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Heterocyclic Chemistry

λ^5-Phospha[7]helicenes: Synthesis, Properties, and Columnar Aggregation with One-Way Chirality**

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Helical extension of π-conjugated systems is of great interest for the production of novel molecules and materials with unusual properties and applications. A typical example is helical polyacetylenes, in which continuous π conjugation is achieved through covalent bonds.[1,2] Another example is the assembly of short helical fragments, such as helicenes.[3,4] For instance, helicenebisquinone derivatives were reported to form one-dimensional columnar aggregates with the aid of long alkyl side chains.[5] Unique optical properties, such as high nonlinear optical susceptibility[5c,f] and circularly polarized luminescence, were reported for these aggregates.[5e,6] Single crystals would also be suitable for creating such architectures if the π-conjugated helical molecules are appropriately stacked. Nevertheless, our analysis of the Cambridge Crystallographic Database revealed that structures with one-dimensional columnar helicene packing that is driven by π–π stacking interactions are rather uncommon,[7] and in the majority of structures with helicene packing, the packing is noncolumnar and mostly driven by CH-π interactions. We hypothesized that the use of dipole–dipole interactions in addition to inherent π–π stacking interactions might produce a one-dimensional columnar arrangement of helicenes. Dipole–dipole interactions have been used as part of systems that contain cooperative interactions for the formation of one-dimensional molecular arrangements.[8] Theoretical studies on the corannulene dimer have also demonstrated that dipole–dipole interactions should be a significant part of the binding energy of bowl-shaped molecules.[9] Previously, we have reported the synthesis of oxa- and aza[7]helicenes **3** and **4** by using palladium-catalyzed reactions.[10] These helicenes do not possess dipole-moment vectors that are parallel to their helical axes, and no one-dimentional columnar stack was formed. Herein, we report the preparation of λ^5-phospha[7]helicenes **1** and **2** as a new family of helicenes.[11,12] The phosphole oxide and phosphole sulfide moieties give these helicenes a dipole-moment vector that is parallel to their helical axes, and thus the columnar stacking of **1** and **2** was achieved. More importantly, a racemate of phosphole sulfide **2** crystallized with a unique packing motif: the columns with one dipole direction consist of a single enantiomer and the columns with the opposite dipole direction consist of the other enantiomer (Figure 1).

λ^5-Phospha[7]helicenes **1** and **2** were synthesized as shown in Scheme 1. A racemic 4,4′-biphenanthryl-3,3′-diyl bis(trifluoromethanesulfonate, *rac*-**6**), from which we previously synthesized aza[7]helicene,[10] was selected as the starting compound. The palladium-catalyzed cross-coupling of *rac*-**6** with ethyl phenylphosphinate gave a 46% yield of the monophosphrous compound *rac*-**7** as a mixture of diastereomers (axial chirality and *P*-centered chirality).[13] λ^3-Phospha[7]helicene *rac*-**9**, which has a phosphole moiety, was obtained by the reduction of *rac*-**7** with $LiAlH_4$[13c,14] and a subsequent palladium-catalyzed intramolecular P-arylation.

