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Synthesis of Cyclophanes with Planar and Helical Chirality

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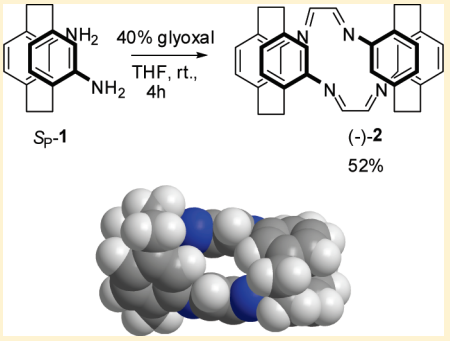
Supporting Information

ABSTRACT: Novel helical macrocyclic imines derived from planar chiral [2.2]-paracyclophane were synthesized. The chiroptical properties of the enantiopure compounds were investigated and their absolute configurations were assigned.



Helicenes and helicene-like systems that consist of aromatic ortho condensed rings with helical chirality have attracted great interest due to their unique structure features[1] as well as potential application in chiral materials,[2] chiral molecular recognition,[3] and asymmetry synthesis.[4] Since the chirality of helicene was discovered by Newman in the 1950s,[5] a variety of derivatives have been prepared,[6] while few helical systems based on planar chiral molecules were chosen for detailed study.[7]

[2.2]Paracyclophane, systematically investigated by Cram and his co-workers from 1951,[8] is still of great interest. [2.2]-Paracyclophane is a three-dimensional aromatic molecule with a rigid arrangement of parallel, eclipsed benzene rings. The rigid framework of these compounds with D_{2h} symmetry becomes planar chiral by substitution of one benzene ring. [2.2]-Paracyclophane derivatives have found applications in synthetic chemistry[9,10] and materials science.[11] Herein, we report a novel class of helical compounds with planar chiral based on [2.2]paracyclophane and describe the intramolecular planar-to-helical chirality transfer.

The strategy for the preparation of our helical scaffold relies on a condensation of glyoxal and diamino[2.2]paracyclophane. Condensation of glyoxal and S_p-4,12-diamino[2.2]paracyclophane (**1**)[12] afforded the macrocyclic imine (−)-**2** in 52% yield accompanied by some polymeric materials (Scheme 1).[13] The yield was not high, but the raw material could be recovered by the reaction of the polymeric material with hydroxylamine. The enantiomer of the macrocyclic imine (+)-**2** was also prepared by the reaction of glyoxal with corresponding R_p-**1** in similar yield.

The analogue imine (−)-**6** was prepared as shown in Scheme 2. After condensation of S_p-4-amino-12-bromo[2.2]paracyclophane (**3**)[12] with glyoxal, the resulting diimine was converted to *N*,*N*′-bis[S_p-12-bromo-4-[2.2]paracyclophanyl]-1,2-ethylenediamine (**4**). The diamine **4** underwent Buchwald−Hartwig reaction, and the resulting *N*,*N*′-Bis[S_p-12-benzhydrylideneamino-4-[2.2]paracyclophanyl]-1,2-ethylenediamine was hydrolyzed into *N*,*N*′-bis[S_p-12-amino-4-[2.2]paracyclophanyl]-1,2-ethylenediamine (**5**). Condensation of glyoxal and the diamine **5** gave the macrocyclic imine (−)-**6** in 48% yield.

Analogous compounds (+)-**10**−**12** were also prepared (Scheme 3). R_p-4-Hydroxyl-12-benzhydrylideneamino[2.2]paracyclophane (**7**)[12] was reacted with *p*-toluenesulfonates **8a**−**c**, and the resulting compounds were hydrolyzed to the diamines **9a**−**c**. Condensation of glyoxal and the diamines **9a**−**c** afforded the macrocyclic imines (+)-**10**−**12** in moderate yield.

First, we studied the absolute configuration of the imine (−)-**2** by X-ray crystallography. Single-crystal X-ray diffraction analysis of (−)-**2**, which was obtained by slow diffusion of *n*-hexane into a chloroform solution in a dark room, showed a unique structure. The X-ray structure of (−)-**2** showed helical twist of the macrocyclic imine system with 72.1° and 71.6° dihedral angles between the planes of the benzene rings linked by C═N bonds in different [2.2]paracyclophane moieties. Thus, we could ascribe unambiguously (*M*)-helicity to the structure.

