HETEROCYCLCES, Vol. 57, No. 6, 2002, pp. 1091-1099, Received, 18th March, 2002

ONE-STEP SYNTHESIS OF OPTICALLY ACTIVE CYCLIC POLYAMINES CONTAINING HELICENE

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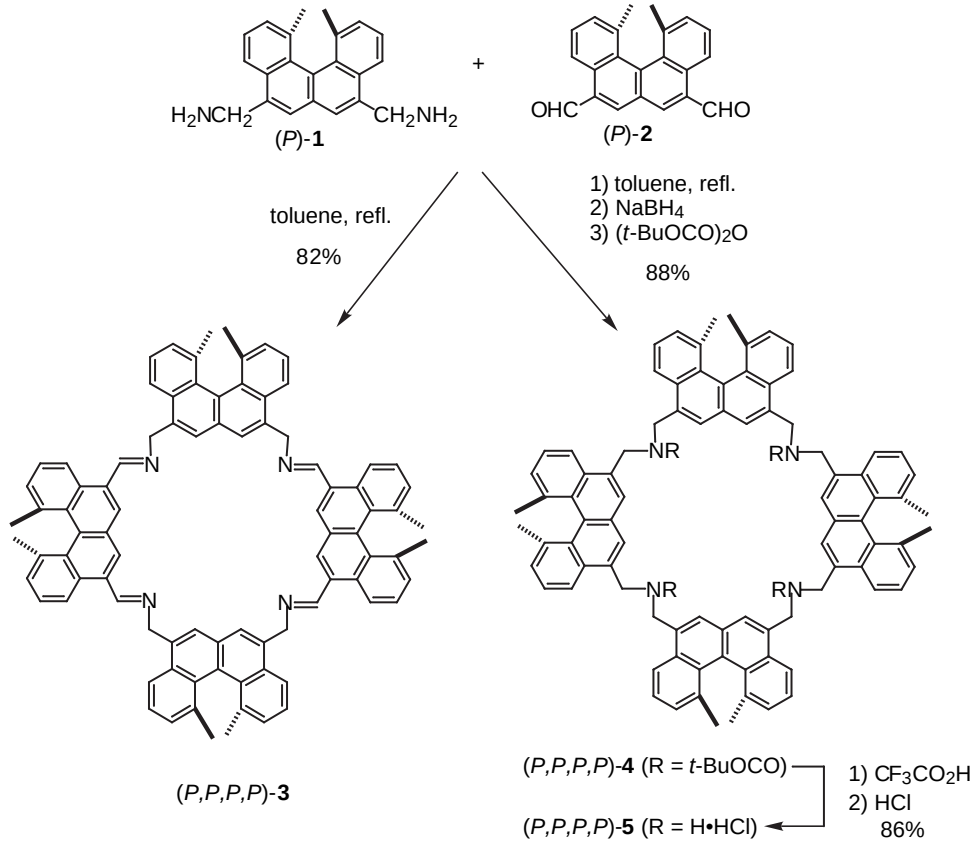
Abstract - Chiral macrocyclic tetraamines containing four helicenes were effectively synthesized in one-step. Reductive coupling of a (*P*)-helicenedi(methylamine) and a (*P*)-helicenedicarbaldehyde gives a cyclic (*P,P,P,P*)-tetramer in 88% yield. The (*P,M,P,M*)-diastereomer was effectively synthesized from the (*M*)-diamine and the (*P*)-dialdehyde in 66% yield. The intermediate (*P,P,P,P*)-imine and (*P,M,P,M*)-imine can be isolated also in high yields. The reductive coupling of achiral arenes, *m*-phenylenedi(methylamine) and *m*-phenylenedicarbaldehyde gives the cyclic tetramer in 47% yield, which is accompanied by the higher cyclic oligomers containing hexamer (18%) and octamer (3%). The condensed benzene ring system of the helicene appears to play an important role in the high yielding cyclic tetramerization.

During our studies on the chemistry of helicenes, 1,12-dimethylbenzo[*c*]phenanthrenes,[1] their 5,8-derivatives were found to show a high tendency to form cyclized compounds.[2-5] For example, when the helicenedicarboxylic acid was treated with the corresponding acid chloride in the presence of a base, trimeric and tetrameric cyclic acid anhydrides were obtained predominantly.[2] The anhydride formation was shown to be under equilibrium. We here provide another example of the high yielding cyclization for the helicene derivative. Reaction of helicenediamine (**1**)[6] with dialdehyde (**2**)[4] gives the tetrameric imine, and the corresponding cyclic amines were obtained after reduction in high yields. Although synthesis of optically active cyclic polyamines and polyimines were reported,[7-9] such compound containing helicene was not known.