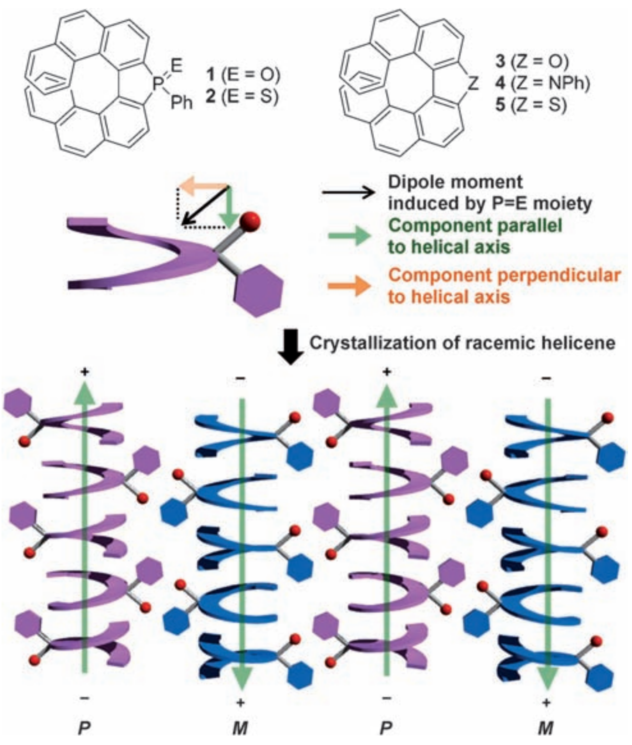

Figure 1. Structures of heterohelicenes and a representation of the columnar packing in a single crystal of *rac*-**2**. Columns with a given dipole moment consist of a single enantiomer (*P* or *M* isomer) and columns with the opposite dipole moment consist of the other enantiomer.

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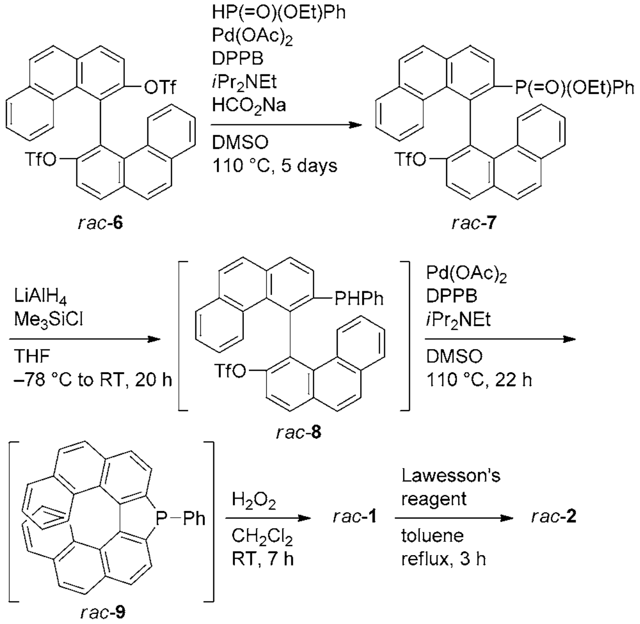

Scheme 1. Synthesis of λ^5-phospha[7]helicenes **1** and **2**. DPPB = 1,4-bis(diphenylphosphino)butane; Tf = trifluoromethanesulfonyl.

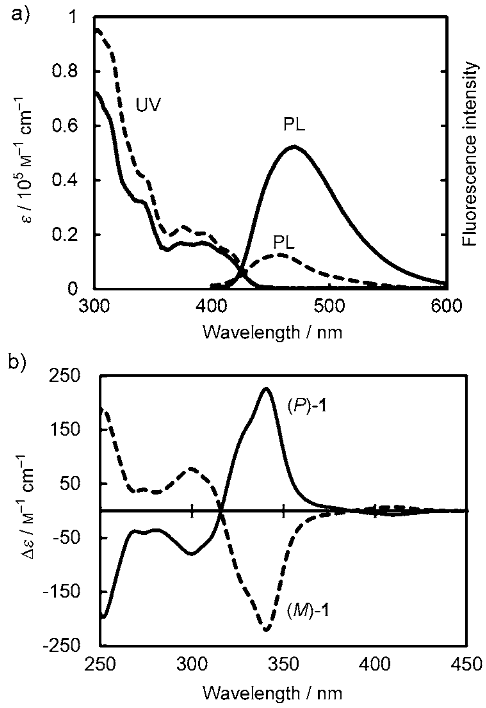

Figure 2. a) UV/Vis absorption (UV) and photoluminescence spectra (PL) of (*P*)-**1** (solid line, 2.4×10^{-6} M) and (*P*)-**2** (dashed line, 7.5×10^{-6} M) in CHCl$_3$ solution. b) CD spectra of **1** (1.6×10^{-5} M for both enantiomers, CHCl$_3$ solution).

