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

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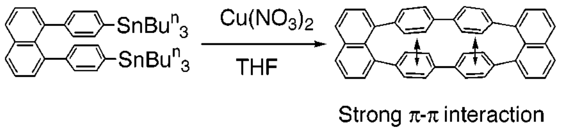
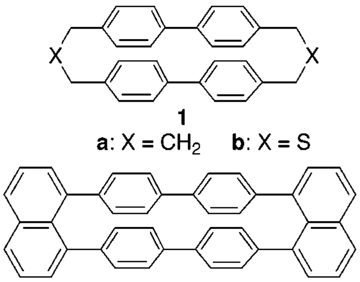
ABSTRACT



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′*-biphenylylene chains with splayed naphthalene rings, and the *p,p′*-biphenylylene chains located face-to-face indicate a fairly strong π−π interaction.

Cyclophanes and cyclic oligophenylenes have attracted considerable interest among experimental and theoretical chemists,[1,2] because of their unique structures, π−π 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 π−π interaction between two biphenyl rings seems to be not very large due to release of strain energy by bending



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a: X = CH$_2$ **b**: X = S

2

Figure 1. 3,3-Biphenylophanes.

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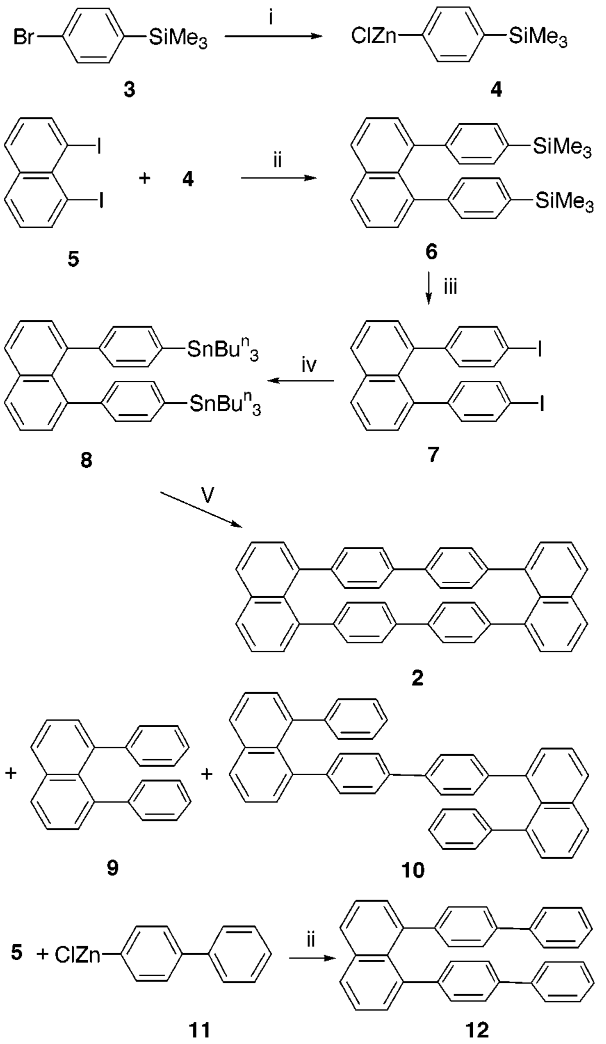
the 2-thiapropano bridges. In contrast, cyclic oligophenylene **2** with a [3.3]biphenylophane framework like **1a** can be expected to have a conformationally rigid structure with a face-to-face arranged 1,8-diphenylnaphthalene system which has been investigated extensively over the last several decades.[4] 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 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(PPh$_3$)$_4$ (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 CCl$_4$ 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(NO$_3$)$_2$•3H$_2$O (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(NO$_3$)$_2$•3H$_2$O (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**.

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



Reagents and conditions: i) 1) Bu^{n}Li, 2) ZnCl$_2$; ii) Pd(PPh$_3$)$_4$ (10 mol%), 0 °C, 30 min, room temp., 15 h; iii) ICl, -20 °C, 10 min, 50 °C, 30 min; iv) 1) Bu^{n}Li, 2) Bu$^n_3$SnCl; v) Cu(NO$_3$)$_2$•3H$_2$O

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 *p*,*p*′-biphenylylene 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−

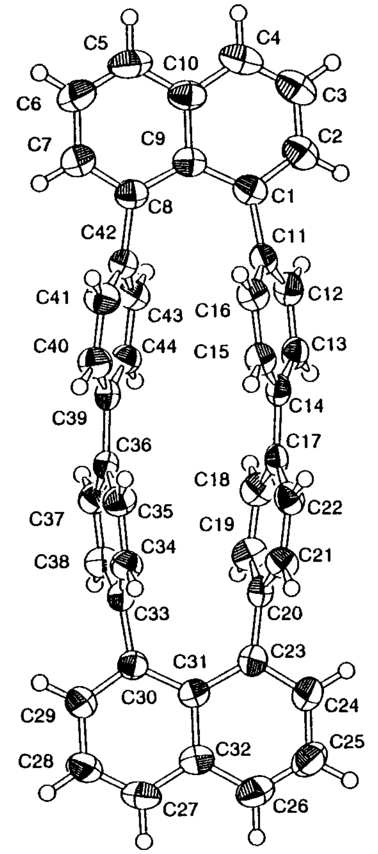


Figure 2. The molecular structure of **2**.

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(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_{sp^2}-C_{sp^2} 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 naphthalenoparacyclophanes 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 (λ_{max} = 638 nm) and DDQ (λ_{max} = 790 nm) in CH_2Cl_2. 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 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.

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

	UV		fluorescence	
compound	λ_{max}/nm	ϵ 10^4/M^{-1} cm^{-1}	λ_{max}/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 (Φ_f = 0.546).

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(4) For general reviews, see (a) Balasubramaniyan, 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 ($CDCl_3$) 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); ^{13}C NMR (CS_2:$CDCl_3$ = 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 $C_{44}H_{28}$ 556.2191, found 556.2185. **10**: colorless cryst, mp 239−240 °C, EI-MS *m/z* 558 (M^+); ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{44}H_{30}$ 558.2348, found 558.2322.

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(7) X-ray intensity data were measured on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with Mo Kα radiations using a crystal with the dimension of 0.20 × 0.40 × 0.05 mm. A total of 6571 reflections were collected up to $2\theta = 55.0°$, 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**: $C_{44}H_{28}$, FW = 556.71, orthorhombic, space group *Pbca* (#61), $a = 24.1982(5)$ Å, $b = 30.3055(7)$ Å, $c = 7.8559(2)$ Å, $V = 5761.0(2)$ Å^3, $Z = 8$, $d_{calcd} = 1.284$ g cm^{-3}, $R_1 = 0.044$ and $_wR_2 = 0.118$ for 397 variables, GOF = 0.62.

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

(14) Cyclic voltammetric analysis: 1,2-dichlorobenzene, 0.05 M Bu_4NPF_6, glassy carbon working, Pt counter, and Ag/Ag^+ reference electrodes, 298 K.