

A Cyclic Oligophenylene Containing Two 1,8-Naphthalene Units Bridged by Two Face-to-Face Biphenyl Linkages Exhibiting Unusual Strain and $\pi-\pi$ Interaction

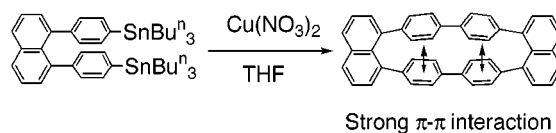
Masahiko Iyoda,* Terumasa Kondo, Kazumi Nakao, Kenji Hara, Yoshiyuki Kuwatani, Masato Yoshida, and Haruo Matsuyama

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

iyoda-masahiko@c.metro-u.ac.jp

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ABSTRACT



1,8-[1,8-Naphthalenediylbis(4',4'-biphenyldiyl)]naphthalene, a very stable strained cyclophane, has been synthesized in moderate yield using the copper-catalyzed coupling of 1,8-bis(4-(tributylstannyl)phenyl)naphthalene. The X-ray analysis of the titled compound discloses bent p,p' -biphenylene chains with splayed naphthalene rings, and the p,p' -biphenylene chains located face-to-face indicate a fairly strong $\pi-\pi$ interaction.

Cyclophanes and cyclic oligophenylenes have attracted considerable interest among experimental and theoretical chemists,^{1,2} because of their unique structures, $\pi-\pi$ interaction, molecular strain, and aromaticity, and as substrates for

host-guest chemistry. Although 2,17-dithia[3,3](4,4')-biphenylophane **1b** has been synthesized (Figure 1),^{3a} the

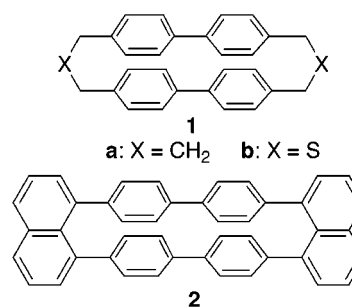


Figure 1. 3,3-Biphenylophanes.

$\pi-\pi$ interaction between two biphenyl rings seems to be not very large due to release of strain energy by bending

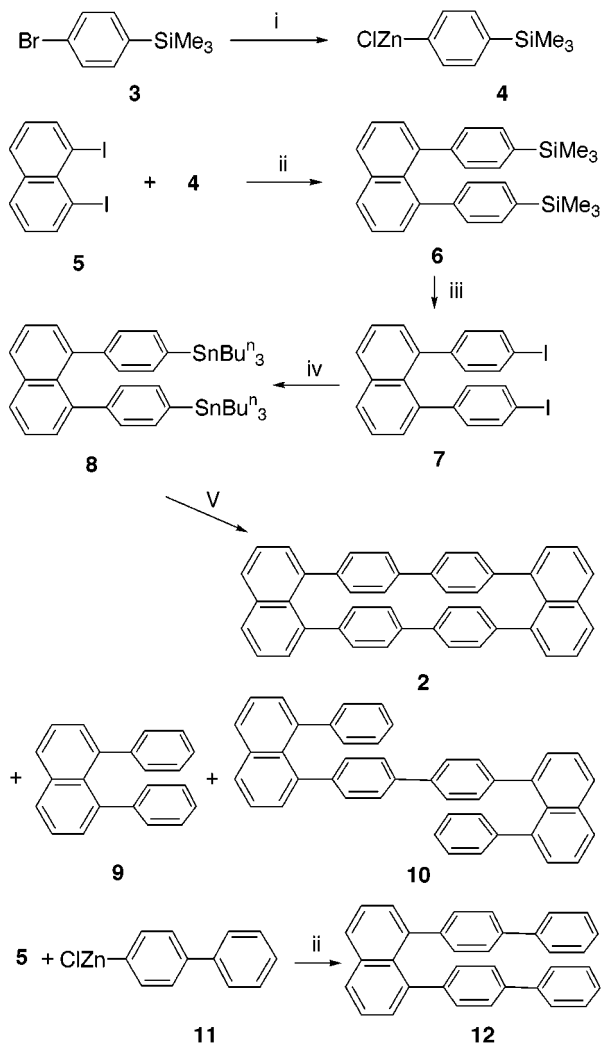
(1) For general reviews of cyclophanes, see Weber, E., Ed. *Cyclophanes*. In *Topics in Current Chemistry*; 1994; Vol. 172. Vögtle, F. *Cyclophane Chemistry*; Wiley: New York, 1993. Diederich, F. *Cyclophanes; Monographs in Supramolecular Chemistry*; The Royal Society of Chemistry: London, 1991.

