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8,14,30,36-Tetramethoxy[2.0.2.0](1,6)naphthalenophane-1,19-diyne: A Double-Helically Twisted Cyclophane by Diastereoselective Dimerization

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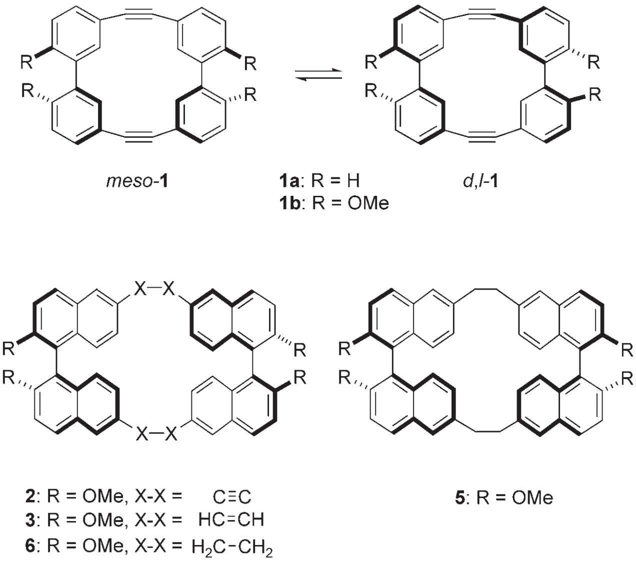
Abstract: The title compound and its corresponding etheno- and ethano-bridged compounds were successfully synthesized in enantiomerically pure form by McMurry coupling of 2,2′-dimethoxy-(*R*)- or -(*S*)-1,1′-binaphthyl-6,6′-dicarbaldehydes as the key reaction. The reaction proceeded in a highly diastereoselective manner; the reaction of the racemic dialdehyde did not afford the *meso* coupling product but gave only the racemic one in poor yield. The diyne crystallized in the chiral monoclinic space group $P2_1$ from toluene/hexane. Structural analysis reveals that it has a considerably twisted double-helical structure in crystal form. The spectral properties (NMR, UV/Vis, and CD) clearly indicate the highly strained nature of the molecule. In particular, its UV/Vis and CD spectra exhibit a bathochromic shift of about 20 nm for the naphthyl π–π* transitions.

Keywords: binaphthols · chiral molecules · cyclophanes · stereoselective synthesis · strained molecules

Introduction

Double-helically twisted chiral cyclophanes are of great interest because their unique structures impart properties with potential applications in optics and electronics.[1,2] However, few compounds composed of strained and curved conjugate systems have been obtained as enantiomerically pure forms. Recently, we synthesized the cyclophanes **1** as a significant segment of double-helically conjugated systems.[3] Variable-temperature NMR spectroscopic experiments indicated that tetramethoxy derivative **1b** exists in an equilibrium mixture of *meso* and *d*,*l* forms in chloroform (Scheme 1). However, crystal analysis of **1b** revealed that it adopts the *meso* form in the crystals. To explore the chiroptical properties of double-helically conjugated systems, suitable model compounds would be needed. In this context, we designed the title cyclophane **2** with binaphthol units.[4–7] The semi-empirical calculation PM3[8] predicted the distorted structure of **2** (Figure 1), which shows considerably bent acetylenic bonds (164.5°) and small dihedral angles between the two naphthylene rings of the binaphthol units (75.6°). In particular, the dinaphthyleneacetylene units are considerably twisted; the dihedral angle between the C3−C12 and C42−C41 bonds is 94.5°. Thus, the front (visible side) of the naphthylenes A and C are twisted but smoothly connected with the back



Scheme 1. Structures of **1**–**6**.

