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[2.0.2.0]Metacyclophane-1,15-diynes. A Potential Fragment of Double-Helical Conjugated Systems

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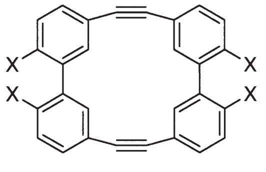
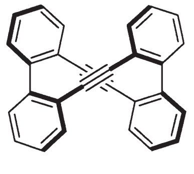
The title cyclophanes as a potential fragment of double-helical π-conjugated system were synthesized, and the spectroscopic and crystallographic characterization shows the strained nature of the π-system; variable-temperature NMR spectra also reveal that the cyclophanes exist as an equilibrium mixture between the *meso*- and *dl*-forms in solution.

Double-helical molecules are of great interest because of their unique structures as well as potential applications in optics and electronics; therefore, synthetic chemists have been interested in the double-helical arylacetylene oligomers.[1] The combination of the cyclophanes **1** and **2** may construct a half pitch of the double-helical oligomers. Although the cyclophane **2** has been synthesized by Staab's group 30 years ago,[2] **1** has remained unknown. Recently we have synthesized several macrocyclic cyclophanes with strained acetylenic bonds using the McMurry coupling as a key step, and studied the molecular functions based on the novel structures.[3,4] Here we report the synthesis, properties and the molecular structure of **1**.



1a : X = H
1b : X = OMe



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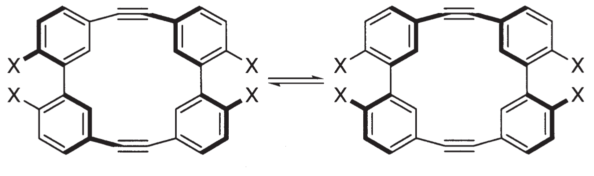
The cyclophanes **1** have two possible diastereomers, *meso*- and *dl*-form owing to two asymmetric axes of the biphenyl units. The semiempirical calculation (AM-1)[5] predicts the distorted structures of **1** with bent triple bonds (*meso*-**1a**; 162.4°, *dl*-**1a**; 162.4°, *meso*-**1b**; 163.6°, and *dl*-**1b**; 163.7°). The introduction of four methoxy groups seems to induce the further deformation not to the acetylenic bonds but to the aromatic rings (twisted angle of biphenyl units: *meso*-**1a**; 29.5°, *dl*-**1a**; 30.0°, *meso*-**1b**; 38.7°, and *dl*-**1b**; 39.9°). The calculation also predicts that the diastereomers have small differences in the heat of formation ($\Delta H_f = 0.04$ kcal/mol for **1a**, and $\Delta H_f = -0.34$ kcal/mol for **1b**).[6] Thus, **1** may exist as an equilibrium mixture in solution.

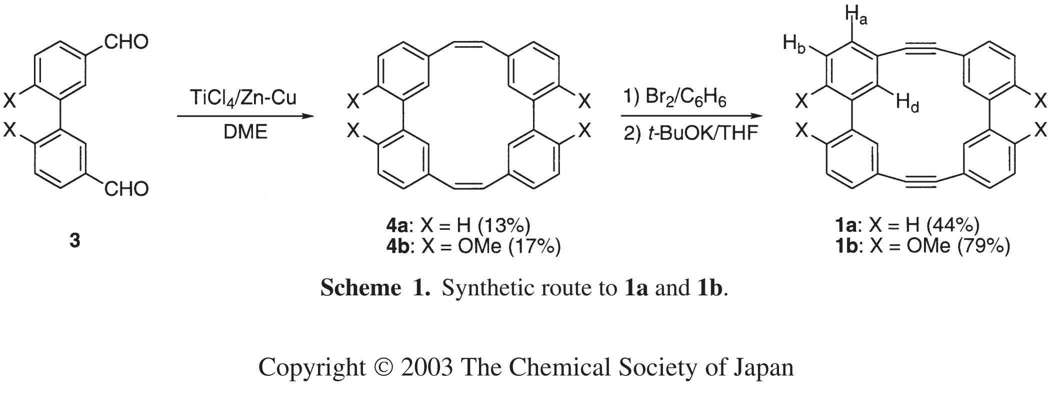


dl-**1** *meso*-**1**

Scheme 1 outlines the synthesis of **1**. Thus, the McMurry coupling of 3,3′-biphenyldicarbaldehydes **3**[7] afforded the corresponding [2.0.2.0]metacyclophanedienes **4** in better yields than the known synthesis using the bis-Wittig reaction (**4a**: 4%).[8] Bromination and dehydrobromination of **4** led to the cyclophanes **1**[9] as stable crystalline substances in moderate yields.