As the phosphorus center of *rac*-**9** is susceptible to oxidation under ambient conditions, *rac*-**9** was directly oxidized without purification to give racemic λ^5-phospha[7]helicene *rac*-**1**, which has a phosphole oxide moiety, in a 34 % overall yield from *rac*-**7**. λ^5-Phospha[7]helicene *rac*-**2**, which has a phosphole sulfide moiety, was synthesized from *rac*-**1** in 97 % yield by using Lawesson's reagent. Racemic **1** was separated into enantiopure (*P*)-**1** and (*M*)-**1** by HPLC on a chiral stationary phase. The absolute configuration of enantiopure **1** in each fraction was determined by X-ray crystallographic analysis (see below). In contrast, *rac*-**2** could not be separated into enantiopure forms by HPLC. Therefore, both (*P*)-**2** and (*M*)-**2** were synthesized from enantiopure (*P*)-**1** and (*M*)-**1**, respectively.[15]

The photophysical properties of λ^5-phospha[7]helicenes **1** and **2** were evaluated by UV/Vis absorption and photoluminescence spectroscopy (Figure 2), cyclic voltammetry, and theoretical calculations. The photophysical data are summarized in Table S5 in the Supporting Information. Both λ^5-phospha[7]helicenes **1** and **2** have almost identical spectra. The longest absorption maxima (λ_{abs}) at 416 nm of **1** and **2** (Figure 2 a) are significantly red-shifted relative to that of 5-phenyldibenzophosphole-5-oxide (332 nm), 5-phenyldibenzophosphole-5-sulfide (330 nm),[12f] and phenanthrene (293 nm), which indicates effective π conjugation over the helical frameworks. The absorption edges of **1** and **2** were both at 432 nm, which are red-shifted relative to the related hetero[7]helicenes **3**–**5**.[10,16] The HOMO–LUMO energy gaps of 2.87 eV that were estimated from the absorption edges agree with those calculated by DFT calculations at the B3LYP/6-31G(d) level (see the Supporting Information). Cyclic voltammetry experiments show two irreversible oxidation waves for **1** and **2**, and the HOMO energy levels (E_{HOMO}) of **1** and **2** were estimated to be −5.90 eV and −5.87 eV, respectively (see the Supporting Information). λ^5-Phospha[7]helicenes **1** and **2** have similar broad luminescent spectra with maxima (λ_{em}) at 462 nm and 460 nm, respectively, in solution. Thus, larger Stokes shifts were observed for both λ^5-phospha[7]helicenes (2390 cm^{-1} for **1** and 2800 cm^{-1} for *rac*-**2**) than for **3** and **4** (650 cm^{-1} for **3** and 580 cm^{-1} for **4**). Such large Stokes shift are common for phosphole-containing compounds and suggest a large rearrangement of the π-conjugated framework upon photoexcitation.[17] The quantum yield of **1** in solution is 7.8 %, whereas the quantum yield in the solid state is much lower (0.1 %). In contrast, **2** has a low quantum yield of 0.1 % both in solution and in the solid state. Based on DFT calculations for **1** and **2**, the HOMOs are mainly located on the two phenanthrene moieties and chalcogen atoms, and contain a nodal plane at the phosphorus atom (see the Supporting Information). In contrast, the LUMOs are largely located on the phosphole/chalcogenide moieties, where (thio)phosphoryl groups work as an electron-withdrawing group through σ*–π* hyperconjugation. Such electronic perturbation of the phosphole/chalcogenide moieties may cause an intramolecular charge transfer to induce a large Stokes shift.

The optical properties of **1** and **2** that are imparted by their chiral structures were characterized. Similar to other known (*P*)-heterohelicenes, both (*P*)-**1** and (*P*)-**2** are dextrorotatory. The specific rotations $[\alpha]_D$ of (*P*)-**1** and (*P*)-**2** are +3014 (c = 0.10, CHCl$_3$) and +3198 (c = 0.10, CHCl$_3$), respectively, which are much larger than those of **3** and **4** (see below). The circular dichroism (CD) spectra of (*P*)-**1** and (*P*)-**2** had a small negative dichroic signal at around 410 nm, a intense positive signal around 340 nm, and a relatively intense negative signal around 250 nm (Figure 2b). This trend is similar to that of the known (*P*)-heterohelicenes.[10,16b,18] In contrast, the dichroic signs of (*P*)-**1** and (*P*)-**2** at around 300 nm are opposite to that of the known (*P*)-heterohelicenes.