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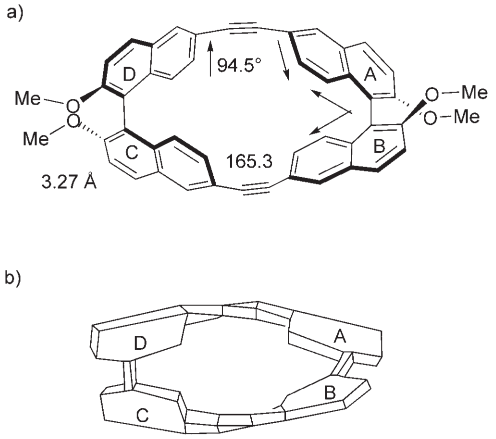


Figure 1. a) Molecular structure of **2** by PM3 calculation and selected bond and dihedral angles. b) Schematic representation of the conjugation of the naphthylene groups.

(blind side) of B and D through an acetylenic bond to construct a doubly folded Möbius loop.[9] On the other hand, the corresponding cyclophanediene **3** has a nomal "Hückel" conjugation because of the low dihedral angles (81°). The considerably high energy of the racemization barrier of a binaphthol skeleton ($37.8\,\mathrm{kcal\,mol^{-1}}$)[10] should enable the obtaining of the compound in enantiomerically pure forms. Herein we report the synthesis, properties, and molecular structure of **2**.

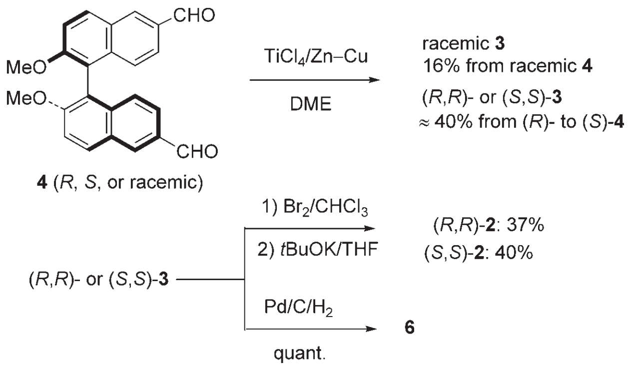
Results and Discussion

Synthesis

McMurry coupling of 2,2′-dimethoxy-(*R*)- or -(*S*)-1,1′-binaphthyl-6,6′-dicarbaldehydes (**4**)[11] afforded the corresponding cyclophanediene **3** (*R*,*R* or *S*,*S*) in approximately 40% yield.[12] The reaction of racemic **4** proceeded in a diastereoselective manner to yield racemic **3** alone in 16% yield. The low yield of **3** suggests that the reaction of (*R*)- and (*S*)-**4** would lead to the corresponding polymeric materials. Similar selectivity was observed in the zirconocene coupling of binaphthol derivatives by Schafer and Tilley.[6f] According to theoretical calculations (PM3) of the ethano-bridged cyclophanes, the enthalpy of formation of the *meso* form **5** is about $2.7\,\mathrm{kcal\,mol^{-1}}$ higher than that of the *d,l* form **6**. The results suggest that the inherent strain would prevent the formation of the *meso* coupling products. Bromination and dehydrobromination of **3** afforded the diyne **2** as pale-yellow crystalline substances in moderate yields. This crystal is rather susceptible to oxygen. When exposed to air at ambient temperature, it decomposed to form an insoluble material within a few days. The hydrogenation of **2** and **3** with Pd/C/H$_2$ led to the ethano-bridged cyclophane **6** quantitatively in enantiomerically pure form (Scheme 2).

Abstract in Japanese:

ねじれた共役系をもつ光学的に純粋な表題化合物をジアステレオ選択的なマクマリー反応を鍵反応に合成した。結晶構造解析やスペクトルの解析結果から分子が非常にねじれた構造をもつことが明らかとなった。



Scheme 2. Synthesis of **2**, **3**, and **6**. DME = 1,2-dimethoxyethane.

