## o-Carborane-based Biphenyl and p-Terphenyl Derivatives

Yasuhiro Morisaki,\* Masato Tominaga, Takuya Ochiai, and Yoshiki Chujo\*<sup>[a]</sup>

**Abstract:** The synthesis and properties of biphenyl- and *p*-terphenyl-fused *o*-carboranes are described. Aryl rings in the biphenyl and *p*-terphenyl skeletons are highly coplanar because of the presence of the *o*-carborane unit. *o*-Carborane exhibits an electron-withdrawing character via the inductive effect, resulting in a decrease in both the HOMO and LUMO levels of oligophenyls without causing electronic perturbation.

Recently, icosahedral carboranes  $(C_2H_{12}B_{10})^{[1]}$  have been used as building blocks for  $\pi$ -conjugated molecules<sup>[2]</sup> and polymers.<sup>[3]</sup> In particular, o-carborane (o-C<sub>2</sub>H<sub>12</sub>B<sub>10</sub>), containing two adjacent carbon atoms, imparts aggregation-induced emission (AIE)<sup>[4]</sup> properties to the molecules in which it is incorporated.<sup>[2e-k,3e-h]</sup> Optoelectronic properties, including AIE, are drastically altered by changes in orientation between the  $\pi$ -conjugated systems and the two adjacent carbon atoms in the o-carborane unit.<sup>[2i,j]</sup> When the torsion angle between the  $\pi$ -conjugated plane and the carboncarbon bond approaches 90°, AIE is observed due to intramolecular charge transfer (CT) from the  $\pi$ -conjugated system to the o-carborane cluster, as well as suppression of molecular motion. On the other hand, at a torsion angle close to 0°, o-carborane withdraws electrons inductively from the  $\pi$ -conjugated unit. Previously, we synthesized a bithiophene-fused o-carborane,<sup>[5]</sup> in which bithiophene and the o-carborane's carbon-carbon bond were fused; that is, the bithiophene unit and the carbon-carbon bond were on the same plane (dihedral angle of 0°). As a result, the o-carborane moiety acted as a strong electron-withdrawing group through an inductive effect rather than a conjugation effect. Recently, the bithiophene-fused o-carborane has attracted attention for optoelectronic materials.<sup>[6]</sup> Sun, Su, and coworkers predicted that bithiophene-fused o-carborane derivatives would exhibit large hyperpolarizability values by virtue of the electron-withdrawing character, which is ex-

[a]	Dr. Y. Morisaki, M. Tominaga, T. Ochiai, Prof. Dr. Y. Chujo
	Department of Polymer Chemistry
	Graduate School of Engineering
	Kyoto University
	Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
	Fax: (+81)75-383-2607
	E-mail: ymo@chujo.synchem.kyoto-u.ac.jp
	chujo@chujo.synchem.kyoto-u.ac.jp
	Supporting information for this article is available on the WWW

under http://dx.doi.org/10.1002/asia.201400067.

pected to be beneficial for applications in nonlinear optical (NLO) materials.<sup>[6a]</sup> Marshall, Heeney, and co-workers reported on the transistor performance of conjugated polymers containing the bithiophene-fused *o*-carborane as an acceptor.<sup>[6b]</sup> A variety of electron-deficient and highly planar oligoaryls can be obtained by the combination of *o*-carborane and oligoaryl systems; from this perspective, *p*-oligophenyls were chosen for investigation in this study. Herein, we report the synthesis and optoelectronic properties of *p*-oligophenyl-fused *o*-carboranes; that is, compounds in which biphenyl and *p*-terphenyl are attached to the two adjacent carbons of *o*-carborane.

Synthetic routes to biphenyl- and *p*-terphenyl-fused *o*-carboranes (**4** and **7**) are shown in Scheme 1. Treatment of bis-(2-bromophenyl)acetylene<sup>[7]</sup> (**1**) with decaborane ( $B_{10}H_{14}$ , **2**) in *N*,*N*-dimethylaniline afforded bis(2-bromophenyl)-*o*-car-



Scheme 1. Synthesis of compounds 4 and 7.