(2) For oligophenylenes, see, Staab, H. A.; Binnig, F. *Chem. Ber.* **1967**, *100*, 293. Irgartinger, H.; Leiserowitz, L.; Schmidt, G. M. *J. Chem. Ber.* **1970**, *103*, 1132. Wittig, G.; Rümpler, K.-D. *Liebigs Ann.* **1971**, *751*, 1. Fujioka, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3494. Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. B.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645. Chan, C. W.; Wong, H. N. C. *J. Am. Chem. Soc.* **1985**, *107*, 4790; **1988**, *110*, 462. König, B.; Heinze, J.; Meerholz, K.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1361. Percec, V.; Okita, S. *J. Polym. Sci. Polym. Chem. Ed.* **1993**, *31*, 877. Wong, T.; Yuen, M. S. M.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **1993**, *58*, 3118. Rajca, A.; Safronov, A.; Rajca, S.; Shoemaker, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 488. Hensel, V.; Lützwow, K.; Jacob, J.; Gessler, K.; Saenger, W.; Schlüter, A.-D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2654. Kelly, T. R.; Lee, Y.-J.; Mears, R. J. *J. Org. Chem.* **1997**, *62*, 2774. Hensel, V.; Schlüter, A. D. *Chem. Eur. J.* **1999**, *5*, 421.

the 2-thiapropano bridges. In contrast, cyclic oligophenylene **2** with a [3.3]biphenylophane framework like **1a** can be expected to have a conformationally rigid structure with a face-to-face arranged 1,8-diphenylnaphthalene system which has been investigated extensively over the last several decades.⁴ We now report here the first synthesis of the cyclic oligophenylene **2** using the copper-catalyzed coupling of 1,8-bis(4-(tributylstannyl)phenyl)naphthalene.

Compound **2** was synthesized according to the reaction sequence outlined in Scheme 1. The arylzinc reagent **4** was

Scheme 1. Syntheses of **2** and Related Compounds



Reagents and conditions: i) 1) BuⁿLi, 2) ZnCl₂; ii) Pd(PPh₃)₄ (10 mol%), 0 °C, 30 min, room temp., 15 h; iii) ICl, -20 °C, 10 min, 50 °C, 30 min; iv) 1) BuⁿLi, 2) Buⁿ₃SnCl; v) Cu(NO₃)₂·3H₂O

prepared from **3** in THF by successive treatment with butyllithium (1.2 equiv) and zinc chloride (1.3 equiv). The reaction of 1,8-diiodonaphthalene **5** with **4** (4 equiv) in the presence of Pd(PPh₃)₄ (10 mol %) in THF at room temperature for 15 h proceeded smoothly to give **6**⁵ in 60% yield. Treatment of **6** with ICl (2.0 equiv) in CCl₄ at -20 to +50 °C produced **7** in 74% yield. Although attempted couplings

of **7** with transition metal catalysts were unsuccessful, the coupling reaction of 1,8-bis(4-(tributylstannyl)phenyl)naphthalene **8** with Cu(NO₃)₂·3H₂O (2.2 equiv) in THF resulted in the formation of **2** in moderate yield. Thus, the reaction of **7** with butyllithium (3.2 equiv), followed by treatment with chlorotributyltin(IV) (3.5 equiv) gave **8** in 76% yield. The reaction of **8** with Cu(NO₃)₂·3H₂O (2.2 equiv) in THF at room temperature for 1 h produced **2** in 41% yield, together with **9** (9%) and **10** (5%). To clarify the properties of the face-to-face arranged biphenyl units in **2**, the open chain analogue **12**⁶ was synthesized in 50% yield by the palladium-catalyzed cross-coupling reaction of **5** with **11**.

Recrystallization of **2** from chlorobenzene gave single crystals, and the crystal structure of **2** was determined by X-ray diffraction method.⁷ As shown in Figure 2, the two

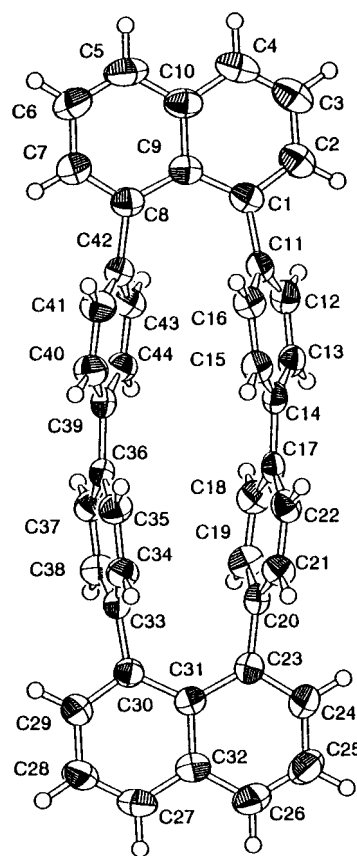


Figure 2. The molecular structure of **2**.

