0.797	C4′	C5′	1.334
	C4′	H4	0.677	C5′	C6′	1.382	C5′	H5	1.058
	C6′	C7′	1.345	C6′	C11′	1.498	C7′	C8′	1.419
	C7′	H7	0.906	C8′	C9′	1.383	C8′	H8	0.901
	C9′	C10′	1.385	C9′	H9	0.909	C11′	H11a′	0.905
	C11′	H11b′	1.153						

(b)	C2	C1	C10	131.1	C2	C1	C11	117.3
	C10	C1	C11	111.0	C1	C2	C3	118.5
	C1	C2	C2′	124.6	C3	C2	C2′	116.9
	C2	C3	C4	129.2	C3	C4	C5	127.3
	C4	C5	C6	122.0	C5	C6	C7	126.8
	C5	C6	C11	117.1	C7	C6	C11	115.4
	C6	C7	C8	124.0	C7	C8	C9	127.0
	C8	C9	C10	128.0	Br1	C10	C1	119.6
	Br1	C10	C9	115.5	C1	C10	C9	124.9
	C1	C11	C6	101.8	C2′	C1′	C10′	132.4
	C2′	C1′	C11′	115.5	C10′	C1′	C11′	111.7
	C2	C2′	C1′	123.6	C2	C2′	C3′	116.3
	C1′	C2′	C3′	120.0	C2′	C3′	C4′	128.1
	C3′	C4′	C5′	131.1	C4′	C5′	C6′	121.2
	C5′	C6′	C7′	126.8	C5′	C6′	C11′	116.9
	C7′	C6′	C11′	115.9	C6′	C7′	C8′	122.0
	C7′	C8′	C9′	127.9	C8′	C9′	C10′	127.2
	Br1′	C10′	C1′	120.2	Br1′	C10′	C9′	115.5
	C1′	C10′	C9′	124.2	C1′	C11′	C6′	101.6

Table 3. Torsional angles (in °): e.s.d. < 1.1°

C10	C1	C2	C3	151.6	C10	C1	C2	C2′	− 26.8
C11	C1	C2	C3	− 18.6	C11	C1	C2	C2′	162.9
C2	C1	C10	Br1	39.5	C2	C1	C10	C9	− 140.7
C11	C1	C10	Br1	− 149.8	C11	C1	C10	C9	30.0
C2	C1	C11	C6	83.6	C10	C1	C11	C6	− 88.5
C1	C2	C3	C4	− 29.4	C2′	C2	C3	C4	149.1
C1	C2	C2′	C1′	72.1	C1	C2	C2′	C3′	− 113.0
C3	C2	C2′	C1′	− 106.4	C3	C2	C2′	C3′	68.6
C2	C3	C4	C5	4.8	C3	C4	C5	C6	23.7
C4	C5	C6	C7	− 149.0	C4	C5	C6	C11	20.4
C5	C6	C7	C8	145.6	C11	C6	C7	C8	− 23.9
C5	C6	C11	C1	− 84.1	C7	C6	C11	C1	86.5
C6	C7	C8	C9	− 18.6	C7	C8	C9	C10	− 0.5
C8	C9	C10	Br1	− 164.7	C8	C9	C10	C1	15.4
C10′	C1′	C2′	C2	31.0	C10′	C1′	C2′	C3′	− 143.8
C11′	C1′	C2′	C2	− 156.4	C11′	C1′	C2′	C3′	28.8
C2′	C1′	C10′	Br1′	− 25.8	C2′	C1′	C10′	C9′	149.6
C11′	C1′	C10′	Br1′	161.5	C11′	C1′	C10′	C9′	− 23.2
C2′	C1′	C11′	C6′	− 87.7	C10′	C1′	C11′	C6′	86.4
C2	C2′	C3′	C4′	− 156.0	C1′	C2′	C3′	C4′	19.1
C2′	C3′	C4′	C5′	− 3.8	C3′	C4′	C5′	C6′	− 16.5
C4′	C5′	C6′	C7′	146.6	C4′	C5′	C6′	C11′	− 25.3
C5′	C6′	C7′	C8′	− 148.8	C11′	C6′	C7′	C8′	23.3
C5′	C6′	C11′	C1′	85.0	C7′	C6′	C11′	C1′	− 87.8
C6′	C7′	C8′	C9′	20.0	C7′	C8′	C9′	C10′	3.2
C8′	C9′	C10′	Br1′	151.8	C8′	C9′	C10′	C1′	− 23.8