Optically active helicenediamine ((*P*)-**1**)[6] and helicenedicarbaldehyde ((*P*)-**2**)[4] were condensed in the presence of a catalytic amount of benzoic acid (5 mol%) in refluxing toluene, and the mixture was added to sodium borohydride in methanol and tetrahydrofuran. The crude product was *t*-butoxycarbonylated giving (*P,P,P,P*)-**4** in 88% yield (Scheme 1). While the ^{1}H-NMR spectral

absorptions of (*P*,*P*,*P*,*P*)-**4** in DMSO-d_6 were broadened at room temperature, they were sharpened at above 60 °C. The simple NMR spectrum indicates the cyclic structure of (*P*,*P*,*P*,*P*)-**4**, and FAB MS as well as vapor pressure osmometry in chloroform confirms the tetrameric structure. The protecting group was removed by reacting with trifluoroacetic acid at 0 °C, and treatment with hydrochloric acid gave (*P*,*P*,*P*,*P*)-**5** in 86% yield. Analogously, the antipodes ((*M*,*M*,*M*,*M*)-**4**) and ((*M*,*M*,*M*,*M*)-**5**) were obtained from (*M*)-**1** and (*M*)-**2**.



Scheme 1.

The imine ((*P*,*P*,*P*,*P*)-**3**), which is the intermediate for (*P*,*P*,*P*,*P*)-**4,** can be isolated by concentration of the reaction mixture and washing the crystals with ether in 82% yield. The imine proton was observed at δ 9.18 by ^{1}H-NMR spectrum and IR spectrum indicated the presence of C=N bond at 1633 cm^{-1}. CD spectra of (*P*,*P*,*P*,*P*)-**3,** (*P*,*P*,*P*,*P*)-**4** , and (*P*,*P*,*P*,*P*)-**5** are shown in Figure 1.

The diastereomer ((*P*,*M*,*P*,*M*)-**4**) being a *meso*-compound was obtained from (*M*)-**1** and (*P*)-**2** in 66% yield, which was converted to (*P*,*M*,*P*,*M*)-**5**. (Scheme 2). The imine ((*P*,*M*,*P*,*M*)-**3**), being less soluble than (*P*,*P*,*P*,*P*)-**3**, precipitated from the reaction mixture, and was isolated in 87% yield. Because of the low solubility of (*P*,*M*,*P*,*M*)-**3** use of dichloromethane and acetic acid gave better results in the reduction than methanol and tetrahydrofuran. As judged from yields, the stereochemistry at the helicene moiety does not largely affect the efficiency of the tetramerization. As expected from its structure (*P*,*M*,*P*,*M*)-**3** exhibited Cotton effects by CD, while (*P*,*M*,*P*,*M*)-**4** was inert (Figure 2).