The structures of **1** and **2** were confirmed by single-crystal X-ray analysis.[19] Single crystals that were suitable for X-ray analysis were obtained from *rac*-**1**, enantiopure (*P*)-**1**, enantiopure (*M*)-**1**, *rac*-**2**, and enantiopure (*M*)-**2**. It is noteworthy that whereas a single crystal of *rac*-**1** contained only one enantiomer by spontaneous resolution, a racemic crystal that contained both enantiomers was obtained with *rac*-**2**. The absolute configuration of enantiopure **1** with the longer HPLC retention time was confirmed to be the *P* configuration by the refinement of the Flack parameter with data collected by using Cu *K*α radiation (see the Supporting Information). Accordingly, the absolute configuration of enantiopure **1** and **2** was determined. Helicenes **1** and **2** have more distorted structures than the other heterohelicenes: the sums of the five dihedral angles that are derived from the seven C–C bonds [C(17)-C(17a)-C(17b)-C(17c), C(17a)-C(17b)-C(17c)-C(17d), C(17b)-C(17c)-C(17d)-C(17e), C(17c)-C(17d)-C(17e)-C(17f), and C(17d)-C(17e)-C(17f)-C(1)] are 95.2° for **1** (based on the crystallographic data of enantiopure (*M*)-**1**, Figure 3) and 99.6° for **2** (based on the crystallographic data of *rac*-**2**). These angles are larger than those of hetero[7]-helicenes **3**–**5** (79–88°). This can be attributed to the larger angles between the two double bonds of phosphole oxide (50°) and phosphole sulfide (50°) relative to furan (32°), pyrrole (35°), and thiophene (45°): the larger angle causes a larger overlap of the two terminal benzene rings in the λ^5-phospha[7]helicenes and, therefore, a stronger steric repulsion (see the Supporting Information). These larger distortions in **1** and **2** explain the higher tolerance of **1** and **2** towards racemization. The enantiopurity of **1** and **2** did not decrease after heating the compounds to 170 °C for 68 h in CH_2Cl_2, whereas the enantiopurity of **3** and **4** did decrease after heating (**3**: from > 90 % *ee* to 40 % *ee* at 150 °C for 20 min in mesitylene; **4**: from 99 % *ee* to 40 % *ee* at 150 °C for 68 h in mesitylene). The larger specific rotations of enantiopure **1** and **2** might also be attributed to their more-distorted structures.

The packing structures in the single crystals of *rac*-**2** and enantiopure (*M*)-**2** are shown in Figure 3b–3e.[20] Columnar alignments of the π systems were detected for the racemate and for the single enantiomer of **2**, as well as the single enantiomer of **1**. In these structures, each column consists of helicenes with a staggered packing pattern (Figure 3b,c). The intermolecular, face-to-face, π–π interaction distances of (*M*)-**1**, *rac*-**2**, and (*M*)-**2** are 3.44 Å, 3.35 Å, and 3.46 Å, respectively. The dipole-moment vectors that are perpendicular to the helical axis cancel each other through the two interacting molecules, whereas the vectors that are parallel to the axis are aligned in one column. Neighboring columns have opposite dipole-moment vectors that cancel each other and the overall dipole moment. Most notable is the packing of *rac*-**2**. Each column contains a single enantiomer of either (*P*)-**2** or (*M*)-**2**. As shown in Figure 3d, all of the columns that contain (*P*)-**2** have dipole moments from the bottom to the top and all of the columns that contain (*M*)-**2** have dipole moments in the opposite direction, from the top to the bottom. Thus, the crystal is chirally anisotropic. In other words, if chirality can be sensed to differentiate (*P*)-**2** from (*M*)-**2** (or (*M*)-**2** from (*P*)-**2**), the moment is a one-way street from bottom to top (or top to bottom, Figure 1).[21]