The chirality of (−)-**2** was also reflected by its optical properties (Figure 1, Table 1). The magnitudes of the specific rotation ($[\alpha]^{20}_{D}$ −4350) and the CD spectrum are both large. It is well-known that the negative sign of specific rotation is usually found for *M* [*n*]helicenes and a positive sign for *P* [*n*]helicenes.[1a,b,14] For (−)-**2**, we found an agreement with the phenomenon. The CD spectrum of (*M*)-helical (−)-**2** is dominated by strongly negative dichroisms, and the CD spectrum of (+)-**2** is opposite in sign, but equal in magnitude, which reveals that the (−)-**2** and (+)-**2** are enantiomers, and (+)-**2** is (*P*)-helical.

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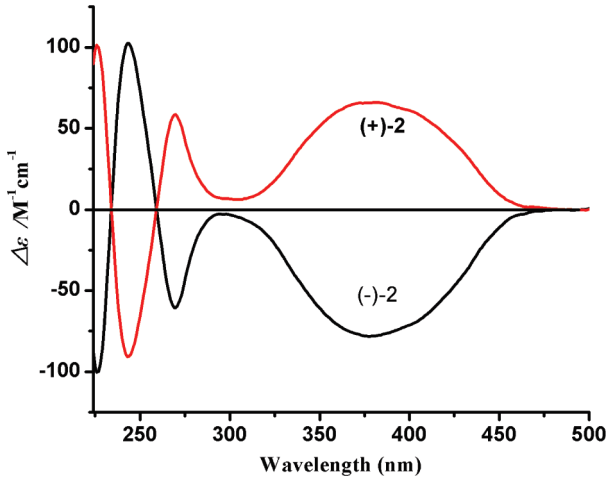
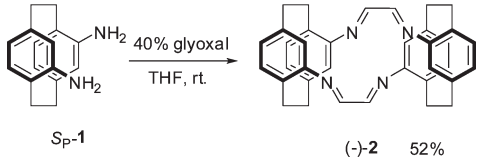
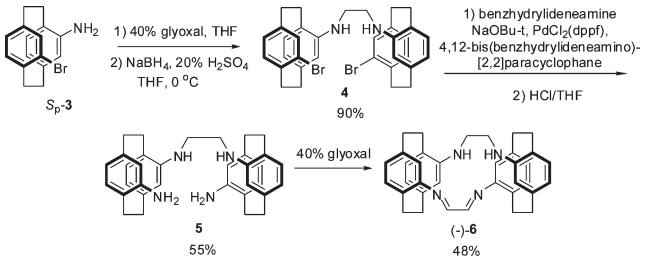


Figure 1. CD spectra of (−)-**2** and (+)-**2** in CH_2Cl_2.

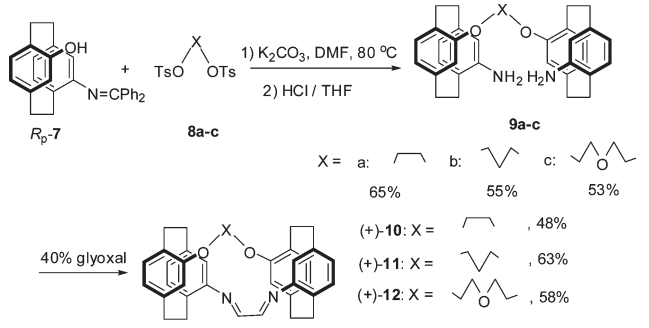
Scheme 1. Synthesis of Macrocyclic Imine (−)-2



Scheme 2. Synthesis of Macrocyclic Imine (−)-6



Scheme 3. Synthesis of Macrocyclic Imine (+)-10−12



Macrocyclic imine (−)-**6** and (+)-**10**−**12** formed yellow needlelike crystals upon recrystallization, but none of them were suitable for single-crystal X-ray diffraction analysis. To assign the helicity of the compounds, their CD spectra in CH_2Cl_2 were measured (Figure 2). (−)-**6** was compared with (−)-**2**, as they have similar structure. For (−)-**6**, the dichroisms at 244, 272, 286, and 381 nm are similar in shape to the dichroisms at 243, 270, 305, and 381 nm in (−)-**2**, indicating that (−)-**6** is (*M*)-helical. (+)-**10** was compared to (−)-**6**, as they could be viewed as *pseudo*-enantiomers. Not surprisingly, the curves observed for the two imines are almost mirror imagines. This comparison implies that (+)-**10** is (*P*)-helical. Similarly, (+)-**11** and (+)-**12** could also be assigned to (*P*)-helicity. Overall, these observations are consistent with *P* helicity for dextrorotatory [*n*]helicene and *M* helicity for the laevorotatory [*n*]helicene.