Table 4. Summary of crystal data, data for intensity measurements and crystal structure refinement (Stoe four-cycle diffractometer; graphite monochromatized MoKα radiation; $2\Theta/\omega$ scan mode; 50 steps/reflexion + (α_1, α_2)-splitting)

a [Å]	13.813(3)	Range of h, k, l	$\pm h$, k, $\pm l$
b [Å]	8.127(1)	Measured reflexions	6686
c [Å]	15.657(4)	Unique reflexions	3105
β [°]	92.58(2)	Intern. consist.	0.068
Volume [Å]	1755.9	Reflexions with $F_0 > 3\sigma F_0$	2113
ρ_{calc} [$g \cdot cm^{-3}$]	1.665	Number of variables	281
Cell content	$4\{C_{22}H_{16}Br_2\}$	R and wR; $w = [\sigma(F_0)]^{-2}$	0.053/0.039
Space group	$P2_1/a - C^5_{2h}$	Least squares shift	
μ (MoKα) [cm^{-1}]	45	to error $(\Delta/\sigma)_{max}$	$< 10^{-3}$
Step width [°]	0.03	Final difference Fourier	
Time/step [sec]	0.5–1.5	$(\Delta p)_{max}$; $(\Delta p)_{min}$	0.87/− 0.72
$2\Theta_{max}$ [°]	50	Temperature	25°C

methods. Fig. 1 depicts a stereoscopic view of the molecule. The atomic coordinates, bond lengths and angles as well as some selected torsional angles are presented in Tables 1–3.

This structure analysis confirms the configuration $(R)_p(S)_p$ of the annulenyl moieties as proposed from the results of ^1H and ^{13}C-nmr spectroscopy and from stereochemical correlations [1, 2]. The torsional angle around the 2,2′-bond (C3-C2-C2′-C3′) is 68.6° (C1-C2-C2′-C1′: 72.1°). With regard to previous studies [1], it seems remarkable that the colours of the crystals of the stereoisomers of **1** obviously depend on the torsional angle and therefore on the potential conjugation of the π-systems of the annulene moieties. They are for meso-**1** (70.3°): light yellow, for the optical inactive racemate (56.2°): yellow and for the enantiomer of the racemate (34.4°): orange [1] (average angles τ).

The "best planes" through the annulene perimeter carbon atoms (C3, C4, C5, C7, C8, C9) are twisted to approximately 23° (± 3) around the 2,2′-bond. This twist seems to be responsible for the strong shifts of the protons H3 and H3′ in the ^1H-nmr spectra (with signals at 7.70 and 6.41 ppm, resp. in $CDCl_3$) [2]. One proton suffers deshielding by the "opposite" annulenyl moiety whereas the other experiences the shielding effects of *two* such residues. This effect has also been observed for the racemic forms of **1**.

Structure Determination

The X-ray intensity data and the data for the lattice constants refinement (58 *hkl* data within $20° < 2-\theta < 30°$) were collected on a Stoe four cycle diffractometer. In Table 4 the crystal data, the conditions for the intensity measurements and structure refinements are compiled. Corrections were applied for Lorentz and polarization effects as well as for adsorption corrections (36 Φ scan data).

The positions of the nonhydrogen atoms were determied by direct method strategy [5], the positions of the hydrogen atoms by subsequent difference Fourier summations. The refined structure parameters – least squares techniques – are compiled in Table 1. All calculations were performed with neutral atomic scattering functions (International Tables for X-Ray Crystallography, 1974).

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