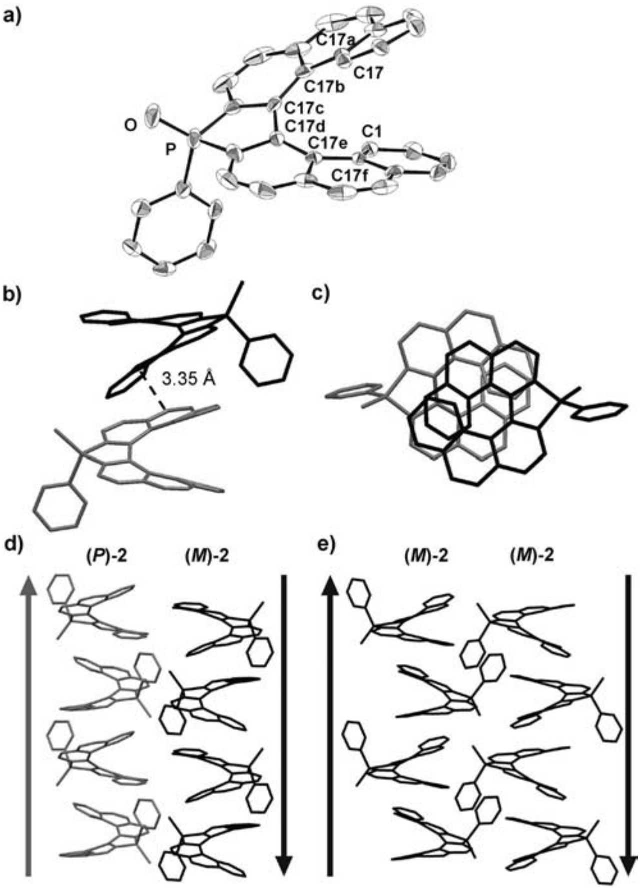

Figure 3. X-ray structures of λ^5-phospha[7]helicenes: a) ORTEP drawings of (*M*)-**1** packing in the single-crystal structure of *rac*-**2** (the single crystal was obtained from enantiopure (*M*)-**1**; 50 % thermal ellipsoids; all hydrogen atoms are omitted for clarity). b) Side and c) top views of (*P*)-**2** and (*M*)-**2** in the racemic crystal structure of *rac*-**2**. d) Columnar arrangement of (*P*)-**2** and (*M*)-**2** in the single-crystal structure of *rac*-**2**. e) Columnar arrangement of (*M*)-**2** in the single-crystal structure of (*M*)-**2**.

In conclusion, we have developed a new synthetic approach to λ^5-phospha[7]helicenes and revealed their unique packing structures. One-dimentional columnar packing of the λ^5-phospha[7]helicenes, which achieves the ideal π–π stacking of the helicenes, was successfully created with the aid of dipole moments. A racemate of phosphole sulfide **2** exhibited a unique packing structure that creates "one-way chirality".

Experimental Section

A mixture of $LiAlH_4$ (55 mg, 1.46 mmol) in THF (7.3 mL) was placed in a 20 mL Schlenk tube under argon and cooled to −78 °C in a dry ice/acetone bath. Me_3SiCl (126 μL, 1.46 mmol) was added to the white suspension of $LiAlH_4$ and the resulting mixture was warmed to room temperature and stirred for 1 h. The resulting colorless solution was then cooled to −42 °C in a dry ice/acetonitrile bath. *rac*-**7** (210 mg, 0.31 mmol) was dissolved in tetrahydrofuran (6.0 mL) and this solution was added slowly to the $Me_3SiCl/LiAlH_4$ mixture. The reaction mixture was warmed to room temperature and stirred for 16 h, then cooled to 0 °C and quenched with degassed ethyl acetate (0.5 mL) and degassed water (0.5 mL). After stirring the mixture at room temperature for 15 min, it was filtered through a pad of basic alumina, under argon. The filtrate was concentrated under reduced pressure to yield a diastereomeric mixture of *rac*-**8** (187 mg). ^{31}P NMR (500 MHz, $[D_8]THF$): $\delta = -44.9, -45.1$ ppm].