p,p'-biphenylene chains are located face-to-face. The intramolecular distances between two phenyl carbons are 2.99–3.66 Å (C11–C42, 3.03 Å; C20–C33, 2.99 Å; C14–

(3) For biphenylophanes, see (a) Staab, H. A.; Haenel, M. *Chem. Ber.* **1973**, *106*, 2190. (b) Thulin, B.; Wennerström, O.; Somfai, I.; Chmielarz, B. *Acta Chem. Scand.* **1977**, *B31*, 135. (c) Nishimura, J.; Doi, H.; Ueda, E.; Ohbayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 5293. (d) Tani, K.; Seo, H.; Maeda, M.; Imagawa, K.; Nishiwaki, N.; Ariga, M.; Tohda, Y.; Higuchi, H.; Kuma, H. *Tetrahedron Lett.* **1995**, *36*, 1883. (e) van Eis, M. J.; de Kanter, F. J. J.; de Wolf, W. H.; Bickelhaupt, F. J. *Am. Chem. Soc.* **1998**, *120*, 3371.

C39, 3.66 Å; C17–C36, 3.65 Å). Thus, the benzene rings stand nearly parallel in contrast to 1,8-diphenylnaphthalene **9**.⁸ Each benzene carbon's C_{sp²}-C_{sp²} contact is 2–12% shorter than the sum of the van der Waals radii (3.40 Å). On the other hand, the naphthalene parts indicate a splayed structure, and the intramolecular distances (C4–C5 and C26–C27) are 2.44 and 2.45 Å, respectively, whereas the C1–C8 and C23–C30 distances are 2.59 and 2.58 Å, respectively. Therefore, the structure of the naphthalene parts is almost the same as that of 3-bromo-1,8-dimethylnaphthalene.⁹ Noteworthy is the high coplanarity of the benzene rings, the maximum atomic deviations from the least-squares planes of the four benzene rings being 0.02–0.05 Å. In contrast, the X-ray analyses of [2.2]- and [3.3]paracyclophanes revealed bending of the benzene rings.¹⁰ Therefore, the ring strain in **2** is mainly released by bending six pivot bonds. The out-of-plane deformation angles of the C–C bonds between the two phenyl rings of the biphenyl chains have an average value of 4.1°, and those between the phenyl and naphthalene groups have an average value of 2.2° to the phenyl rings. Thus, **2** can be regarded as a very stable strained molecule, melting at 460–462 °C without decomposition.

Although strained cyclophanes and oligophenylenes such as 1,2:9,10-dibenzo[2.2]paracyclophane-1,9-diene and naph-

thalenoparacyclophanes are known as π -acids and can be reduced chemically and electrochemically to produce the corresponding radical anions and dianions,^{11,12} [3.3]paracyclophane behaves as a π -base to form the CT-complex with tetracyanoethylene (TCNE) in solution and in the solid state.¹³ The cyclic oligophenylene **2**, like [3.3]paracyclophane, forms CT-complexes with TCNE ($\lambda_{\text{max}} = 638$ nm) and DDQ ($\lambda_{\text{max}} = 790$ nm) in CH₂Cl₂. Interestingly, the oxidation potential of **2** measured by cyclic voltammetry is fairly low ($E_{1/2}^{(1)} = 0.85$ V vs F_c/F_c^+),¹⁴ whereas **9**, **10**, and **12** show no oxidation peak under similar conditions.

The title compound **2** and related compounds (**9**, **10**, and **12**) show strong fluorescence in solution and in the solid state. UV and fluorescence spectra of **2**, **9**, **10**, and **12** in benzene are summarized in Table 1. The absorption maxima

Table 1. Fluorescence Quantum Yields and Absorption Coefficients of **2**, **9**, **10**, and **12**

compound	UV		fluorescence	
	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/10^4/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	Φ_f^a
9	302	1.23	377	0.11
12	304	4.30	389	0.34
10	315	3.49	393	0.41
2	313	5.67	427	0.12

^a The quantum yield was calculated in benzene by using a 0.5 M solution of quinine sulfate as a standard ($\Phi_f = 0.546$).

of **2**, **9**, **10**, and **12** are similar, whereas **2** shows the largest Stokes shift (114 nm), presumably due to the dimerized structure. It is worth noting that **2** shows much lower fluorescence quantum yield as compared to **10**, although the conformational mobility of **2** seems to be smaller than that of **10**. Further studies on the electronic structure and properties of **2** are now under way.

