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1,1′-Bi(trishomobarrelenyl) – Synthesis and Chiroptic Properties

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Dedicated to Professor Josef Michl on the occasion of his 70th birthday

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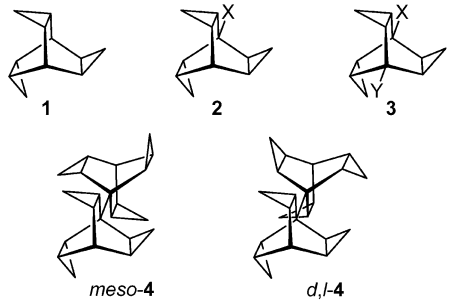
1,1′-Bi(*endo*,*exo*,*syn*-pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecyl)[1,1′-bi(trishomobarrelenyl)] (**4**) has been prepared as a 1:1 mixture of its *meso*- and *d*,*l*-diastereomers in six steps from trishomobarrelene **1** via the amine **5**, the *N*,*N*′-bis(trishomobarrelenyl)sulfamide **6** and the 1,2-(trishomobarrelenyl)diazene **7** in 16 % overall yield. Crystals of *meso*-**4** were grown from a pentane solution of the mixture and subjected to an X-ray structure analysis. The (+)- and the (–)-enantiomer were isolated by HPLC on a chiral-phase column. They exhibited significantly enhanced molar optical rotations which are consistent with the presence of three helically arranged 1,2-dicyclopropylethane units in their skeletons. The absolute configuration of the (+)-enantiomer was assigned on the basis of DFT computed optical rotations of both enantiomers to be *all*-(*S*).

Introduction

Our long-standing interest in propeller- and helix-shaped chiral oligocyclic hydrocarbons and their peculiar chiroptic properties[1–5] has led us to conceive 1,1′-bi(trishomobarrelenyl) [1,1′-bi(*endo*,*exo*,*syn*-pentacyclo[3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecyl)] (**4**). While unsubstituted trishomobarrelene **1**, because of its plane of symmetry, is achiral, any bridgehead-monosubstituted **2** or unsymmetrically 1,5-disubstituted derivative **3** only has C_3 symmetry and thereby is chiral.

As the two monosubstituted halves in 1,1′-bi(trishomobarrelenyl) **1** can either be enantiomeric or identical, **1** exists in two diastereomeric forms, i.e., *meso*-**4** and *d*,*l*-**4**. The latter two double-cage molecules, due to their presumably preferred staggered conformation, would enclose three helically arranged 1,2-dicyclopropylethane units having the central bridgehead-bridgehead bond in common, and therefore might exhibit interesting chiroptic properties such as enhanced optical rotations. Although enantiomerically pure bridgehead derivatives **2** have been prepared,[1] and bridgehead–bridgehead coupling of an appropriate enantiomerically pure bridgehead derivative would lead to enantiopure *d*- or *l*-**1**, we chose to proceed along the shorter route and prepare a mixture of *meso*- and *d*,*l*-**4**, hoping for a possible separation of all three stereoisomers.



Results and Discussion

The synthesis of *meso*-/*d*,*l*-**4** started with photochlorination of the hydrocarbon **1** with *tert*-butyl hypochlorite.[6] Treatment of the thus obtained chloride with ammonia in

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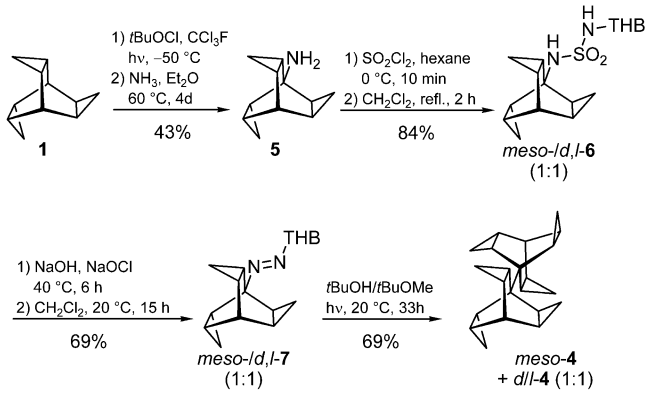
diethyl ether at 60 °C for 4 d gave the bridgehead amine **5** in 43% yield over both steps which was subsequently converted into the *N*,*N*′-bis(trishomobarrelenyl)sulfamide *meso*-/*d*,*l*-**6** by reaction with sulfuryl chloride (84% yield based on SO_2Cl_2). Chlorination of the latter with sodium hypochlorite under basic conditions (sodium hydroxide) proceeded with ring closure to a thiadiaziridine *S*,*S*-dioxide and subsequent elimination of sulfur dioxide to yield 1,2-bis(trishomobarrelenyl)diazene *meso*-/*d*,*l*-**7**. Photolysis of this azo compound in a 4:1 mixture of *tert*-butyl alcohol and *tert*-butyl methyl ether provided a 1:1 mixture of *meso*- and *d*,*l*-1,1′-bi(trishomobarrelenyl) *meso*-/*d*,*l*-**4** in 69% yield (Scheme 1).[7]