A mixture of *rac*-**8** (187 mg, 0.31 mmol), $Pd(OAc)_2$ (6.9 mg, 0.031 mmol), 1,4-bis(diphenylphosphino)butane (DPPB, 13 mg, 0.031 mmol), $i\text{Pr}_2NEt$ (186 µL, 1.07 mmol) in DMSO (3.0 mL) was placed in a 100 mL Schlenk tube and degassed by three freeze-pump-thaw cycles. After stirring under argon at 110 °C for 79 h, the reaction mixture was cooled to ambient temperature and diluted with CH_2Cl_2 (10 mL), then aqueous H_2O_2 (30–35 %) was added. The resulting mixture was stirred at room temperature for 12 h. Water (20 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (10 mL × 5). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel with gradient elution from CH_2Cl_2 to CH_2Cl_2/ethyl acetate (4:1) to give *rac*-**1** as a yellow solid (49 mg, 34 % from *rac*-**7**, $R_f = 0.30$(ethyl acetate)).

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[15] Although the enantiopurity of (*P*)-**2** and (*M*)-**2** could not be estimated by HPLC analysis, the transformation of (*P*)-**1** and (*M*)-**1** to (*P*)-**2** and (*M*)-**2**, respectively, was assumed to proceed without any loss of enantipurity, as no decrease in the enantiopurity of (*P*)-**1** was observed after heating it to 170 °C for 64 h in 1,2-dichlorobenzene.

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[19] Crystal data for (*P*)-**1**: $C_{34}H_{22}O_{1.5}P$; $M_r = 485.52$; $a = 10.113(4)$, $b = 12.110(6)$, $c = 19.665(9)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 2408(2)$ Å^3; $T = 93(2)$ K; orthorhombic; space group $P2_12_12_1$; $Z = 4$; $\mu = 1.231$ mm^{-1}; $\rho_{calcd} = 1.339$ g cm^{-3}; 35 543 reflections measured; 4404 unique reflections ($R_{int} = 0.1014$); final $R_1 = 0.0826$; $wR_2 = 0.2177$ [$I > 2.0\sigma(I)$]. (*M*)-**1**: $C_{34}H_{21}OP$; $M_r = 476.48$; $a = 10.050(6)$, $b = 12.175(7)$, $c = 19.520(11)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 2389(2)$ Å^3; $T = 103(2)$ K; orthorhombic; space group $P2_12_12_1$; $Z = 4$; $\mu = 0.142$ mm^{-1}; $\rho_{calcd} = 1.325$ g cm^{-3}; 15 536 reflections measured; 4187 unique reflections ($R_{int} = 0.0319$), final $R_1 = 0.0630$; $wR_2 = 0.1397$ [$I > 2.0\sigma(I)$]. *rac*-**2**: $C_{34}H_{21}PS$; $M_r = 492.54$; $a = 26.353(10)$, $b = 12.458(4)$, $c = 19.163(8)$ Å; $\alpha = \gamma = 90°$; $\beta = 130.0975(11)°$; $V = 4813(3)$ Å^3; $T = 103(2)$ K; monoclinic; space group $C2/c$; $Z = 8$; $\mu = 0.224$ mm^{-1}; $\rho_{calcd} = 1.360$ g cm^{-3}; 15 314 reflections measured; 4187 unique reflections ($R_{int} = 0.0566$); final $R_1 = 0.0681$; $wR_2 = 0.1217$ [$I > 2.0\sigma(I)$]. (*M*)-**2**: $C_{34}H_{21}PS$; $M_r = 492.54$; $a = 10.055(3)$, $b = 12.389(4)$, $c = 20.027(6)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 2494.6(13)$ Å^3; $T = 93(2)$ K; orthorhombic; space group $P2_12_12_1$; $Z = 4$; $\mu = 0.216$ mm^{-1}; $\rho_{calcd} = 1.311$ g cm^{-3}; 16 935 reflections measured; 4376 unique reflections ($R_{int} = 0.0591$); final $R_1 = 0.1024$; $wR_2 = 0.2833$ [$I > 2.0\sigma(I)$]. CCDC 851214 [(*P*)-**1**], 841807 [(*M*)-**1**], 841809 [*rac*-**2**], and 841808 [(*M*)-**2**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystal data of the single crystal from *rac*-**1** is not described since the enantiopure crystal was obtained by spontaneous resolution, and the crystallographic data was the same as that for the single crystal of enantiopure (*M*)-**1**.

[20] Note that none of the previous O-, S-, or N-containing [7]helicenes form such columnar aggregates.

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