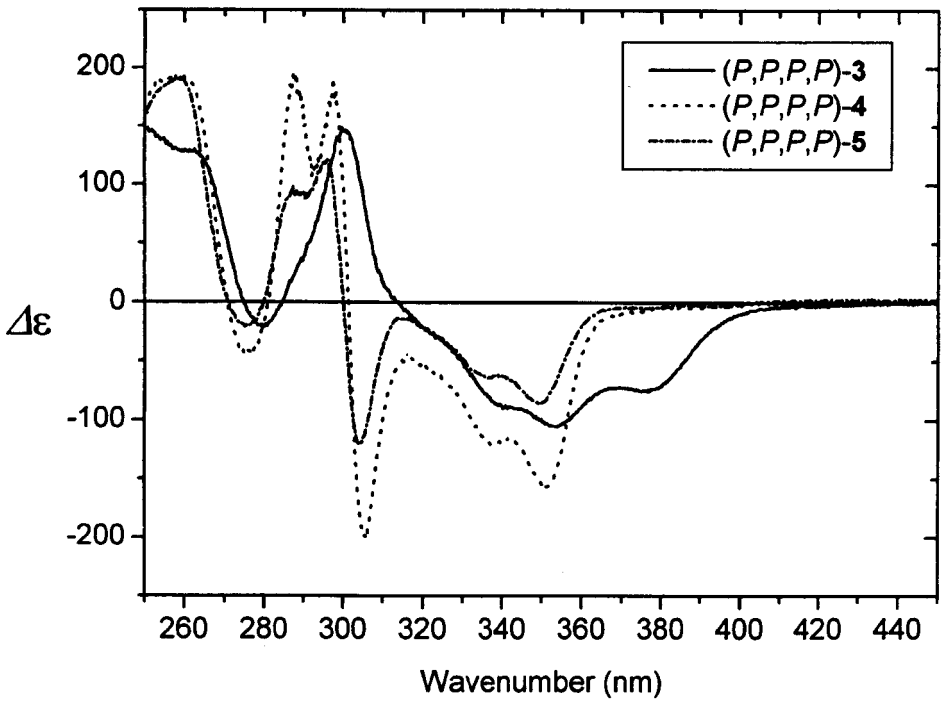


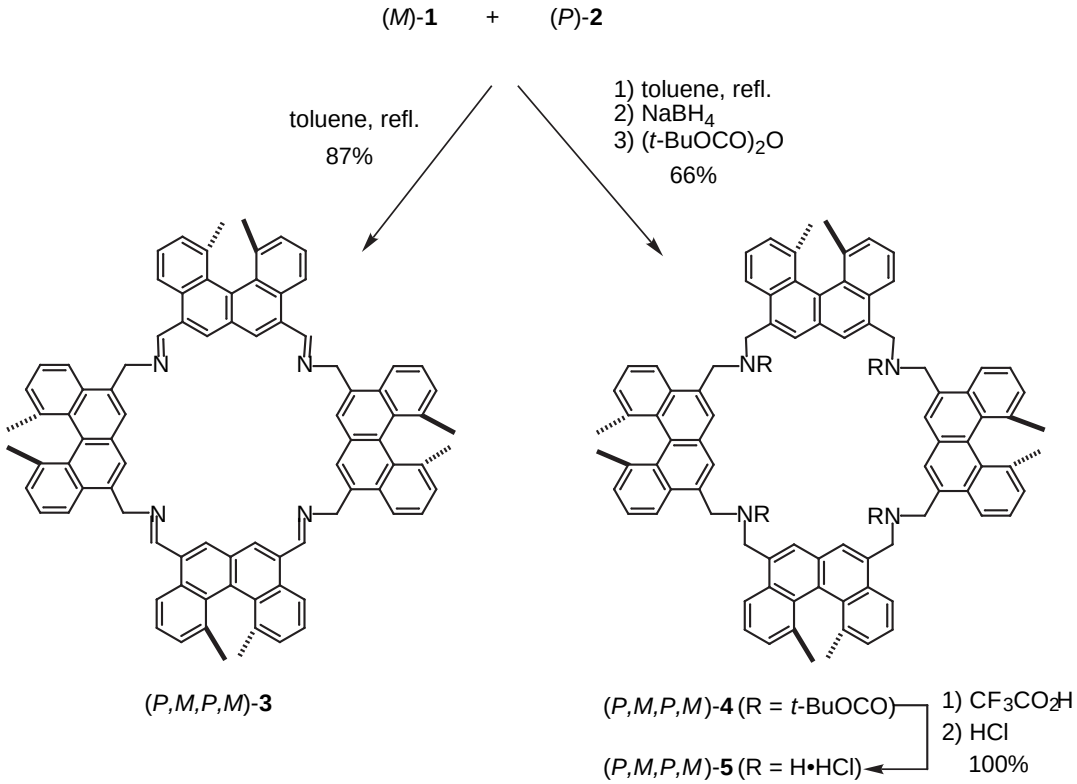
Figure 1. The CD spectra of (*P*,*P*,*P*,*P*)-**3** ($CHCl_3$, 14 μM), (*P*,*P*,*P*,*P*)-**4** ($CHCl_3$, 10 μM), and (*P*,*P*,*P*,*P*)-**5** (MeOH, 10 μM) at 25 °C.