Scheme 1. Synthesis of *meso*- and *d*,*l*-1,1′-bi(trishomobarrelenyl) *meso*-/*d*,*l*-**4** from pentacyclo[3.3.3.0^{2,4}.0^{6,8}.0^{9,11}]undecane (trishomobarrelene) **1**. THB = 1-trishomobarrelenyl.

The *meso*-diastereomer crystallized from a solution of the mixture in pentane. Its structure and configuration was proved by an X-ray single crystal structure analysis (Figure 1).[8] The stereoisomers that remained in the solution were separated and purified by preparative scale high performance liquid chromatography (HPLC) on a chiral-phase column (Chiralcel OD). The (+)- and the (–)-enantiomer (+)- and (–)-**4** were thus obtained with 72 and 97% enantiomeric excess as determined by analytical HPLC on the same type of column.

The length of the central bond [1.541(3) Å] between the two trishomobarrelenyl moieties is completely normal for a C(sp^3)–C(sp^3) bond and not elongated like the one in hexacyclopropylethane (1.636 Å).[9] As expected, the conformation around the central single bond is staggered. This can be assumed to be the case also for *d*-**4** and *l*-**4** and even in solution, though the rotational barrier around that bond should not be very high. The absolute values of the molar rotations $[M]_D^{26}$, i.e., the specific rotations $[\alpha]_D^{26}$ normalized with respect to the relative molecular masses are higher than those of any other known enantiomerically pure trishomobarrelene bridgehead derivative (Table 1).

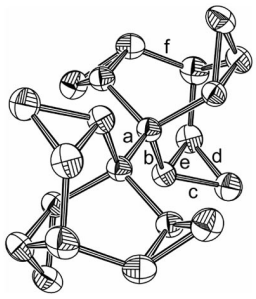


Figure 1. Structure of *meso*-1,1′-bi(trishomobarrelenyl) *meso*-**4** in the crystal.[8] Selected bond lengths: a: 1.541(3) Å, b: 1.5372(15) Å, c: 1.4949(18) Å, d: 1.496(2) Å, e: 1.5098(18) Å, f: 1.5252(18) Å.

Apparently, the second propeller-shaped chiral trishomobarrelenyl residue attached to the first one enhances the optical rotation to a greater extent than a simple alkyl substituent, and this must be attributed to the helicity of the three 1,2-dicyclopropylethane units incorporated in the skeleton of the chiral 1,1′-bi(trishomobarrelenyl) **4**.

Without having a heavy-atom containing enantiomerically pure bridgehead derivative of **4** for an X-ray analysis at hand, the absolute configuration of (+)- and (–)-**4**, can only be determined computationally. Indeed, density functional theory computations at the B3W91/cc-pVDZ level of theory[10] determine an *all*-(*S*)-configuration for the (+)-enantiomer (Figure 2).

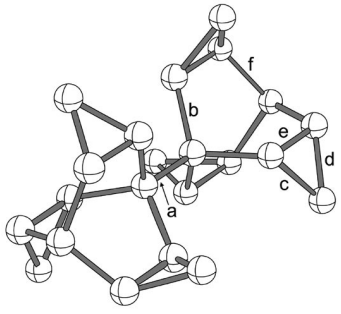


Figure 2. B3PW91/cc-pVDZ optimized geometry of (+)-1,1′-bi(trishomobarrelenyl), computed $[\alpha]_D^{25}$ = 204. Selected bond lengths: a: 1.558 Å, b: 1.542 Å, c: 1.507 Å, d: 1.507 Å, e: 1.516 Å, f: 1.531 Å.