Molecular Structure of 2

Compound **2** was crystallized in the chiral monoclinic space group $P2_1$ from toluene/hexane. The observed structure indicates the high molecular deformation of **2** (Figure 2a). Although the structure is basically similar to that predicted, the observed dihedral angles of C3−C12−C42−C41 (84°) and C19−C20−C34−C25 (86°) are smaller than 90°. Thus, **2** does not have a doubly folded Möbius structure in the crystalline form. The observed dihedral angles of the binaphthol units (average 61.3°) and the bond angles of the acetylenic carbon atoms (average 161.0°) are 14.6 and 3.5° smaller than those predicted, respectively. The unexpectedly large deviation from the predicted structure decreases the twist of the molecule as a whole. The crystal includes hexane molecules in a 1:1 ratio. Figure 2b shows the crystal packing of **2**. Despite its macrocyclic structure, it contains no cavity but has only a shallow dishlike structure. The hexane molecule is sandwiched in the space between the macrocycles.

NMR Spectral Properties

The ^{1}H and ^{13}C NMR spectra of the cyclophanes **2**, **3**, and **6** exhibit the expected simple patterns in agreement with the D_2 symmetry of the molecule (Figure 3). The relatively high-field chemical shift of the etheno protons of **3** (6.83 ppm) is indicative of the *Z* configuration, as shown by the chemical shifts of the corresponding protons of 1,2-(*E*)- and -(*Z*)-(2,2′)-dinaphthylethenes (*E* 7.61 ppm, *Z* 6.85 ppm).[13] The ethano-bridge protons of **6** appear as one set of doublets ($J = 9.1$ Hz), thus indicating the conformational rigidity of the ethano bridges. Figure 3 shows the ^{1}H NMR spectra of **2**, **3**, and **6** in the aromatic range. The signals for the protons at the 8-positions of the binaphthol units in **2** and the 7-positions in **6** appear considerably upfield in the ^{1}H NMR spectra due to the anisotropy effect of

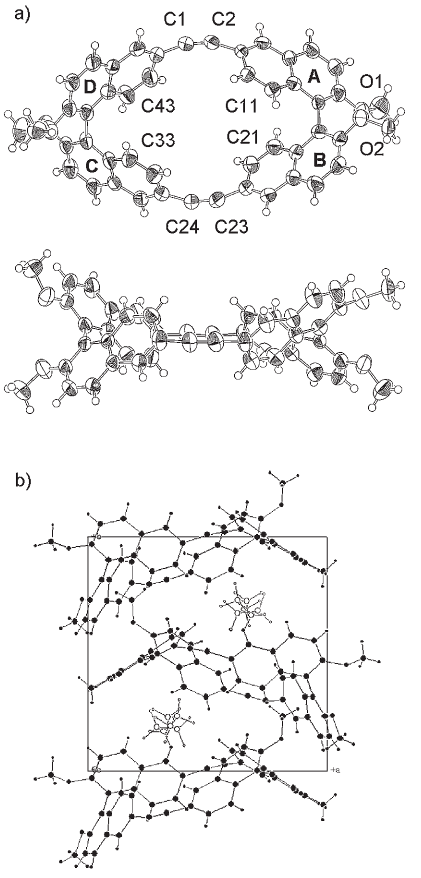


Figure 2. a) Molecular structures of **2** (thermal ellipsoids set at 50% probability). An included hexane molecule is omitted for clarity. Selected atomic distances (Å) and bond and dihedral angles (°): O1–O2 3.31(1), O3–O4 3.01(1), C11–C21 3.43(1), C33–C43 3.14(1); C41–C1–C2 162.6(6), C1–C2–C3 159.0(6), C19–C23–C24 162.3(6), C23–C24–C25 160.3(6); ∢AB = 56.5(1), ∢CD = 66.1(1), C(3)–C(12)–C(42)–C(41) = 84, C(19)–C(20)–C(34)–C(25) = 86. b) Crystal packing of **2**·hexane.