Chem. Asian J. 2014, 9, 1247-1251

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borane (3) in 16% yield.<sup>[8]</sup> Subsequently, the reaction of 3 with *n*BuLi was carried out to obtain the dilithiated species, and successive treatment with ZnBr<sub>2</sub> and CuCl<sub>2</sub> in situ afforded biphenyl-fused *o*-carborane 4 in 41% isolated yield. Target compound 7 was prepared by the same method from 1,4-dibromo-2,5-bis(2-bromophenylethynyl)benzene (5)<sup>[9]</sup> (Scheme 1). Compounds 4 and 7 were obtained as air- and moisture-stable white solids, and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectroscopy, high-resolution mass spectrometry (HRMS), and X-ray crystallography.

Compound 4 was soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, toluene, benzene, and DMF. Single crystals of 4 were readily obtained from CHCl<sub>3</sub> and MeOH, and the molecular structure, as determined by Xray crystallography, is shown in Figure 1.<sup>[10]</sup> The crystal structure of 4 revealed a high planarity of the biphenyl skeleton with a torsion angle (C1-C2-C3-C7) of 179.2(2)° between the two aromatic rings,<sup>[10a]</sup> which is almost same as that of phenanthrene (178.38°).<sup>[11]</sup> The C5-C6 bond length (1.643(2) Å) of the carborane cage in 4 is longer than those in benzene (1.397 Å), a general carbon–carbon double bond, and a single bond. The solubility of 7 in organic solvents was much lower than that of 4; the former could be dissolved only in hot CHCl<sub>3</sub>, benzene, and toluene. Single crystals of 7 were obtained from hot benzene and MeOH, and its molecular structure was confirmed by X-ray crystallography (Figure 1 B).<sup>[10b]</sup> The structure of **7** revealed the highly



Figure 1. ORTEP drawings of compounds **4** (A) and **7** (B). Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): **4** C1–C2 1.410(3); C2–C3 1.483(2); C3–C4 1.407(3); C4–C5 1.502(3); C5–C6 1.643(2); C6–C1 1.492(3); **7** C1–C2 1.402(5); C2–C3 1.477(5); C3–C4 1.407(5); C4–C5 1.510(5); C5–C6 1.633(5); C6–C1 1.497(5).

planar *p*-terphenyl skeleton with a torsion angle of  $178.9(4)^{\circ}$  (C1-C2-C3-C7). From the structures of **4** and **7**, it appears as if the 2- and 2'-positions in the two adjacent phenyl rings are rigidly held in the same plane by a clasp.

To obtain further insight into the aromaticity of the C1-C6 benzocarborane rings in 4 and 7, nucleus-independent chemical shift (NICS) values were calculated at the B3LYP/ 6-31G(d,p)//B3LYP/6-31G(d,p) level.<sup>[12]</sup> The results are summarized in Figure 2, together with values for the related compounds phenanthrene and 9,10-dihydrophenanthrene. The NICS(1) value of central aromatic ring of phenanthrene was -9.2 ppm, whereas that of the central 6-membered ring of 9,10-dihydrophenanthrene was -0.1 ppm. In compound 4, the NICS(1) values of the arene ring and C1-C6 benzocarborane ring were found to be -10.3 and -1.2 ppm, respectively. The NICS(1) calculation of the C1-C6 benzocarborane ring of 7 was also carried out, and the value was estimated to be -1.0 ppm (Figure 2). These results indicate that the C1-C6 benzocarborane rings of 4 and 7 are non-aromatic rings.



Figure 2. NICS values (ppm) of 4, phenanthrene, 9,10-dihydrophenanthrene, and 7 calculated at the B3LYP/6-31G(d,p)//B3LYP/6-31(d,p) level.

