DOI: 10.1002/ange.201408390

Helical Structures

Construction of a Highly Distorted Benzene Ring in a Double Helicene**

Sigma Hashimoto, Soichiro Nakatsuka, Masaharu Nakamura,* and Takuji Hatakeyama*

***Abstract:** A P-fused double helicene consisting of a highly distorted benzene ring, with a bending angle of 23°, has been synthesized by a tandem intramolecular phospha-Friedel–Crafts reaction. Despite the distortion and reduced aromaticity, the double helicene shows thermal and chemical stability. These are important features that make these compounds attractive for applications as a new C_2-symmetric bisphosphine ligand. The simple strategy proposed in this work can be used to prepare a diverse range of distorted molecules.*

Distorted molecules with unique properties are the focus of study of many research groups.[1] In particular, the construction of distorted benzene rings has received great attention in the fields of physical and structural chemistry.[2] The conventional approach for the construction of distorted benzene rings is to tether two benzene rings.[3] This tether can induce the maximum bending angle of 24.9° as in [1.1]paracyclophane[3b] (Figure 1 a). Another approach involves the introduction of bulky substituents on the benzene rings of acene[4] to avoid steric repulsion, thus neighboring substituents favor the twisting of the benzene rings. The twist and bending angles for each benzene ring are in the range of 27 to 30° and 19 to 22°, respectively (Figure 1 b).[5] We herein report an alternative approach based on the twisting of a benzene ring promoted by two identical helical distortions as shown in Figure 2 a. We have demonstrated the validity of this approach with the synthesis of the double helicene **1**, which has a benzene ring surrounded by two [5]helicene substructures as double helical moieties (Figure 2 b). To achieve an efficient helical distortion, **1** has been substituted with methyl groups at the end position of the [5]helicene substructures. We have also introduced two phosphorus atoms at a position *para* to the central benzene ring as this ensures the facile construction of a highly distorted structure by a tandem phospha-Friedel–Crafts reaction.[6]

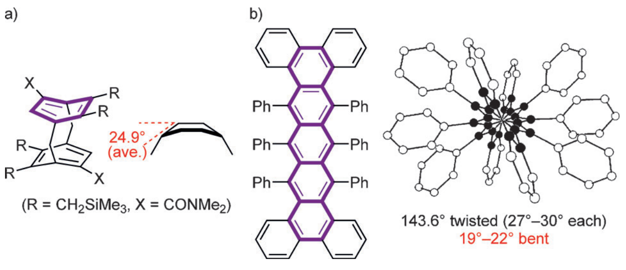


Figure 1. Distorted benzene rings obtained with conventional strategies: a) Kinetically stabilized [1.1]paracyclophane.[3b] b) 9,10,11,20,21,22-Hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene.[4c]

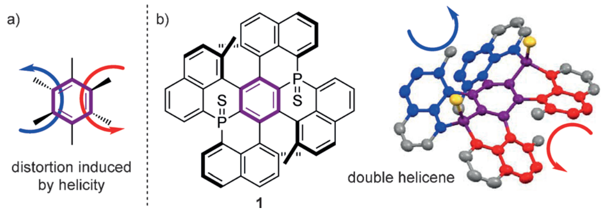


Figure 2. a) Proposed strategy for the construction of distorted benzene rings. b) The target distorted benzene in P-fused double helicene (*M*,*M'*)-**1**. Each of the two homochiral [5]helicene fragments is shown in red/blue color.