In order to know the effect of the aromatic ring system on the cyclization reaction, a reaction of achiral *m*-phenylene derivatives was examined (Scheme 3). We have conducted studies to regard the helicene as a chiral equivalent of *m*-phenylene, and to compare behaviors of the chiral and achiral compounds.[2-4] *m*-Phenylenedi(methylamine) (**6**) was condensed with isophthalaldehyde (**7**), and the reduction followed by the *t*-butoxycarbonylation gave cyclic polyamines, which contained tetramer (**8)** (47%), hexamer (**9)** (18%), and octamer (**10)** (3%). The tendency to form tetrameric compound was observed in the achiral version of the compound as well as the chiral helicene. The selectivity, however, is higher in the helicene derivative, which may be due to the presence of the four condensed benzene rings of the helicene.

To summarize, condensation of helicenedi(methylamine) and helicenedicarbaldehyde gives optically active tetrameric polyamines in high yields. Studies on the synthesis and properties of the metal complexes derived from the cyclic polyamines are now underway.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Varian Mercury (400 MHz). Spectra taken in $CDCl_3$ were referenced to tetramethylsilane (δ 0.00) as an internal standard. Spectra taken in DMSO-d_6 (δ 2.49) and CD_3OD (δ 3.30) were referenced to the residual solvents. ^{13}C-NMR spectra were recorded on a Varian Mercury (100 MHz). Spectra taken in $CDCl_3$ (δ 77.0), DMSO-d_6 (δ 39.7), and CD_3OD (δ 49.0) were referenced to the residual solvents. Melting points were determined with Yanagimoto micro melting point apparatus without correction. Optical rotations were measured on a JASCO DIP-



Scheme 2.

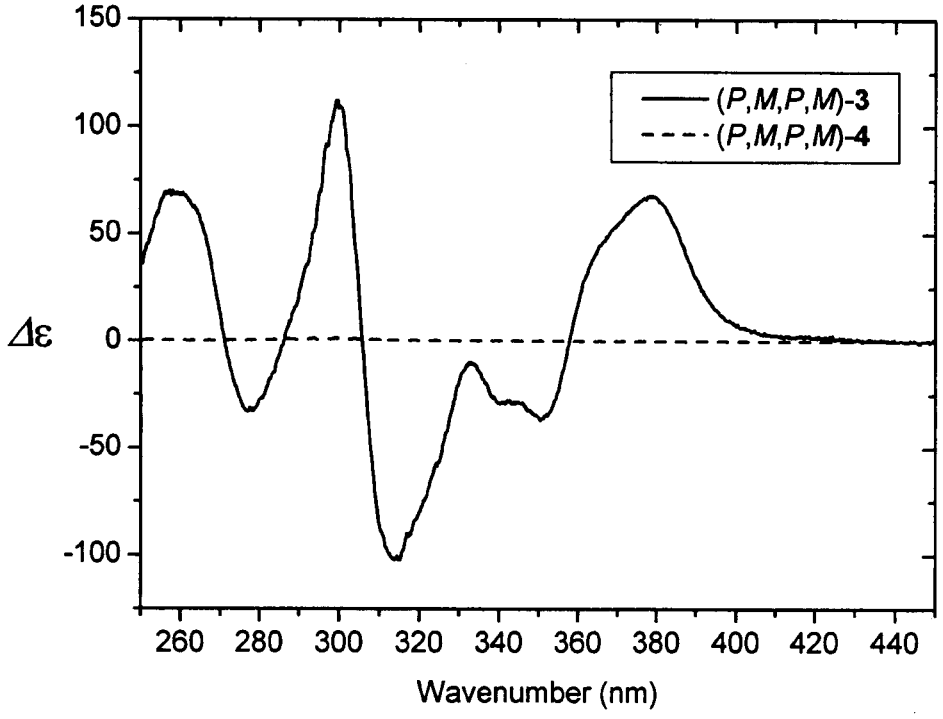
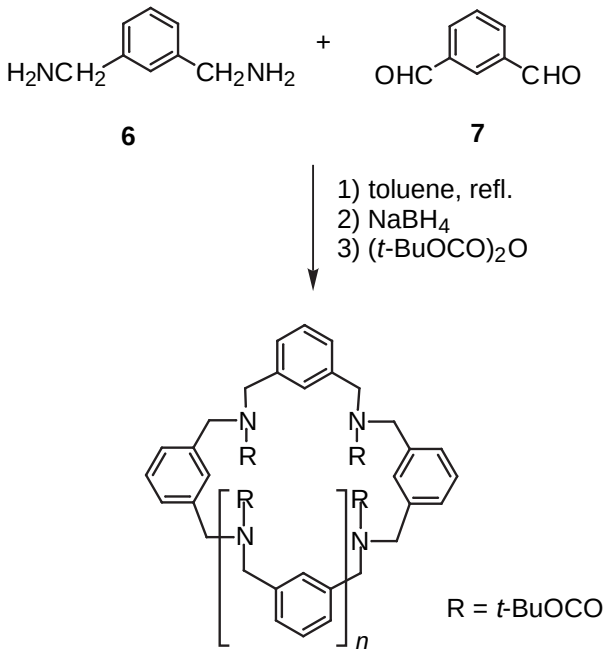