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(11) de Meijere, A.; Gerson, F.; König, B.; Reiser, O.; Wellauer, T. *J. Am. Chem. Soc.* **1990**, *112*, 6827; Gerson, F.; Scholz, M.; de Meijere, A.; König, B.; Heinze, J.; Meerholz, K. *Helv. Chim. Acta* **1992**, *75*, 2307.

(12) Bieber, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 175. Gerson, F.; Heckendorf, R.; Möckel, R.; Vögtle, F. *Helv. Chim. Acta* **1985**, *68*, 1923.

(13) Sheehan, M.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3553.

(14) Cyclic voltammetric analysis: 1,2-dichlorobenzene, 0.05 M Bu₄NPF₆, glassy carbon working, Pt counter, and Ag/Ag⁺ reference electrodes, 298 K.

(4) For general reviews, see (a) Balasubramanian, V. *Chem. Rev.* **1966**, *66*, 567. (b) König, P. *Topics Curr. Chem.* **1998**; *196*, 91.

(5) All new compounds were fully characterized by spectroscopic analyses. The selected data are as follows: **2**, colorless cryst, mp 460–462 °C, EI-MS m/z 556 (M^+); ¹H NMR (CDCl₃) δ 6.928 (8H, d, $J = 7.7$ Hz), 7.104 (8H, d, $J = 7.7$), 7.548 (4H, dd, $J = 7.2$ and 1.3), 7.605 (4H, dd, $J = 7.8$ and 7.2), 7.985 (4H, dd, $J = 7.8$ and 1.3); ¹³C NMR (CS₂:CDCl₃ = 3:1) δ 124.99, 125.58, 129.03, 129.08, 130.06, 130.55, 135.35, 138.15, 139.65, 140.97; HRMS m/z calcd for C₄₄H₂₈ 556.2191, found 556.2185. **10**: colorless cryst, mp 239–240 °C, EI-MS m/z 558 (M^+); ¹H NMR (CDCl₃) δ 6.939–7.008 (10H, m), 6.973 (4H, d, $J = 8.3$), 7.000 (4H, d, $J = 8.3$), 7.456 (2H, dd, $J = 7.0$ and 1.5), 7.500 (2H, dd, $J = 7.0$ and 1.5), 7.580 (2H, dd, $J = 8.0$ and 7.0), 7.591 (2H, dd, $J = 8.0$ and 7.0), 7.981 (2H, dd, $J = 8.0$ and 1.5), 7.984 (2H, dd, $J = 8.0$ and 1.5); ¹³C NMR (CDCl₃) δ 125.14, 125.42, 125.76, 127.08, 128.33, 128.64, 128.66, 129.45, 129.96, 130.10, 130.73, 131.03, 135.44, 138.61, 140.16, 140.51, 141.80, 143.16; HRMS m/z calcd for C₄₄H₃₀ 558.2348, found 558.2322.

(6) Ibuki, E.; Ozasa, S.; Fujioka, Y.; Mizutani, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 845.

(7) X-ray intensity data were measured on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with Mo K α radiations using a crystal with the dimension of 0.20 \times 0.40 \times 0.05 mm. A total of 6571 reflections were collected up to $2\theta = 55.0^\circ$, of which 6565 had $I > -10.00\sigma(I)$, and were used in the refinement. The crystal structure was solved by a direct method (SIR92), expanded using Fourier techniques (DIRDIF94), and refined by the full matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. Crystal data for **2**: C₄₄H₂₈, FW = 556.71, orthorhombic, space group *Pbca* (#61), $a = 24.1982(5)$ Å, $b = 30.3055(7)$ Å, $c = 7.8559(2)$ Å, $V = 5761.0(2)$ Å³, $Z = 8$, $d_{\text{calcd}} = 1.284$ g cm⁻³, $R_1 = 0.044$ and $wR_2 = 0.118$ for 397 variables, GOF = 0.62.

(8) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003; Vögtle, F.; Papkalla, T.; Koch, H.; Nieger, M. *Chem. Ber.* **1990**, *123*, 1097.

(9) Jameson, M. B.; Penfold, B. R. *J. Chem. Soc.* **1965**, 528.

(10) Brown, C. J. *J. Chem. Soc.* **1953**, 3265; Lonsdale, D. K.; Milledge, H. J.; Rao, K. V. K. *Proc. R. Soc.* **1960**, *A255*, 82; Gantzel, P. K.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *18*, 958; Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr.* **1972**, *B28*, 1733.