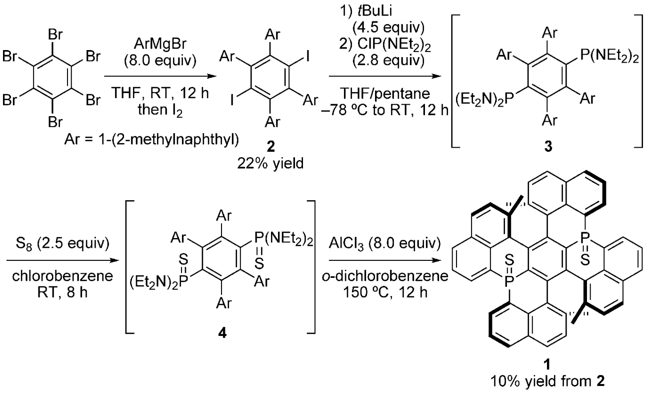
Synthesis of the P-fused double helicene **1** was achieved according to the procedure illustrated in Scheme 1. In particular, hexabromobenzene was treated with 8 equivalents of the aryl Grignard reagent, which gave the 2,3,5,6-tetraaryl-1,4-diiodobenzene **2** in 22 % yield upon quenching with

---

[*] S. Nakatsuka, Prof. Dr. T. Hatakeyama
Department of Chemistry, School of Science and Technology
Kwansei Gakuin University
2-1 Gakuen, Sanda, Hyogo 669-1337 (Japan)
E-mail: hatake@kwansei.ac.jp
Dr. S. Hashimoto, Prof. Dr. M. Nakamura
International Research Center for Elements Science (IRCELS)
Institute for Chemical Research (ICR)
Kyoto University, Uji, Kyoto 611-0011 (Japan)
and
Department of Energy and Hydrocarbon Chemistry
Graduate School of Engineering, Kyoto University
Nishikyo-ku, Kyoto 615-8510 (Japan)
E-mail: masaharu@scl.kyoto-u.ac.jp
Prof. Dr. T. Hatakeyama
PRESTO, the Japan Science and Technology Agency (JST)
5, Sanbancho, Chiyoda, Tokyo, 102-0075 (Japan)
and
Elements Strategy Initiative for Catalysts and Batteries (ESICB)
Kyoto University, Katsura, Kyoto 615-8510 (Japan)

[**] This study was supported by the Precursory Research for Embryonic Science and Technology (PRESTO) from the Japan Science and Technology Agency (JST), a Grant-in-Aid for Young Scientists (23685020), and a Grant-in-Aid for Scientific Research (26288095) from the Ministry of Education, Culture, Sports, Science & Technology in Japan (MEXT), and the "Funding Program for Next-Generation World-Leading Researchers (NEXT Program)," initiated by the Council for Science and Technology Policy (CSTP) from the Japan Society for the Promotion of Science (JSPS). We are grateful to Professors Takahiro Sasamori and Hikaru Takaya (Kyoto University) for their guidance in the X-ray crystallography experiments.

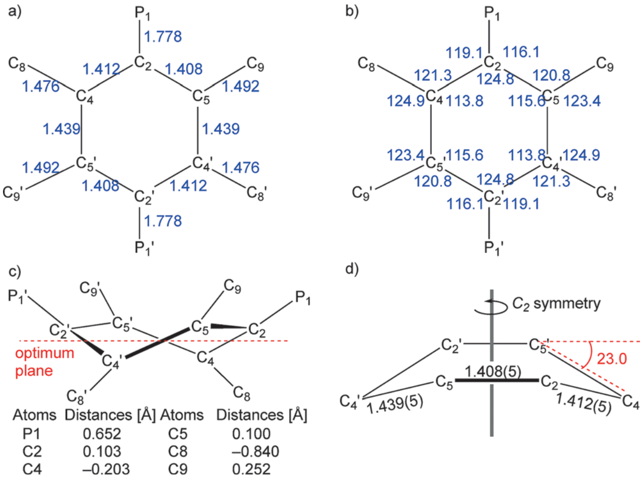
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408390.



Scheme 1. Synthesis of **1**.