Figure 2. The CD spectra of (*P*,*M*,*P*,*M*)-**3** (10 μM) and (*P*,*M*,*P*,*M*)-**4** (10 μM) in chloroform at 25 °C.



8 (*n* = 1) 47%
9 (*n* = 2) 18%
10 (*n* = 3) 3%

Scheme 3.

340 digital polarimeter. IR spectra were recorded on a JASCO FT/IR-400 spectrophotometer, and CD spectra on a JASCO J-720 spectropolarimeter. Low- and high-resolution MS spectra as well as FAB MS (*m*-nitrobenzyl alcohol) spectra were recorded on a JEOL JMS-DX-303 or a JMS-AX-500 spectrometer. MALDI TOF-MS spectra were recorded on a PerSeptive Biosystems Voyager^{TM} DE SI using dithranol matrix. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5. Vapor pressure osmometry (VPO) was conducted with KNAUER K-7000 in chloroform using benzil as standard. Merck silica gel 60 (230-400 mesh) was employed for flash column chromatography. The ratios of solvent mixtures for chromatography are shown in volume/volume.

(*P,P,P,P*)-Cyclic Tetramer Imine ((*P,P,P,P*)-3). Under an argon a mixture of (*P*)-**1**[6] (31 mg, 0.10 mmol), (*P*)-**2**[4] (31 mg, 0.10 mmol), and benzoic acid (0.6 mg, 0.005 mmol) in toluene (10 mL) was heated at reflux for 2 h. The solution was concentrated, and the solid was washed with ether giving essentially pure (*P,P,P,P*)-**3** (48 mg, 82%). $[\alpha]_D^{25}$ –629° (c 0.23, $CHCl_3$). mp 260 °C (decomp). Anal. Calcd for $C_{88}H_{68}N_4 \cdot 3H_2O$: C, 85.54; H, 6.04; N, 4.53. Found: C, 86.08; H, 6.11; N, 4.57. FAB MS calcd for $^{12}C_{87}{}^{13}CH_{68}N_4$: 1181.6. Found: 1182 ($M^+$+1). IR (KBr) 1633 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.85 (12H, s), 2.01 (12H, s), 5.58 (4H, d, *J* = 15 Hz), 5.62 (4H, d, *J* = 15 Hz), 7.38 (4H, d, *J* = 6.8 Hz), 7.45 (4H, d, *J* = 6.8 Hz), 7.61 (4H, t, *J* = 6.8 Hz), 7.65 (4H, t, *J* = 6.8 Hz), 7.74 (4H, s), 8.24 (4H, d, *J* = 6.8 Hz), 8.26 (4H, s), 9.03 (4H, d, *J* = 6.8 Hz), 9.18 (4H, s). ^{13}C-NMR ($CDCl_3$) δ 24.9, 25.0, 64.3, 121.8, 123.2, 125.8, 125.9, 126.9, 128.3, 129.3, 129.9, 130.4, 131.8, 131.9, 132.3, 132.7, 132.9, 133.3, 135.7, 138.0, 138.0, 163.8. (*M,M,M,M*)-**3**: $[\alpha]_D^{25}$ +600° (c 0.24, $CHCl_3$). mp 260 °C (decomp).