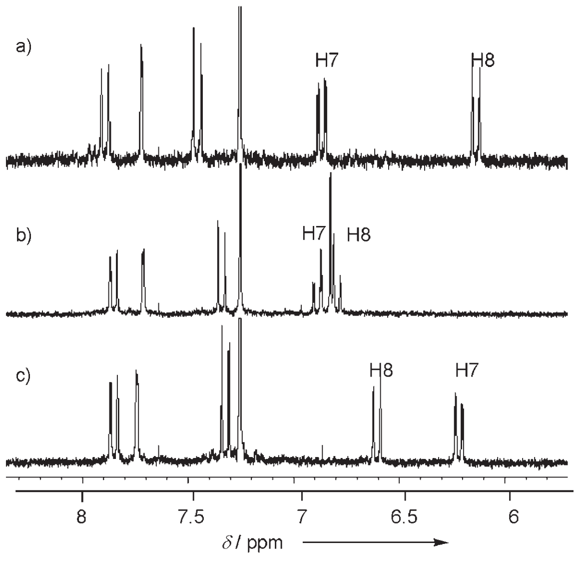
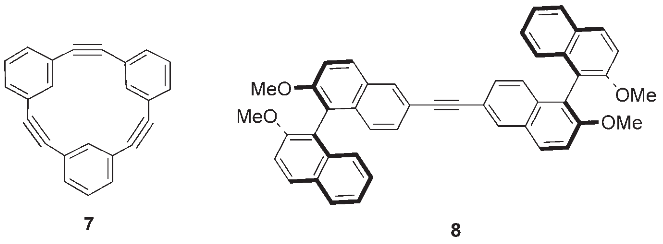


Figure 3. Partial ^{1}H NMR spectra of a) **2**, b) **3**, and c) **6** in CDCl$_3$. The numbering of the protons is based on that of 2-naphthol as a segment.

the facing naphthylene rings (ring A to ring B in **2** and ring A to ring C in **6**; Figure 1). The large deviations in the signals of the protons at the 7- and 8-positions indicate that the conformation of these molecules changes largely with the hybridization of the bridge carbon atoms. The considerably low-field chemical shift of the sp-hybridized carbon atoms of **2** (99.0 ppm) is consistent with the high distortion of the acetylenic bonds. This value is almost comparable to that of [2.2.2]metacyclophane-1,9,17-triyne **7** (99.86 ppm);[12b] however, the observed average bond angle of the acetylenic carbon atoms of **7** (158.6°) is 2.5° smaller than that in **2**. The sp-hybridized carbon atoms of diarylacetylene **8** with binaphthol units resonate at 89.5 ppm (Scheme 3).[14] This value is almost identical to that of diphenylacetylene (89.4 ppm). These results indicate that the difference in the electronic effects between benzene and naphthalene rings is not so significant. Thus, the packing force would deform the structure of **2** in the crystal.



Scheme 3. [2.2.2]Metacyclophane-1,9,17-triyne **7** and diarylacetylene **8**.

UV/Vis and CD Spectral Properties

Figure 4 shows the circular dichroism (CD) and UV/Vis spectra of **2**, **3**, and **6**. The CD signal intensities of the enantiomers are of opposite sign but equal in magnitude, and they did not change upon heating at 150 °C for 4 h. The results clearly indicate that no racemization occurred during the conversions. The cyclophanes exhibit two characteristic absorption bands in the UV/Vis spectra and bisignate curves in the CD spectra in the 220–270- and 270–370-nm ranges. The bands in the 220–270-nm range correspond to the π–π* transitions of the binaphthyl units.[6,7,15,16] The absorption maxima in the UV/Vis spectra and the zero points in the CD spectra are generally independent of the substituents at the 6,6′-positions. Actually, the absorption maxima and zero points for **3** and **6** were observed at almost the same wavelengths (237 and 238 nm). However, those for **2** exhibit a bathochromic shift of about 20 nm, probably due to the high distortion of the naphthylene rings. The higher intensity of the CD absorption of **2** relative to those of **3** and **6** are due to the small dihedral angles (average 61.3°) of the binaphthyl units.[17] On the other hand, the relatively large absorptions of **2** in the 270–370-nm range correspond to the π–π* transitions of the dinaphthylacetylene systems, because the absorptions of **6** in the same range are considerably smaller. The highly distorted double-helical structure of **2** also decreased the intensity of the absorption at around 350 nm relative to that of **3**. The CD spectra of **2** and **3** are very differ-