Figure 3 shows the molecular orbitals of 4, 9,10-dihydrophenanthrene, biphenyl, and phenanthrene obtained by density functional theory (DFT) calculations. In compound 4, no overlap of orbitals between the biphenyl moiety and carborane skeleton was observed. Thus, the molecular orbital of 4 was identical to those of 9,10-dihydrophenanthrene and biphenyl. The energy band gaps of 4 (4.90 eV) and 9,10-dihydrophenanthrene (4.99 eV) were narrower than that of bi-



Figure 3. The HOMO/LUMO orbitals and their energy levels calculated at the B3LYP/6-31G(d,p) level of theory for compound 4, 9,10-dihydrophenanthrene, biphenyl, and phenanthrene.

phenyl (5.37 eV) since the phenyl rings of biphenyl are twisted due to the repulsion of hydrogen atoms. The highly coplanar biphenyl moiety of 4 narrows the energy band gap in comparison with 9,10-dihydrophenanthrene. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of 4 were estimated to be -6.55 and -1.65 eV, respectively; these values were lower than those of the other compounds examined. Since a contribution of the electrical perturbation of the o-carborane skeleton to the biphenyl moiety was not observed, the deep HOMO and LUMO levels arose from the electron-withdrawing feature of o-carborane via the inductive effect. The LUMO energy level of 4 was estimated from the cyclic voltammogram (CV) peak onset potentials measured in the DMF solution, as shown in Figure S15 in the Supporting Information. A reduction signal with a peak onset at -1.2 V (vs. ferrocene/ferrocenium) appeared, whereas no peak was observed in biphenyl.<sup>[13]</sup>

In the case of the molecular orbitals of **7**, a similar tendency as for **4** was observed (see Figure S16 in the Supporting Information). The orbitals of **7** were identical to those of 5,6,12,13-dibenz[a,h]anthracene and p-terphenyl, and the energy band gap (4.18 eV) was similar to that of 5,6,12,13dibenz[a,h]anthracene (4.26 eV). Deep HOMO (-6.53 eV) and LUMO (-2.35 eV) energy levels were estimated, which were derived from the inductive electron-withdrawal of ocarborane.

UV/Vis absorption spectra of compounds 4 and 7 in  $CHCl_3$  (1.0×10<sup>-5</sup> M) are shown in Figure 4 together with the

spectra of biphenyl and p-terphenyl. Biphenyl exhibited a broad absorption peak (Figure 4A), whereas 4 exhibited a peak with a vibronic structure. In addition, the absorption peak edge of 4 was bathochromically shifted compared with that of biphenyl. As shown in Figure 4B, the spectrum of 7 also exhibited a vibronic structure, which was bathochromically shifted in comparison with that of *p*-terphenyl. These results are consistent with the suppression of the rotary motion of the phenylene rings by the *o*-carborane skeleton.  $\pi$ -Electrons are more effectively delocalized through the highly planar oligophenyl moieties fixed by o-carborane than the corresponding oligophenyls.

Photoluminescence (PL) spectra of **7** and *p*-terphenyl are shown in Figure S18 in the Supporting Information (in CHCl<sub>3</sub>;  $1.0 \times 10^{-5}$  M). The PL spectrum

of 7 exhibited a clear vibrational structure, and 7 emitted bright purple fluorescence with a PL quantum efficiency  $(\Phi_{\rm PL})$  of 0.52.<sup>[14]</sup> The Stokes shift was considerably small; the absorption peak at 336 nm (Figure 4B) and the PL peak at 337 nm (Figure S18, Supporting Information) indicated a 0-0 transition band. On the other hand, the PL peak top of pterphenyl appeared at 340 nm with a higher  $\Phi_{\rm PL}$  of 0.93. A broad vibrational PL spectrum of *p*-terphenyl was observed, thus suggesting that similar structures of p-terphenyl moieties in both 7 and *p*-terphenyl are formed in the excited state. To understand the decrease in  $\Phi_{\rm PL}$  of 7 (=0.52), PL measurements in a frozen medium were carried out (in 2-MeTHF;  $1.0 \times 10^{-5}$  M at 77 K), as shown in Figure S19 in the Supporting Information. The PL intensity of 7 increased apparently at 77 K; therefore, the main non-radiative deactivation process is caused by the molecular motion of the o-carborane moiety rather than by an intramolecular CT process.