(*P*,*P*,*P*,*P*)-Cyclic Tetramer Tetra(*t*-butoxycarbonyl) Derivative ((*P*,*P*,*P*,*P*)-4). Under an argon atmosphere a mixture of (*P*)-**1** (99 mg, 0.32 mmol), (*P*)-**2** (98 mg, 0.32 mmol), and benzoic acid (2 mg, 0.016 mmol) in toluene (30 mL) was heated at reflux for 2 h. After cooled the solution was added to a suspension of sodium borohydride (920 mg, 24 mmol) in methanol (100 mL) and tetrahydrofuran (100 mL) at 0 °C. The mixture was stirred for 10 min at the same temperature, and water was added. The organic materials were extracted with chloroform, and the extract was washed with brine, dried over potassium carbonate, and concentrated. The residue was diluted with dichloromethane (10 mL), to which 1 M aqueous sodium hydroxide (10 mL) and di(*t*-butyl) dicarbonate (687 mg, 3.2 mmol) were added. After stirred for 3 h, the organic materials were extracted with dichloromethane. The organic layer was dried over potassium carbonate, and concentrated under reduced pressure. Purification by silica gel chromatography (ethyl acetate/hexane = 1/8) gave (*P*,*P*,*P*,*P*)-**4** (212 mg, 88%). $[\alpha]_D^{25}$ -72° (c 0.14, $CHCl_3$). mp 300 °C (decomp) (EtOH). Anal. Calcd for $C_{108}H_{108}N_4O_8 \cdot 2H_2O$: C, 79.77; H, 6.94; N, 3.45. Found: C, 79.61; H, 6.83; N, 3.36. FAB MS calcd for $^{12}C_{107}{}^{13}CH_{108}N_4O_8$: 1589.8. Found: 1590 ($M^+$+1). IR (KBr) 2973, 2927, 1692 cm^{-1}. VPO ($CHCl_3$, 35 °C) Calcd: 1590. Found: 1560 ± 130 (9 mM). ^{1}H-NMR (DMSO-d_6 at 90 °C) δ 1.39 (36H, s), 1.75 (24H, s), 4.27 (8H, d, *J* = 16 Hz), 5.40 (8H, d, *J* = 16 Hz), 7.27 (8H, s), 7.34 (8H, d, *J* = 7 Hz), 7.50 (8H, dd, *J* = 7,8 Hz), 8.06 (8H, d, *J* = 8 Hz). ^{13}C-NMR (DMSO-d_6 at 90 °C) δ 22.8, 28.1, 47.1, 79.8, 120.6, 124.5, 125.4, 125.7, 127.8, 130.2, 131.1, 131.9, 135.8, 154.3. (*M*,*M*,*M*,*M*)-**4**: $[\alpha]_D^{25}$ +72° (c 0.23, $CHCl_3$). mp 300 °C (decomp) (EtOH).

(*P*,*P*,*P*,*P*)-Cyclic Tetramer ((*P*,*P*,*P*,*P*)-5). The compound ((*P*,*P*,*P*,*P*)-**4**) (39 mg, 0.025 mmol) was dissolved in dichloromethane (2.5 mL), to which trifluoroacetic acid (0.5 mL) was added at 0 °C. After stirred for 2 h at the same temperature, the solvent was evaporated under reduced pressure. Methanol (5 mL) and 1 M hydrochloric acid (1 mL) were added, and the solution was concentrated under reduced pressure. Essentially pure (*P*,*P*,*P*,*P*)-**5** (30 mg, 86%) was obtained by washing with ether. $[\alpha]_D^{25}$ –360° (c 0.21, MeOH). mp 230 °C (decomp). Anal. Calcd for $C_{88}H_{80}N_4Cl_4 \cdot 6H_2O$: C, 73.22; H, 6.42; N, 3.88. Found: C, 73.24; H, 6.44; N, 3.59. FAB MS calcd for $^{12}C_{87}{}^{13}CH_{76}N_4$: 1189.6. Found: 1190 ($M^+$+1). IR (KBr) 3389, 2961, 2924, 1614, 1591 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ 1.85 (24H, s), 5.08 (8H, d, *J* = 14 Hz), 5.14 (8H, d, *J* = 13 Hz), 7.55 (8H, d, *J* = 7.2 Hz), 7.76 (8H, dd, *J* = 7.2, 8 Hz), 8.29 (8H, s), 8.38 (8H, d, *J* = 8 Hz). ^{13}C-NMR (DMSO-d_6) δ 23.2, 48.0, 121.2, 125.5, 126.7, 127.5, 128.0, 128.7, 130.0, 130.3, 130.5, 136.2. (*M*,*M*,*M*,*M*)-**5**: $[\alpha]_D^{25}$ +355° (c 0.35, MeOH). mp 235 °C (decomp).