Table 1. Optical rotations of enantiomerically pure 1,1′-bi(trishomobarrelenyl) and some other trishomobarrelene bridgehead derivatives.

Compound	$[M]_{365}^{26}$	$[\alpha]_{365}^{26}$	$[M]_D^{26}$	$[\alpha]_D^{26}$	Ref.
(+)-**4**	+281	+814	+92	+266	this work
(–)-**4**[a]	–258	–748	–86	–250	this work
(+)-**2** (X = CO_2H)	–	–	+66	+125(3)[b]	[1]
(+)-**2** (X = Cl)	–	–	+88	+159(4)[b]	[1]
(+)-**2** (X = OH)	–	–	+43	+70(2)[b]	[1]
(+)-**2** (X = OAc)	–	–	+50	+103(4)[b]	[1]

[a] Contains a small fraction of (+)-**4**. [b] Measured at 20 °C.

The agreement between the computed (gas phase) and measured ($CHCl_3$) optical rotations is quite good (Table 2) and comparable to that of the conformationally fully restricted triangulanes.[4a,4b,11] On this basis, we can assign the absolute configuration of the (*M*)-isomer being (+).

Table 2. DFT-computed optical rotations (at the B3PW91/cc-pVDZ level of theory) at various wavelengths for (+)-**4** with the configuration depicted in Figure 2 (hydrogens omitted for clarity).

Wave length	Computed $[\alpha]^{25}$ (gas phase)	Experimental $[\alpha]^{26}$ (in $HCCl_3$)
589	204	266
578	212	–
546	240	–
436	397	–
365	604	814

Conclusions

The experimentally determined and computed optical rotations of the *all*-(*S*)- and *all*-(*R*)-1,1′-bi(trishomobarrelenyl) once more confirm that helical substructures as the 1,2-dicyclopropylethane units in (+)- and (–)-**4** lead to enhanced amplitudes of the Cotton effects.

Experimental Section

General Remarks: Trishomobarrelene (**1**)[6] was prepared according to the previously published procedure. All operations in anhydrous solvents were performed under nitrogen or argon in flame-dried glassware. Hexane and Et_2O were dried by distillation from sodium/benzophenone, and CH_2Cl_2 by distillation from P_2O_5. SO_2Cl_2 was distilled prior to use. All other chemicals were used as commercially available. NMR spectra were recorded on a Bruker AM 250 (250 MHz for ^1H and 62.9 MHz for ^{13}C NMR) and a Varian Inova 600 (599.8 MHz for ^1H and 150 MHz for ^{13}C NMR) instrument. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) or APT (Attached Proton Test) measurements. Chemical shifts refer to $\delta_{TMS} = 0.00$ according to the chemical shifts of residual solvent signals. IR spectra were recorded on a Bruker IFS 66 FT-IR for KBr pellets. Low resolution mass spectra were measured with a Finnigan LCQ (ESI) or a Finnigan MAT 95 (EI at 70 eV and DCI) spectrometer. High resolution mass spectra (HRMS) were obtained with an APEX IV 7T FTICR, Bruker Daltonic (HR-ESI) or a Finnigan MAT 95 spectrometer (HR-EI). The enantioseparation of *d*,*l*-1,1′-bi(trishomobarrelenyl) (*d*,*l*-**4**) was performed by HPLC using a Chiracel OD column, (25 × 2.0 cm), EtOH/H_2O, 9:1 (4.5 mL/min), detector: RI: JASCO RI-2031 (prep. scale) or (25 × 0.46 cm), EtOH/H_2O, 9:1 (4.5 mL/min), detector: RI: JASCO RI-2031 and α: JASCO OR-990 (anal. scale). Optical rotations were measured on a JASCO *P*-1030 polarimeter. Melting points were determined on a Büchi 510 capillary melting point apparatus, values are uncorrected. TLC analyses were performed on precoated sheets, 0.25 mm Sil G/UV254 (Macherey–Nagel). Silica gel grade 60 (230–400 mesh) (Merck) was used for column chromatography.