In conclusion, the synthesis, characterization, and properties of oligophenyl-fused *o*-carboranes have been described. Owing to the effect of the *o*-carborane unit, high coplanarity of the oligophenyl moieties was achieved. As a result, extension of  $\pi$ -conjugation, small Stokes shift, 0–0 transition band, and clear vibronic structures in UV and PL spectra were observed. In addition, *o*-carborane acted as a strong electron-withdrawing group; in particular, *o*-carborane withdrew electrons inductively. *o*-Carborane decreased both HOMO and LUMO levels of oligophenyls without providing electronic perturbation. The energy levels of *p*-terphenyl-fused *o*-carboranes were lower than those of the corre-



Figure 4. UV/Vis absorption spectra in  $CHCl_3$  (1.0×10<sup>-5</sup>M). (A) Biphenyl and 4. (B) *p*-Terphenyl and 7.

sponding thiophene-fused benzocarborane. Further syntheses of various oligoaryl-fused *o*-carboranes and evaluation of the properties of completely coplanar oligoaryls are presently under investigation. Functionalization of the obtained biphenyl- and *p*-terphenyl-fused *o*-carboranes toward electron deficient  $\pi$ -conjugated building blocks is currently underway.

## Acknowledgements

This work was supported by Grant-in-Aid for Exploratory Research (No. 24655102) and Grant-in-Aid for Scientific Research on Innovative Areas "Element-Blocks" (No. 24102013) from the Japan Society for the Promotion of Science. M.T. appreciates Research Fellowships (No. 12J03404) from the Japan Society for the Promotion of Science for Young Scientists.

**Keywords:** benzocarborane  $\cdot$  biphenyl  $\cdot$  carboranes  $\cdot$  electron-deficient compounds  $\cdot$  *p*-terphenyl