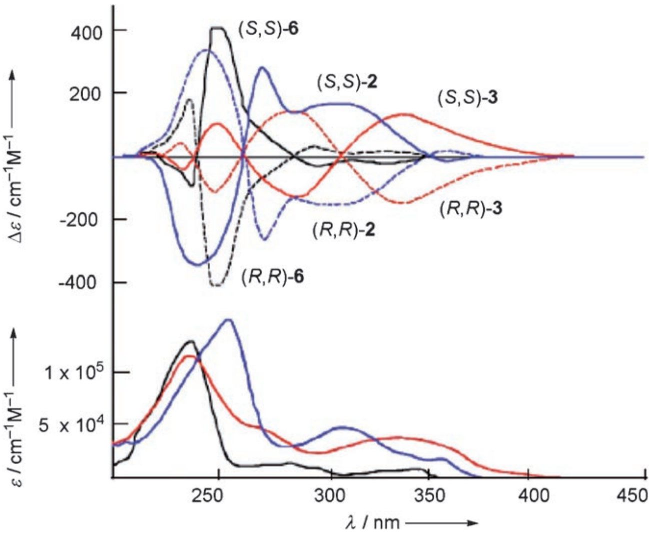


Figure 4. CD (top) and UV/Vis (bottom) spectra of **2** (blue), **3** (red), and **6** (black) in THF.

ent. The results indicate the large deformation of **2**, and that it might have the doubly folded Möbius structure in solution.

Conclusions

The chiral cyclophanes **2**, **3**, and **6** were synthesized in a highly diastereoselective manner. These cyclophanes with a chiral cavity surrounded by electron-rich π systems provide potential utility as chiral host molecules. Notably, **2** has a double-helical conjugation with a large deviation from planarity. Crystal-structure and spectroscopic analysis indicate the highly strained nature of **2**. We have presented herein a new approach to accessing compounds with a novel topological conjugation. Further studies from the theoretical and experimental points of view will be reported in due course.

Experimental Section

General Remarks

Melting points were measured on a Yanaco MP 500D apparatus and are uncorrected. FAB and EI mass spectra were recorded on JEOL JMS-SX 102 and Shimadzu GCMS-QP5050A instruments. ^{1}H NMR (tetramethylsilane as internal standard: 0 ppm) and ^{13}C NMR spectra (CDCl$_3$ as internal standard: 77.0 ppm) were recorded on a JEOL EX-270 spectrometer. Chemical shifts are given in ppm. IR spectra were obtained on a Perkin–Elmer 1650 spectrometer. UV/Vis and CD spectra were obtained on Jasco V-570 and J-725 spectrophotometers, respectively. Column chromatography was performed with Merck Kiesel-gel 60. All reagents were of commercial quality and used as supplied unless otherwise stated; THF and DME were dried where necessary by using standard procedures.

Syntheses

4:[11] A suspension of (*S*)-6,6′-dibromo-2,2′-dimethoxy-1,1′-binaphthyl (1.01 g, 2.1 mmol) in diethyl ether (50 mL) was treated with *n*-butyllithium (1.4 M in hexane, 5.6 mL, 7.8 mmol) for 5 h at 0 °C under N$_2$. *N*,*N*-dimethylformamide (DMF; 1.2 mL, 16 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After the mixture was stirred for 2 h, hydrochloric acid (2 M, 50 mL) was added, and the mixture was extracted with ethyl acetate. The organic layer was separated, dried with anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (40 g, CH$_2$Cl$_2$) gave (*S*)-2,2′-dimethoxy-1,1′-binaphthyl-6,6′-dicarbardehyde ((*S*)-**4**; 0.387 g, 49 %) as a pale-yellow solid. M.p.: 243.6–244.2 °C (ethanol); IR (KBr): $\tilde{\nu}$ = 915 (s), 1059 (s), 1168 (s), 1269 (s), 1342 (s), 1409 (s), 1475 (s), 1619 (s), 1687 (s), 2738 (m), 2790 (m), 2841 (s), 2941 (s), 3018 (m), 3359 cm^{-1} (w); ^{1}H NMR (270 MHz, CDCl$_3$): δ = 10.10 (s, 2 H), 8.37 (d, J = 1.6 Hz, 2 H), 8.17 (d, J = 9.0 Hz, 2 H), 7.69 (dd, J = 1.6, 8.8 Hz, 2 H), 7.54 (d, J = 9.0 Hz, 2 H), 7.15 (d, J = 8.8 Hz, 2 H), 3.79 ppm (s, 6 H); MS (EI): m/z (%) = 370 $[M]^+$ (100), 324 $[M-C_2H_6O]^+$ (19); elemental analysis: calcd (%) for $C_{24}H_{18}O_2$: C 77.82, H 4.90; found: C 77.61, H 4.83.