Table 1. Specific Rotation of (−)-2, (+)-2, (−)-6, and (+)-10−12

compd	$[\alpha]^{20}_D$	$[M]_D$
(−)-**2**	−4351	−22627
(+)-**2**	+4316	+22442
(−)-**6**	−2342	−12270
(+)-**10**	+2032	+10687
(+)-**11**	+2344	+12658
(+)-**12**	+1570	+8949

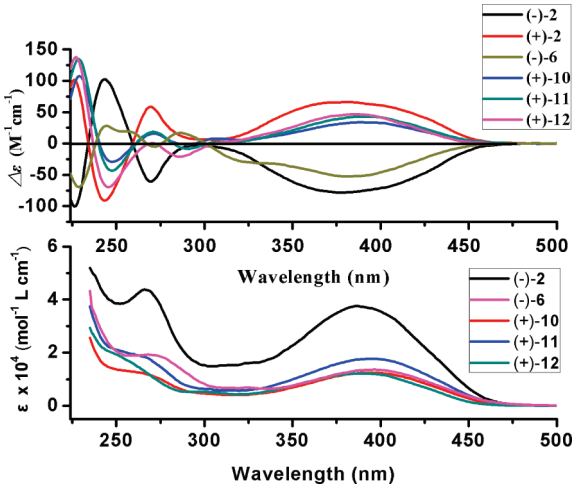


Figure 2. CD and UV−vis spectra of (−)-**2**, (+)-**2**, (−)-**6**, and (+)-**10**−**12** in CH_2Cl_2.

In conclusion, we have asymmetrically synthesized a novel class of helical macrocyclic imines derived from planar chiral [2.2]paracyclophane. All these compounds were characterized in detail. From the X-ray crystallography and CD spectra, the absolute helicity of the compounds was determined.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Macrocyclic Imine (−)-2. S_p-4,12-Diamino[2.2]paracyclophane (**1**) (280 mg, 1.18 mmol) and 40% glyoxal (0.22 mL, 1.76 mmol) in THF (5.0 mL) were stirred at room temperature for 4 h. After completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure to give a residue, which was purified by column chromatography on silica gel, using CH_2Cl_2 as eluent, to give the desired product (−)-**2** as a yellow solid. Yield 160 mg (52%); mp >250 °C dec; $[\alpha]^{20}_D$ −4351 (*c* 0.048, CH_2Cl_2); $[M]_D$ = −22627; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.77−2.97 (m, 8H), 3.31−3.43 (m, 4H), 3.83−3.95 (m, 4H), 6.40 (s, 4H), 6.56−6.64 (m, 8H), 8.11 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ

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(ppm) 30.1, 34.4, 123.0, 133.7, 134.0, 137.6, 142.2, 147.1, 156.9; HRMS (ESI) mass calcd for $C_{36}H_{33}N_4$ [$M^+ + H$] 521.2705, found 521.2722; UV−vis (CH_2Cl_2, 2.0×10^{-5} M) λ_{max} (ε_{max}) = 387 (3.75×10^4), 266 nm (4.37×10^4); CD (CH_2Cl_2, 1.92×10^{-4} M, 0.1 cm cell) 377 nm (θ = −49.5, $\Delta\varepsilon$ = −78.1), 270 nm (θ = −38.3, $\Delta\varepsilon$ = −60.4), 243 nm (θ = 65.0, $\Delta\varepsilon$ = 102.6), 226 nm (θ = −63.6, $\Delta\varepsilon$ = −100.5).