- a) "Icosahedral carboranes: 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>", R. N. Grimes in *Carboranes*, Academic Press, **2011**, Chap. 9, pp. 301–540; b) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223; c) A. González-Campo, E. J. Juárez-Pérez, C. Viñas, B. Boury, R. Sillanpää, R. Kivekäs, R. Núñez, *Macromolecules* **2008**, *41*, 8458–8466; d) F. Issa, M. Kassiou, L. M. Rendina, *Chem. Rev.* **2011**, *111*, 5701–5722.
- [2] a) M. Lamrani, R. Hamasaki, M. Mitsuishi, T. Miyashita, Y. Yamamoto, Chem. Commun. 2000, 1595-1596; b) N. Tsuboya, M. Lamrani, R. Hamasaki, M. Ito, M. Mitsuishi, T. Miyashita, Y. Yamamoto, J. Mater. Chem. 2002, 12, 2701-2705; c) J.-F. Morin, T. Sasaki, Y. Shirai, J. M. Guerrero, J. M. Tour, J. Org. Chem. 2007, 72, 9481-9490; d) C. J. Villagómez, T. Sasaki, J. M. Tour, L. Grill, J. Am. Chem. Soc. 2010, 132, 16848-16854; e) B. P. Dash, R. Satapathy, E. R. Gaillard, K. M. Norton, J. A. Maguire, N. Chug, N. S. Hosmane, Inorg. Chem. 2011, 50, 5485-5493; f) K. Kokado, Y. Chujo, J. Org. Chem. 2011, 76, 316-319; g) K.-R. Wee, W.-S. Han, D. W. Cho, S. Kwon, C. Pac, S. O. Kang, Angew. Chem. 2012, 124, 2731-2734; Angew. Chem. Int. Ed. 2012, 51, 2677-2680; h) K.-R. Wee, Y.-J. Cho, S. Jeong, S. Kwon, J.-D. Lee, I.-H. Suh, S. O. Kang, J. Am. Chem. Soc. 2012, 134, 17982-17990; i) L. Weber, J. Kahlert, R. Brockhinke, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder, M. A. Fox, Chem. Eur. J. 2012, 18, 8347-8357; j) L. Weber, J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder, P. J. Low, M. A. Fox, Dalton Trans. 2013, 42, 2266-2281; k) K.-R. Wee, Y.-J. Cho, J. K. Song, S. O. Kang, Angew. Chem. Int. Ed. 2013, 52, 9682-9685.
- [3] a) H. M. Colquhoun, P. L. Herbertson, K. Wade, I. Baxter, D. J. Williams, *Macromolecules* 1998, *31*, 1694–1696; b) E. Hao, B. Fabre, F. R. Fronczek, M. G. H. Vicente, *Chem. Commun.* 2007, 4387–4389; c) F. Barrière, B. Fabre, E. Hao, Z. M. LeJeune, E. Hwang, J. C. Garno, E. E. Nesterov, M. B. H. Vicente, *Macromolecules* 2009, *42*, 2981–2987; d) J. J. Peterson, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Chem. Commun.* 2009, 4950–4952; e) K. Kokado, Y. Chujo, *Macromolecules* 2009, *42*, 1418–1420; f) J. J. Peterson, M. Werre, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Macromolecules* 2009, *42*, 8594–8598; g) J. J. Peterson, A. R. Davis, M. Werre, E. B. Coughlin, K. R. Carter, *ACS Appl. Mater. Interfaces* 2011, *3*, 1796–1799; h) A. R. Davis, J. J. Peterson, K. R. Carter, *ACS Macro Lett.* 2012, *1*, 469–472.
- [4] J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* 2001, 1740–1741.
- [5] Y. Morisaki, M. Tominaga, Y. Chujo, Chem. Eur. J. 2012, 18, 11251– 11257.
- [6] a) Y. Li, H.-Q. Wu, H.-L. Xu, S.-L. Sun, Z.-M. Su, J. Mol. Model. 2013, 19, 3741–3747; b) J. Marshall, B. C. Schroeder, H. Bronstein, I. Meager, S. Rossbauer, N. Yaacobi-Gross, E. Buchaca-Domingo, T. D. Anthopoulos, N. Stingelin, P. Beavis, M. Heeney, Macromolecules 2014, 47, 89–96; c) Heeney and co-workers reported the synthesis of 1,4-benzocarborane-containing conjugated polymers for the use in transistors; see: J. Marshall, Z. Fei, C. P. Yau, N. Yaacobi-Gross, S. Rossbauer, T. D. Anthopoulos, S. E. Watkins, P. Beavis, M. Heeney, J. Mater. Chem. C 2014, 2, 232–239.
- [7] S. Yamaguchi, T. M. Swager, J. Am. Chem. Soc. 2001, 123, 12087– 12088.
- [8] Steric hindrance of bromides at 2,2'-positions resulted in low yields. As shown in equation S2 in the Supporting Information, 2,2'-dichlorotolane yielded the carborane compound in 27% yield. 4,4'-Dibromotolane and tolane itself yielded the corresponding carboranes in 69% and 60% yields [Eqs. (S3) and (S4)], respectively.
- [9] G. Mao, A. Orita, D. Matsuo, T. Hirate, T. Iwanaga, S. Toyota, J. Otera, *Tetrahedron Lett.* 2009, 50, 2860–2864.
- [10] a) CCDC 978228 for 4; see Table S1 and Figure S13 in the Supporting Information; b) CCDC 978229 for 7; see Table S2 and Figure S14 in the Supporting Information. The crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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- [11] V. Petricek, I. Cisarova, L. Hummel, J. Kroupa, B. Brezina, Acta Crystallogr. Sect. B 1990, 46, 830–832.
- [12] Cartesian coordinates of the optimized structures are shown in Tables S3–S6 in the Supporting Information.
- [13] Due to the low solubility of **7** in organic solvents, it was difficult to compare the cyclic voltammograms.
- [14] PL intensities of **4** and biphenyl were weak ( $\Phi_{PL} < 0.01$ ), and noisy PL spectra were obtained (Figure S17, Supporting Information).

Received: January 14, 2014 Published online: March 3, 2014