(*S*,*S*)-3: A mixture of Zn (1.35 g, 20.6 mmol), CuI (0.188 g, 0.987 mmol), and TiCl$_4$ (1.3 mL, 11.8 mmol) in DME (30 mL) was heated for 3.5 h at reflux under N$_2$. A solution of (*S*)-**4** (0.349 g, 0.942 mmol) in DME (30 mL) was added dropwise to the resulting dark-gray suspension over a period of 0.5 h. The mixture was stirred for 17 h at room temperature and heated at reflux for 6 h. The black suspension was cooled to room temperature and passed through a column of alumina gel (50 g, CH$_2$Cl$_2$). The crude product obtained was purified by column chromatography on silica gel (15 g, CH$_2$Cl$_2$) to give 8,14,30,36-tetramethoxy[2.0.2.0]-(1,6)naphthalenophane-1,19-diene ((*S*,*S*)-**3**; 147 mg, 46 %) as pale-yellow solid. Racemic **3**: M.p.: 300 °C (decomp.). (*S*,*S*)-**3**: M.p.: 290 °C (decomp.); UV/Vis (THF): λ (log ε) = 333 (4.63), 237 nm (5.09); IR (KBr): $\tilde{\nu}$ = 801, 896 (m), 1043 (s), 1068 (s), 1095 (s), 1256 (s), 1328 (m), 1483 (s), 1591 (s), 1619 (m), 2833 (m), 2932 (m), 3004 cm^{-1} (w); ^{1}H NMR (270 MHz, CDCl$_3$): δ = 7.85 (d, J = 9.1 Hz, 4 H), 7.71 (d, J = 1.5 Hz, 4 H), 7.34 (d, J = 9.1 Hz, 4 H), 6.89 (dd, J = 1.5, 8.7 Hz, 4 H), 6.83 (s, 4 H), 6.80 (d, J = 8.9 Hz, 4 H), 3.69 ppm (s, 12 H); ^{13}C NMR (68 MHz, CDCl$_3$): δ = 155.1, 133.0, 132.5, 130.2, 129.0, 128.9, 127.9, 127.7, 124.5, 119.4, 114.2, 56.9 ppm; MS (EI): m/z (%) = 676 $[M]^+$ (100); HRMS (EI): m/z calcd for $C_{48}H_{36}O_4$: 676.2614; found: 676.2606.