General Procedure for the Synthesis of Macrocyclic Imine (−)-6. Following the general procedure for the synthesis of (−)-**2**, starting from S_p-4-amino-12-bromo[2.2]paracyclophane (**3**), *N*,*N*′-bis-[S_p-12-bromo-4-[2,2]paracyclophanyl]glyoxal diimine was obtained. To a suspension of the diimine and $NaBH_4$ (0.79 g, 20.81 mmol) in THF (4.0 mL) were added a mixture of 20% aqueous solution of sulfuric acid (1.4 mL, 3.26 mmol) and 2.0 mL of THF dropwise over a period of 1 h at 0 °C. After the mixture was stirred at 0 °C for another 2 h, the yellow color fading, a white precipitate formed. To the mixture were added 5.0 mL of ice−water and subsequently 5.0 mL of 3 M hydrochloric acid. A colorless solid precipitated and saturated NaOH was added dropwise until the stirred mixture tested basic (pH 9). The solution was extracted with CH_2Cl_2 (3 × 3.0 mL), and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 10:1), and pure product **4** was isolated as a crystalline white solid. Yield 0.92 g (89%); mp 233−234 °C; $[\alpha]^{20}_D$ −93.2 (*c* 0.43, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.55−2.87 (m, 4H), 2.90−3.23 (m, 10H), 3.32−3.54 (m, 4H), 3.54−3.68 (m, 2H), 3.74 (br, 2H), 6.06−6.15 (m, 2H), 6.15−6.25 (m, 2H), 6.25−6.45 (m, 4H), 6.51−6.59 (m, 2H), 7.05−7.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 32.2, 32.7, 33.3, 35.6, 42.9, 113.0, 121.4, 124.2, 125.8, 131.4, 131.9, 134.4, 135.1, 138.2, 141.1, 141.6, 146.3. Anal. Calcd for $C_{34}H_{34}Br_2N_2$ (630.45): C, 64.77; H, 5.44; N, 4.44. Found: C, 64.47; H, 5.42; N, 4.22.

The amination reaction was performed according to our published work.[12] In a glovebox, an oven-dried Schlenk flask was charged with aryl diamine **4** (840 mg, 1.33 mmol), $PdCl_2$(dppf) (10.9 mg, 1.33×10^{-2} mmol), 4,12-bis(benzhydrylideneamino)[2.2]paracyclophane (7.5 mg, 1.33×10^{-2} mmol), benzhydrylideneamine (0.9 mL, 3.99 mmol), sodium *tert*-butoxide (396 mg, 3.99 mmol), and toluene (4.0 mL). The mixture was stirred at 110 °C under nitrogen for 8 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to give a residue. To the residue was added concentrated HCl (12 M, 0.33 mL, 4.0 mmol) in THF (4.0 mL), then the solution was stirred at room temperature for 4 h. After the yellow color faded, saturated NaOH was added dropwise until the stirred mixture tested basic (pH 9). The solvent was removed, and the residue was purified by chromatography on silica gel, using CH_2Cl_2 as eluent, to furnish the desired product *N*,*N*′-Bis[S_p-12-amino-4-[2.2]paracyclophanyl]-1,2-ethylenediamine (**5**) as a white solid. Yield 365 mg (54%); mp >220 °C dec; $[\alpha]^{20}_D$ −58.0 (*c* 0.18, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.49−2.71 (m, 4H), 2.79−3.21 (m, 16H), 3.37 (br, 4H), 3.77 (br, 2H), 5.83−5.88 (d, *J* = 1.5 Hz, 2H), 5.95−6.05 (m, 4H), 6.26−6.39 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 32.0, 32.6, 32.8, 33.1, 42.5, 111.9, 116.9, 121.7, 122.9, 123.8, 124.3, 135.0, 135.1, 140.7, 141.6, 144.6, 146.0; HRMS (ESI) mass calcd for $C_{34}H_{39}N_4$ [$M^+ + H$] 503.3175, found 503.3172.

Following the general procedure for the synthesis of (−)-**2**, starting from the arylamine **5**, the desired product (−)-**6** was obtained. Yield 48%; mp >250 °C dec; $[\alpha]^{20}_D$ −2342 (*c* 0.24, CH_2Cl_2); $[M]_D$ = −12270; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.64−2.79 (m, 4H), 2.89−3.38 (m, 14H), 3.51 (br, 2H), 3.72−3.85 (m, 2H), 5.99−6.04 (d, *J* = 1.2 Hz, 2H), 6.09−6.15 (m, 2H), 6.30−6.35 (d, *J* = 7.5 Hz, 2H), 6.49−6.55 (m, 2H), 6.56−6.60 (d, *J* = 1.8 Hz, 2H), 6.62−6.68 (d, *J* = 7.8 Hz, 2H), 8.22 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 31.1, 31.9, 33.1, 34.4, 44.4, 114.2, 120.3, 122.1, 123.6, 133.1, 134.1, 134.6, 137.5, 141.2, 142.7, 145.9, 147.8, 157.1; HRMS (ESI) mass calcd for $C_{36}H_{37}N_4$ [$M^+ + H$] 525.3018, found 525.3003; UV−vis (CH_2Cl_2, 4.76×10^{-5} M) λ_{max} (ε_{max}) = 268 (1.93×10^4), 396 nm (1.36×10^4); CD (CH_2Cl_2, 1.59×10^{-4} M, 0.1 cm cell) 381 nm (θ = −27.5, $\Delta\varepsilon$ = −52.6), 286 nm (θ = 8.8, $\Delta\varepsilon$ = 16.8), 272 nm (θ = −2.6, $\Delta\varepsilon$ = −4.9), 244 nm (θ = 14.8, $\Delta\varepsilon$ = 28.3), 229 nm (θ = −36.5, $\Delta\varepsilon$ = −69.6).