(*P*,*M*,*P*,*M*)-Cyclic Tetramer Imine ((*P*,*M*,*P*,*M*)-3). Under an argon a mixture of (*M*)-**1** (31 mg, 0.10 mmol), (*P*)-**2** (31 mg, 0.10 mmol), and benzoic acid (0.6 mg, 0.005 mmol) in toluene (10 mL) was heated at reflux for 2 h. The precipitate was collected, and washed with toluene giving essentially pure (*P*,*M*,*P*,*M*)-**3** (51 mg, 87%). $[\alpha]_D^{25}$ –142° (c 0.08, C_6H_5Cl). mp 285 °C (decomp) (C_6H_5Cl). Anal. Calcd for $C_{88}H_{68}N_4 \cdot 3H_2O$: C, 85.54; H, 6.04; N, 4.53. Found: C, 85.70; H, 5.81; N, 4.12. FAB MS calcd for $^{12}C_{87}{}^{13}CH_{68}N_4$: 1181.6. Found: 1182 ($M^+$+1). IR (KBr) 1638 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.85 (12H, s), 2.00 (12H, s), 5.09 (8H, br d, *J* = 13 Hz), 5.17 (8H, br d, *J* = 13 Hz), 7.38 (4H, d, *J* = 7.2 Hz), 7.44 (4H, d, *J* = 7.6 Hz), 7.60 (4H, d, *J* = 7.6 Hz), 7.66 (4H, t, *J* = 7.6 Hz), 7.70 (4H, s), 8.21

(4H, s), 8.27 (4H, d, J = 8.0 Hz), 9.01 (4H, d, J = 7.6 Hz), 9.14 (4H, s). ^{13}C-NMR ($CDCl_3$) δ 23.4, 23.5, 62.9, 120.5, 121.9, 124.5, 125.4, 126.8, 127.8, 128.4, 128.9, 130.3, 130.9, 131.3, 131.4, 134.2, 136.5, 136.5, 162.1.

(*P,M,P,M*)-Cyclic Tetramer Tetra(*t*-butoxycarbonyl) Derivative ((*P,M,P,M*)-4). Under an argon atmosphere a mixture of (*M*)-**1** (31 mg, 0.1 mmol), (*P*)-**2** (31 mg, 0.1 mmol), and benzoic acid (0.5 mg, 5 mol%) in toluene (10 mL) was heated at reflux for 2 h. After cooled to rt, the solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane (10 mL) and acetic acid (1 mL). To this solution was added sodium borohydride (190 mg, 5.0 mmol) at 0 °C, and the mixture was stirred at 0 °C for 10 min and at rt for 10 min. The reaction was quenched by adding 10% aqueous sodium hydroxide. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed with brine, dried over potassium carbonate, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (2.5 mL), to which 1 M aqueous sodium hydroxide (2.5 mL) and di(*t*-butyl) dicarbonate (53 mg, 0.24 mmol) were added at rt. After being stirred overnight, the organic materials were extracted with dichloromethane. The organic layer was dried over potassium carbonate, and concentrated under reduced pressure. Purification by silica gel chromatography (ethyl acetate/hexane = 1/8) gave (*P,M,P,M*)-**4** (53 mg, 66%). mp 250 °C (decomp) (EtOH). Anal. Calcd for $C_{108}H_{108}N_4O_8 \cdot 5H_2O$: C, 77.21; H, 7.08; N, 3.33. Found: C, 77.06; H, 6.73; N, 3.41. FAB MS calcd for $^{12}C_{107}{}^{13}CH_{108}N_4O_8$: 1589.8. Found: 1590 ($M^+$+1). IR (KBr) 2972, 2926, 1692 cm^{-1}. ^{1}H-NMR (DMSO-d_6 at 90 °C) δ 1.32 (36H, s), 1.47 (24H, s), 4.83 (8H, d, J = 15 Hz), 5.05 (8H, d, J = 15 Hz), 7.15 (8H, d, J = 8 Hz), 7.29 (8H, s), 7.46 (8H, t, J = 8 Hz), 8.03 (8H, d, J = 8 Hz). ^{13}C-NMR (DMSO-d_6 at 90 °C) δ 22.3, 27.7, 48.1, 79.2, 120.1, 123.7, 124.6, 125.1, 127.2, 129.8, 129.9, 130.4, 131.8, 135.3, 154.4.