1-Aminotrishomobarrelene (5): According to a literature published procedure,[6] trishomobarrelene (**1**) (5.00 g, 34.2 mmol) was photochlorinated with *tert*-butyl hypochlorite (5.00 g, 46.1 mmol). The crude product (6.50 g) was treated with liquid ammonia (80 mL) and anhydrous Et_2O (20 mL), and kept at 60 °C for 35 h in a Teflon-lined autoclave (500 mL). The reaction mixture was cooled to ambient temperature while evaporating excessive ammonia. The residue was taken up with 5% aq. HCl solution (50 mL) and extracted with Et_2O (5 × 50 mL). The organic extract contained trishomobarrelene (600 mg, 4.10 mmol, 12%) and 1,5-dichlorotrishombarrelene (1.75 g, 8.13 mmol, 24%). The aqueous layer was made basic by careful addition of 15% aq. NaOH and extracted with Et_2O (5 × 50 mL). The combined organic extracts were washed with brine (25 mL), dried (NaOH pellets) and the solvents evaporated. Sublimation of the residue (0.1 Torr, 80 °C) gave 2.37 g of the amine **5** (14.7 mmol, 43% based on the starting material **1**), m.p. 148 °C. IR (KBr): $\tilde{\nu}$ = 3361 (NH), 3081, 3009, 2908, 1447, 1333, 1140, 1022, 954, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.05–0.17 (m, 3 H, Cpr-H), 0.35–0.46 (m, 3 H, Cpr-H), 0.52–0.66 (m, 3 H, Cpr-H), 0.85–0.97 (m, 3 H, Cpr-H), 1.56 (br. s, 2 H, NH_2), 2.34 (q, ^3J = 4.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.6 (–, CH_2), 10.7, 17.2, 22.1 (+, CH), 48.6 (C_{quat}) . MS (EI): *m*/*z* (%) = 77 (48), 94 (89), 107 (78), 120 (100), 133 (42), 146 (37) [$C_{11}H_{14}^+$], 160 (27) [M – H], 161 (10) [M^+]. $C_{11}H_{15}N$ (161.25): calcd. C 81.94, H 9.38, N 8.69; found C 81.77, H 9.21, N 8.54. For further characterization, the amine **5** was converted into its hydrochloride: HCl gas was bubbled for 30 min through a solution of **5** (1.00 g, 6.20 mmol) in anhydrous Et_2O (80 mL). The obtained precipitate was filtered off, washed with anhydrous Et_2O (80 mL) and dried in a desiccator to give 1-aminotrishomobarrelene hydrochloride as colorless crystals, m.p. 255 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3420, 3085, 3015, 2900, 1600, 1502, 1451, 1382, 1339, 1100, 1039, 1009, 949, 922, 891, 828, 808, 708, 659, 521 cm^{-1}. $C_{11}H_{16}ClN$ (197.74): calcd. C 66.83, H 8.16, N 7.08, Cl 17.93; found C 66.48, H 8.32, N 6.95, Cl 17.67.

***N*,*N*′-Bis(trishomobarrelenyl)sulfamide (6):** A solution of the amine **5** (1.60 g, 9.92 mmol) in anhydrous hexane (20 mL) was cooled to 0 °C, and SO_2Cl_2 (243 μL, 3.00 mmol) was added dropwise. After stirring the mixture at 0 °C for 10 min, anhydrous CH_2Cl_2 (40 mL) was added, and the reaction mixture was heated at reflux for 2 h. The mixture was poured into 2 N aq. HCl (120 mL) and diluted with CH_2Cl_2 (120 mL). The phases were separated, and the aq. phase was extracted with CH_2Cl_2 (5 × 50 mL). The combined organic layers were washed with 2 N aq. HCl (40 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give 966 mg of the sulfamide **6** (2.51 mmol, 51% based on the amine, 84% based on SO_2Cl_2) as a colorless solid, m.p. 213 °C (decomp.) which was used in the next step without further purification. The aqueous layers were combined, cooled to 0 °C and made basic by careful addition of solid NaOH. The aqueous mixture was extracted with Et_2O (5 × 100 mL). The combined organic extracts were washed with brine, dried (KOH pellets) and evaporated under reduced pressure to give 891 mg of the starting material **5** which was contaminated with a small amount of Et_2O. IR (KBr): $\tilde{\nu}$ = 3310 (NH), 3080, 3010, 1425, 1331, 1320, 1289, 1258, 1148, 1108 (SO_2), 1023, 819, 802, 582 cm^{-1}. ^1H NMR ([D_6]DMSO, 600 MHz): δ = 0.07–0.12 (m, 6 H, Cpr-H), 0.54–0.59 (m, 6 H, Cpr-H), 0.88–0.92 (m, 6 H, Cpr-H), 0.96–1.02 (m, 6 H, Cpr-H), 2.25–2.29 (m, 2 H, 5,5′-H), 6.58, 6.61 (2 × br. s, 2 H, NH) ppm. ^{13}C NMR (151 MHz, [D_6]DMSO, APT): δ = 0.89, 0.91 (–, CH_2), 10.61, 10.62, 14.27, 14.29, 21.26, 21.27 (+, CH), 53.38, 53.40 (–, C_{quat}) ppm. MS (DCI, NH_3): *m*/*z* (%) = 162 (100), 385 (70) [M + H^+], 402 (97) [M + NH_4^+], 419 (4) [M + NH_3 + NH_4^+]. $C_{22}H_{28}N_2O_2S$ (384.54): calcd. C 68.72, H 7.34; found C 68.52, H 7.39.