Typical Procedure for the Synthesis of Macrocyclic Imine (+)-10. The mixture of R_p-4-hydroxyl-12-benzhydrylideneamino-[2.2]paracyclophane (**7**) (201.5 mg, 1.0 mmol), ethylene glycol bis(*p*-toluenesulfonate) (**8a**) (185 mg, 0.5 mmol), and K_2CO_3 (414 mg, 3.0 mmol) in DMF (2.0 mL) was stirred for 8 h at 80 °C under N_2. After completion of the reaction as indicated by TLC, the mixture was cooled to the room temperature, and then water (10.0 mL) was added to the reaction mixture and yellow precipitate was formed, which was collected by filtration. To the precipitate was added concentrated HCl (12 M, 0.25 mL, 3.0 mmol) in THF (4.0 mL), then the mixture was stirred at room temperature for 4 h. After the yellow color faded, saturated NaOH was added dropwise until the stirred mixture tested basic (pH 9). The solvent was removed, and the residue was purified by chromatography on silica gel, using CH_2Cl_2 as eluent, to furnish the desired product **9a** as a white solid. Yield 163 mg (65%); mp >250 °C dec; $[\alpha]^{20}_D$ +6.7 (*c* 0.56, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.53−2.72 (m, 4H), 2.88−3.13 (m, 10H), 3.29 (br, 4H), 3.46−3.59 (m, 2H), 4.03−4.16 (m, 2H), 4.36−4.50 (m, 2H), 5.95 (s, 2H), 5.99−6.07 (m, 2H), 6.16−6.23 (m, 2H), 6.24−6.31 (d, *J* = 7.8 Hz, 2H), 6.48−6.56 (d, *J* = 7.8 Hz, 2H), 6.59−6.67 (d, *J* = 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 31.5, 31.7, 33.3, 33.8, 65.3, 111.9, 117.9, 123.4, 123.8, 124.6, 127.3, 135.1, 135.2, 142.0, 142.1, 144.6, 156.2; HRMS (ESI) mass calcd for $C_{34}H_{36}N_2NaO_2$ [$M^+ + Na$] 527.2674, found 527.2677.

Following the general procedure for the synthesis of (−)-**2**, starting from the arylamine **9a**, the desired product (+)-**10** was obtained. Yield 48%; mp >250 °C dec; $[\alpha]^{20}_D$ +2032 (*c* 0.10, CH_2Cl_2); $[M]_D$ = +10687; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.58−3.19 (m, 10H), 3.26−3.43 (m, 4H), 3.74−3.89 (m, 2H), 3.89−4.02 (m, 2H), 4.02−4.16 (m, 2H), 6.22−6.33 (m, 4H), 6.36−6.49 (m, 4H), 6.50−6.59 (m, 2H), 6.59−6.66 (d, *J* = 8.1 Hz, 2H), 8.25 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 29.1, 29.7, 31.3, 34.0, 34.5, 64.6, 114.9, 121.7, 125.6, 126.9, 133.5, 134.3, 134.6, 137.3, 142.4, 142.9, 147.8, 156.1, 157.2; HRMS (ESI) mass calcd for $C_{36}H_{35}N_2O_2$ [$M^+ + H$] 527.2699, found 527.2694; UV−vis (CH_2Cl_2, 4.75×10^{-5} M) λ_{max} (ε_{max}) = 396 nm (1.25×10^4); CD (CH_2Cl_2, 2.05×10^{-4} M, 0.1 cm cell) 388 nm (θ = 22.8, $\Delta\varepsilon$ = 33.8), 307 nm (θ = 5.3, $\Delta\varepsilon$ = 7.9), 290 nm (θ = −1.0, $\Delta\varepsilon$ = −1.5), 271 nm (θ = 10.6, $\Delta\varepsilon$ = 15.6), 248 nm (θ = −19.9, $\Delta\varepsilon$ = −29.4), 229 nm (θ = 72.6, $\Delta\varepsilon$ = 107.4).

■ ASSOCIATED CONTENT

Supporting Information. Full experimental details and characterization data plus X-ray crystallographic files (CIF) for (−)-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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