(*S*,*S*)-**2**: An excess of Br$_2$ (0.4 g, 2.5 mmol) was added to a solution of (*S*,*S*)-**3** (49 mg, 0.072 mmol) in dichloromethane (10 mL), and the mixture was stirred for 5 min at room temperature. The solvent and remaining bromine were evaporated. The residue was dissolved with THF. *t*BuOK (69 mg, 0.62 mmol) was added to the solution. The mixture was stirred overnight at room temperature under N$_2$, the reaction was quenched with hydrochloric acid (2 M, 20 mL), and the mixture was extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous MgSO$_4$. The solvent was evaporated, and the residue was subjected to chromatography on silica gel (20 g, CH$_2$Cl$_2$) to give 8,14,30,36-tetramethoxy[2.0.2.0](1,6)naphthalenophane-1,19-diyne ((*S*,*S*)-**2**; 18 mg, 37 %) as colorless prisms after recrystallization from hexane/toluene (5:1). M.p.: 200 °C (decomp.); UV/Vis (CH$_2$Cl$_2$): λ (log ε) = 355 (4.36), 308 (4.75), 255 nm (5.23); IR (KBr): $\tilde{\nu}$ = 801 (m), 824 (m), 884 (s), 1042 (m), 1069 (m), 1097 (m), 1174 (m), 1274 (s), 1334 (s), 1483 (s), 1592 (s), 2163 (w, C≡C), 2837 (m), 2935 cm^{-1} (m); ^{1}H NMR (270 MHz, CDCl$_3$): δ = 7.89 (d, J = 8.9 Hz, 4 H), 7.72 (d, J = 1.5 Hz, 4 H), 7.45 (d, J = 9.1 Hz, 4 H), 6.87 (dd, J = 8.9, 1.6 Hz, 4 H), 6.14 (d, J = 8.9 Hz, 4 H), 3.96 ppm (s, 12 H); ^{13}C NMR (68 MHz, CDCl$_3$): δ = 155.7, 134.3, 130.8, 129.5, 128.6 (two signals overlapped), 126.1, 125.9, 119.1, 114.4, 99.0, 56.8 ppm; MS (FAB): m/z (%) = 672 $[M]^+$ (100). Single crystals deposited from hexane/toluene were subjected to X-ray diffraction, and the results confirmed the molecular structure.

(*S*,*S*)-**6**: Pd/C (10 %, 12 mg) was added to a solution of (*S*,*S*)-**3** (40 mg, 0.059 mmol) in toluene (10 mL), and the suspension was stirred overnight at room temperature under H$_2$. The used catalyst was removed by filtration, and the solvent was evaporated to give 8,14,30,36-tetramethoxy-[2.0.2.0](1,6)naphthalenophane ((*S*,*S*)-**6**; 40 mg, 99 %) as colorless fine needles. M.p.: 290 °C (decomp.); UV/Vis (THF): λ (log ε) = 344 (4.05), 330 (3.98), 294 (4.11), 283 (4.23), 273 (4.21), 237 nm (5.16); IR (KBr): $\tilde{\nu}$ = 818 (m), 910 (w), 1066 (m), 1095 (m), 1178 (w), 1255 (s), 1327 (m), 1354 (m), 1483 (m), 1501 (m), 1596 (s), 2835 (m), 2932 cm^{-1} (m); ^{1}H NMR

(270 MHz, $CDCl_3$): $\delta=7.85$ (d, $J=8.9$ Hz, 4H), 7.74 (d, $J=1.5$ Hz, 4H), 7.32 (d, $J=8.9$ Hz, 4H), 6.61 (d, $J=8.6$ Hz, 4H), 6.22 (dd, $J=8.6$, 1.8 Hz, 4H), 3.62 (s, 12H), 3.35 (d, $J=9.1$ Hz, 4H), 2.84 ppm (d, $J=9.1$ Hz, 4H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta=154.1$, 136.3, 132.2, 129.2, 129.2, 128.2, 126.3, 123.8, 119.7, 114.2, 57.0, 38.5 ppm; MS (EI): m/z (%) = 680 $[M]^+$ (100); HRMS: m/z calcd for $C_{48}H_{40}O_4$: 680.2927; found: 680.2958.

*X-ray Crystallographic Analysis of **2***

Intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71069$ Å). The structure was solved by direct methods on F^2 with SHELXS-97. A total of 5795 reflections were collected, 5116 unique reflections were measured and used in the refinement, 523 parameters, $R1=0.0432$, $wR2=0.1438$ for 1687 reflections with $I>2\sigma(I)$, GOF = 0.923, maximum peak in final difference map 0.78 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by using a rigid model. Crystal data for **2**·C_6H_{14}: $M_r=758.91$, monoclinic, $P2_1$ (#4), $a=13.414(2)$, $b=13.041(2)$, $c=12.213(2)$ Å, $\beta=91.68(1)°$, $V=2135.4(5)$ Å^3, $Z=2$, $\rho=1.046$ g cm^{-3}. CCDC-262753 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/data_request/cif.

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