***N*,*N*′-Bis(trishomobarrelenyl)diazene (7):** The solid sulfamide **6** (738 mg, 1.92 mmol) was treated with 15% aq. NaOH (27 mL) and aq. NaOCl (16 mL, cont. 12% Cl_2), and stirred at 40 °C for 6 h. The reaction mixture was diluted with CH_2Cl_2 (39 mL), and stir-

ring was continued at 20 °C for 15 h. H_2O (50 mL) was added, the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and Et_2O (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (75 g SiO_2, CH_2Cl_2) to give 424 mg (1.33 mmol, 69%) of the diazene **7** as a colorless solid. In a separate run, starting with 192 mg of the sulfamide **6**, 124 mg of **7** (78%) was obtained, m.p. 203–205 °C. IR (KBr): $\tilde{\nu}$ = 3075, 2995, 2900, 1439, 1321, 1258, 1099, 1030, 958, 800, 701, 660, 645 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.18–0.30 (m, 6 H, Cpr-H), 0.64–0.76 (m, 6 H, Cpr-H), 0.80–0.92 (m, 6 H, Cpr-H), 0.97–1.07 (m, 6 H, Cpr-H), 2.49 (q, ^3J = 5.0 Hz, 2 H, 5,5′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.2 (–, CH), 10.5, 13.7, 13.8, 23.5 (+, CH), 70.1 (C_{quat}) ppm. MS (ESI): *m*/*z* (%) = 319 (100) [M$^+$ + H], 341 (96) [M$^+$ + Na], 659 (36) [2M$^+$ + Na]. HRMS (ESI): *m*/*z*: calcd. for $C_{22}H_{27}N_2$: 319.2174; found 319.2169 [M$^+$ + H], calcd. for $C_{22}H_{26}N_2Na$: 341.1994; found 341.1988 [M$^+$ + Na]. $C_{22}H_{26}N_2$ (318.46): calcd. C 82.97, H 8.23, N 8.80; found C 82.11, H 8.24, N 8.62.