Good single crystals of **1b** for X-ray analysis were obtained from *p*-xylene and chlorobenzene solutions, respectively. The latter crystal includes the solvent molecule with 1:1 ratio,[10] while the former has no inclusion.[11] The structural analyses using these crystals reveal that **1b** adopts a *meso*-form with considerably distorted triple bonds. Figure 1 shows the molecular structure of **1b** in the crystal from *p*-xylene. The bond angles of acetylenic carbons (av 160.8° for *p*-xylene and 159.9° for chlorobenzene) are about 13° smaller than those of **2** (173.8°),[2b] and almost comparable to those of [2.2.2]metacyclophanetriyne (av 158.6°).[4b] And the obseved twisted angles of biphenyl units (40.2° for *p*-xylene and 38.8° for chlorobenzene) are almost consistent with those of the calculation.

Table 1 shows the selected spectral data of **1a** and **1b** together with those of the reference compounds **5a** and **5b**.[12] In comparison with **5**, **1** exhibit relatively broad absorption bands and bathochromic shift in fluorescence spectra probably due to the distorted structures.[4d] The ^{1}H- and ^{13}C NMR spectra of **1** show the expected simple pattern in agreement with the high symmetry of the molecule at 30 °C. The considerably low field shifts of the sp carbons also indicate the highly strained nature of the cyclophanes.[4] Although the crystal analyses indicate that **1b** adopts the *meso*-form alone in crystal, variable-temperature NMR experiments reveal that **1b** exists in an equilibrium mixture between *meso*- and *dl*-forms in solution (Figure 2). The signals of



Scheme 1. Synthetic route to **1a** and **1b**.

Table 1. Selected spectral data of tolanophane **1a**-**b** and reference **5a**-**b**

		1a	**5a**	**1b**	**5b**
^{1}H NMR[a]	H$_d$	8.51	7.79	7.79	7.40
^{13}C NMR[a]	sp carbon	99.3	89.5[c]	97.6	88.0[c]
Longest absorption max.	nm (log ε)[b]	282 (4.45)	284 (4.78)	292 (4.70)	297 (4.86)
Emission max.[b]	nm	349	333	367	359

[a]δ in $CDCl_3$. [b]In CH_2Cl_2. [c]Averaged value.

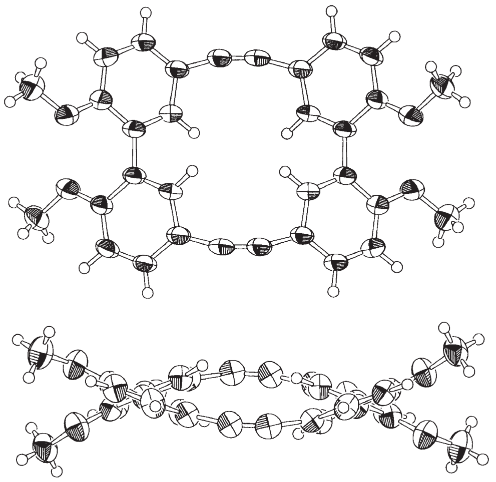


Figure 1. Crystal structure of **1b**. Top: Plan view; bottom: Side view (ORTEP; 50% probability). Selected bond angles and torsion angles (°): C1–C2–C3 160.5(3); C13–C15–C16 161.0(3); C2–C3–C8 115.8(2); C8–C7–C9 117.4(2); C2–C3–C8–C7 163.7(3); C4–C3–C8–C7 7.0(4); C6–C7–C9–C10 54.0(4); C8–C7–C9–C14 40.2(4).