(*P,M,P,M*)-Cyclic Tetramer ((*P,M,P,M*)-5). The compound ((*P,M,P,M*)-**4**) (51 mg, 0.052 mmol) was dissolved in dichloromethane (2.5 mL), to which was added trifluoroacetic acid (0.5 mL) at 0 °C. After stirred for 2 h at the same temperature, the solvents were evaporated under reduced pressure. The residue was dissolved in methanol (5 mL) and 1 M hydrochloric acid (1 mL), and the solution was concentrated again under reduced pressure. Essentially pure (*P,M,P,M*)-**5** (51 mg, 100%) was obtained by washing the residue with ether. mp 280 °C (decomp). Anal. Calcd for $C_{88}H_{80}N_4Cl_4 \cdot 7H_2O$: C, 72.32; H, 6.48; N, 3.83. Found: C, 72.51; H, 6.44; N, 4.04. FAB MS calcd for $^{12}C_{87}{}^{13}CH_{76}N_4$: 1189.6. Found: 1190 ($M^+$+1). IR (KBr) 3425, 1621 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ 1.80 (24H, s), 5.09 (8H, br d, J = 13 Hz), 5.17 (8H, br d, J = 13 Hz), 7.54 (8H, d, J = 7 Hz), 7.80 (8H, dd, J = 7, 8 Hz), 8.31 (8H, s), 8.46 (8H, d, J = 8 Hz). ^{13}C-NMR (DMSO-d_6) δ 23,1, 48.0, 121.3, 125.7, 126.7, 128.0, 128.6, 130.0, 130.4, 130.5, 136.0.

***m*-Phenylene Cyclic Oligomers.** Under an argon atmosphere a mixture of *m*-phenylenedi(methylamine) (**6**, 174 mg, 1.3 mmol), isophthalaldehyde (**7**, 170 mg, 1.3 mmol), and benzoic acid (9 mg, 5 mol%) in toluene (125 mL) was heated at reflux for 1 h. The resulted solution was added to a stirred suspension of sodium borohydride (148 mg, 3.9 mmol) in methanol (125 mL) and tetrahydrofuran (125 mL) at 0 °C. Stirrng was continued for 2.5 h at 0 °C, and the reaction was

quenched by adding water. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed with brine, dried over potassium carbonate, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (8 mL), to which 1 M aqueous sodium hydroxide (5 mL) and di(*t*-butyl) dicarbonate (692 mg, 3.2 mmol) were added. The mixture was stirred at rt overnight. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. Purification by silica gel chromatography (dichloromethane/acetonitrile = 15/1 to 5/1) gave cyclic tetramer (**8)** (262 mg, 47%), cyclic hexamer (**9)** (97 mg, 18%) and cyclic octamer (**10)** (17 mg, 3%). **8**: FAB MS calcd for $C_{52}H_{68}N_4O_8$: 876.5. Found: 877 (M^++1). IR (KBr) 2978, 2929, 1697 cm^{-1}. ^{1}H-NMR ($CDCl_3$ at 45 °C) δ 1.48 (36H, s), 4.29 (16H, br s), 6.75 (4H, br s), 7.11 (8H, br s), 7.24 (4H, t, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$ at 45 °C) δ 28.6, 49.7, 80.2, 126.6, 128.9, 138.0, 155.7. **9**: MALDI TOF-MS calcd for $^{12}C_{77}{}^{13}C\,H_{102}N_6O_{12}$+Na: 1338.7. Found: 1338 (M^++Na). IR (KBr) 2976, 2929, 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$ at 45 °C) δ 1.45 (54H, s), 4.31 (24H, br s), 6.91 (6H, br s), 7.08 (12H, br s), 7.23 (6 H, t, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$ at 45 °C) δ 28.6, 49.6, 80.1, 126.4, 128.7, 138.2, 155.7. **10**: MALDI TOF-MS calcd for $^{12}C_{103}{}^{13}CH_{136}N_8O_{16}$+Na: 1777.0. Found: 1777 (M^++Na). IR (neat) 2976, 2929, 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$ at 45 °C) δ 1.45 (72H, s), 4.33 (32H, br s), 6.99 (8H, br s), 7.07 (16H, br d, *J* = 8 Hz), 7.23 (8H, t, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$ at 45 °C) δ 28.6, 49.6, 80.1, 126.4, 128.6, 138.3, 155.7.

ACKNOWLEDGMENTS

This work was supported by grants from the Japan Society for the Promotion of Science.

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5. The absolute configuration of the helicenes turned out to be erroneous in all of our previous publications. All the absolute structures in the references 1-4 should be reverted.

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