1,1′-Bi(trishomobarrelenyl) (4): A solution of the diazene **7** (263 mg, 826 μmol) in *t*BuOH/*t*BuOMe (ratio 8:2, 75 mL) was irradiated with a medium pressure mercury lamp (450 W, Pyrex filter) for 33 h. The reaction mixture was concentrated under reduced pressure at 30 °C. The residue was taken up with Et_2O (150 mL) and the solution washed with H_2O (3 × 150 mL). The organic layer was dried (Na_2SO_4), and the solvents were removed by distillation through a column packed with glass helices. The residue was purified by column chromatography (20 g SiO_2, CH_2Cl_2) to give 165 mg of 1,1′-bi(trishomobarrelenyl) (**4**) (568 μmol, 69%) as a 1:1 mixture of the *d*,*l*- and *meso*-isomer as a colorless solid. The stereoisomers were separated by preparative HPLC on a chiral phase column. Further elution with Et_2O gave 28 mg 1-hydroxytrishomobarrelene[6] (173 μmol, 10%) as a colorless solid. ***meso*-4:** M.p. 259 °C. IR (KBr): $\tilde{\nu}$ = 3085, 3008, 2963, 2899, 1439, 1333, 1105, 1026, 969, 947, 879, 814, 802, 673 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.03–0.09 (m, 6 H, Cpr-H), 0.46–0.52 (m, 6 H, Cpr-H), 0.68–0.73 (m, 6 H, Cpr-H), 0.79–0.83 (m, 6 H, Cpr-H), 2.37 (q, ^3J = 5.0 Hz, 2 H, 5,5′-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, APT): δ = 1.2 (–, CH_2), 9.1, 10.8, 22.6 (+, CH_3), 37.9 (–, C_{quat}) ppm. MS (EI): *m*/*z* (%) = 145 (100) [$C_{11}H_{14}^+$ – H], 290 (16) [M$^+$]. HRMS (EI): *m*/*z*: calcd. for $C_{22}H_{26}$: 290.2034; found 290.2029 [M$^+$]. $C_{22}H_{26}$ (290.45): C 90.98, H 9.02; found C 90.74, H 8.89. ***d*,*l*-4:** ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.03–0.09 (m, 6 H, Cpr-H), 0.46–0.52 (m, 6 H, Cpr-H), 0.61–0.65 (m, 6 H, Cpr-H), 0.79–0.83 (m, 6 H, Cpr-H), 2.35 (q, ^3J = 5.0 Hz, 2 H, 5,5′-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, APT): δ = 1.0 (–, CH_2), 9.2, 10.8, 22.9 (+, CH_3), 36.9 (–, C_{quat}). (–)-**4:** M.p. 172 °C. (+)-**4:** M.p. 182 °C ppm.

Crystal Structure Determination: Suitable crystals of *meso*-1,1′-bi(trishomobarrelenyl) (**4**) for X-ray crystal structure determination were obtained by slow evaporation of the solvent from a solution of the 1:1 mixture of *meso*- and *d*,*l*-**4** in pentane. The X-ray data were collected on a Bruker SMART CCD 6000 diffractometer at 100 K (λ = 1.54178 Å). The structure was solved by direct methods with SHELXS and refined by full-matrix least-squares on F^2 for all data with SHELXL.[12] Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were placed on calculated positions. Crystallographic data and parameters of the refinements are listed in Table 3.

Computational Methods: Geometries were optimized and structures were classified as minima on the potential energy hypersurface by vibrational frequency analysis using density functional theory computations at the B3PW91/cc-pVDZ level[10] as implemented in Gaussian03.[13] This level has proven to be particularly suitable for the computation of hydrocarbon structures and energies.[14] In order to be able to assign the absolute configuration of 1,1′-bi(trishomobarrelenyl), the optical rotations (ORD) at 589, 578, 546, 436, and 365 nm were computed employing linear response theory; this technique has previously been shown to have similar accuracy as TD-DFT at a significant reduction in computating costs.[15] Furthermore, it has previously provided excellent matches with experimental ORDs for σ-helicenes (triangulanes) and other organic compounds.[4a,4b,11]

Table 3. Crystallographic data and parameters of the refinements of compound *meso*-**4**.

	meso-**4**
Empirical formula	$C_{22}H_{26}$
Formula weight [g/mol]	290.43
Crystal system	trigonal
Space group	$R\bar{3}$
Unit cell dimensions	
a [Å]	10.7645(15)
b [Å]	10.7645(15)
c [Å]	11.061(2)
α [°]	90
β [°]	90
γ [°]	120
Volume [Å^3]	1110.0(3)
Z	3
Density (calculated) [Mg/m^3]	1.303
Absorption coefficient [mm^{-1}]	0.539
F(000)	474
Crystal size [mm^3]	0.30 × 0.20 × 0.20
θ Range for data collection [°]	6.21 to 58.61
Reflections collected	4290
Independent reflections [R_{int}]	352 [0.0358]
Data/restraints/parameters	352/96/55
Goof on F^2	1.051
R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0285, 0.06
R_1, wR_2 indices (all data)	0.0285, 0.0691
Extinction coefficient	0.0071(8)
Largest diff. peak and hole [e·Å^{-3}]	0.131 and –0.148

Supporting Information (see also the footnote on the first page of this article): Gaussian archive entries including levels of theory, *x*,*y*,*z*-coordinates, point groups, and energies of the enantiomeric (+)- and (–)-stereoisomers (+)- and (–)-**4** as well as the diastereomeric *meso*-**4**.

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