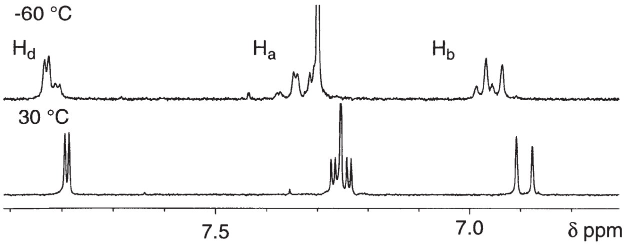


Figure 2. ^{1}NMR spectra of **1b** in $CDCl_3$.

the aromatic protons begin broadening at around −40 °C, and become two sets of three signals at −60 °C (major : minor = ca. 5 : 1, $\Delta G^{\ddagger}$ = ca. 12 kcal/mol, $T_c = -50$ °C). The assignment of the major component in solution is hardly determinable because of the structural similarity between both diastereomers. Although the parent compound **1a** did not show the similar spliting even at −100 °C, the cyclophane would be in equilibrium between two diastereomers with relatively low energy barrier than that of **1b**.

In conclusion, the cyclophanes **1** exist in two inter-changeable diastereomers in spite of the highly strained structure. The energy barrier would be controllable by introducing appropriate substituents on aromatic rings. Thus, the system would be a potential pigment for construction of dynamic chirality sensors[14] as well as a component of double-helical conjugated systems.

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6 ΔH_f represents the difference of the calculated heat of formations (H_f); ΔH_f = (H_f of *meso*-form) – (H_f of *dl*-form).

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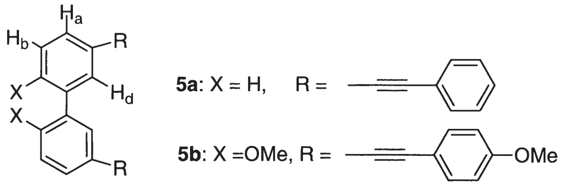
9 [2.0.2.0]metacyclophane-1,15-diyne (**1a**); Colorless plates (from toluene), decomp 280 °C; MS (EI, 70 eV) *m/z* (rel. int.) 352 (100, M$^+$); ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.29 (4H, ddd, J = 7.6, 1.6, 1.0 Hz), 7.45 (4H, dd, J = 7.8, 7.6 Hz), 7.71 (4H, ddd, J = 7.8, 2.0, 1.0 Hz), 8.51 (4H, dd, J = 2.0, 1.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$, δ): 99.3, 124.7, 125.1, 125.7, 129.4, 135.7, 138.2; UV (CH_2Cl_2) λ_{max} (log ε) 228 (4.14), 282 (4.45), 306 nm (3.98); Fluorescence (CH_2Cl_2) λ_{max} 349 nm. 6,10,20,24-Tetramethoxy[2.0.2.0]metacyclophane-1,15-diyne (**1b**); Colorless prisms (from *p*-xylene), decomp 270 °C; MS (EI, 70 eV) *m/z* (rel. int.) 472 (100, M$^+$); ^{1}H NMR (270 MHz, $CDCl_3$, δ): 3.89 (12H, s), 6.89 (4H, d, J = 8.6 Hz), 7.25 (4H, dd, J = 8.6, 2.2 Hz), 7.79 (4H, d, J = 2.2 Hz); ^{13}C NMR (68 MHz, $CDCl_3$, δ): 56.0, 97.6, 111.4, 117.2, 127.4, 128.3, 141.1, 157.2; UV (CH_2Cl_2) λ_{max} (log ε) 230 (4.72), 292 nm (4.70); Fluorescence (CH_2Cl_2) λ_{max} 367 nm.

10 Crystal data for **1b**·C_6H_5Cl: $C_{38}H_{29}O_4Cl$, M_r = 585.09; Orthorhombic, *Pnnm* (#58), a = 7.379(1) Å, b = 12.295(2) Å, c = 16.918(4) Å, V = 1534.8(10) Å^3, Z = 2, D = 1.266 g cm^{-3}; R_1 = 0.077. The data were deposited in Cambridge Crystallographic Data Center (CCDC 204617).

11 Crystal data for **1b**: $C_{32}H_{24}O_4$, M_r = 472.53; Monoclinic, $P2_1/c$ (#14), a = 10.407(1) Å, b = 14.374(2) Å, c = 8.212(1) Å, β = 102.25(1)°, V = 1200.4(3) Å^3, Z = 2, D = 1.307 g cm^{-3}; R_1 = 0.061. The data were deposited in Cambridge Crystallographic Data Center (CCDC 204616).

12 The reference compounds **5a** and **5b** were synthesized by the Wittig reaction of **3** with corresponding phosphonium salts and followed by bromination and dehydrobromination.



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