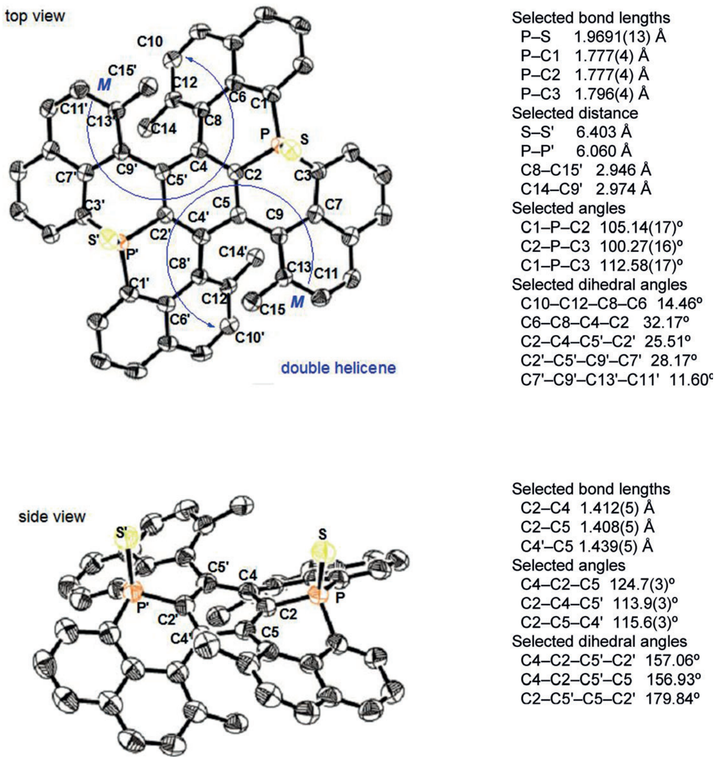
iodine. Lithium–halogen exchange in **2**, and subsequent trapping of the resulting aryllithium with bis(*N*,*N*-diethylamino)chlorophosphine, gave the 2,3,5,6-tetraaryl-1,4-bisphosphine **3**. After sulfurization of **3** by using S_8, **1** was obtained by the tandem phospha-Friedel–Crafts reaction with $AlCl_3$ in 10% yield from **2**.[7] The tandem reaction of the corresponding *p*-phenylenebis(dichlorophosphine) did not give the target compound **1** with or without $NEt(iPr)_2$.

The double-helical structure[8] of **1** was confirmed by X-ray crystallography (Figure 3):[9] **1** possesses a C_2 symmetry with a *cis* arrangement of the two sulfur atoms (S–S′ distance: 6.403 Å). The two [5]helicene-like fragments of the same helicity (the *M*,*M*′-isomer is shown in Figure 1) share the central benzene ring and two phosphorus atoms. The non-bonded contact between the four methyl groups and facing benzene rings are noticeably short (contact distance:[10] 2.962 and 2.871 Å, respectively). In ^{1}H NMR analysis, the chemical shifts of the methyl hydrogen atoms appear at higher field ($\delta = 0.74$ and 1.96 ppm) than that of a typical benzylic proton ($\delta = 2.2$–2.3 ppm) because of aromatic ring current, such as that found in 1-methyl[6]helicene ($\delta = 0.80$ ppm, contact distance: 2.861 Å).[11] In the [5]helicene fragment, the torsion angles for each ring are 14.46° for C10-C12-C8-C6, 32.17° for C6-C8-C4-C2, 25.51° for C2-C4-C5′-C2′, 28.17° for C2′-C5′-C9′-C7′, and 11.60° for C7′-C9′-C13′-C11′.



Atoms	Distances [Å]	Atoms	Distances [Å]
P1	0.652	C5	0.100
C2	0.103	C8	−0.840
C4	−0.203	C9	0.252

Figure 4. Geometric details of the central benzene ring: a) Bond lengths, b) bond angles, c) distances from optimum plane, and d) bending angle.



Selected bond lengths	
P–S	1.9691(13) Å
P–C1	1.777(4) Å
P–C2	1.777(4) Å
P–C3	1.796(4) Å
Selected distance	
S–S'	6.403 Å
P–P'	6.060 Å
C8–C15'	2.946 Å
C14–C9'	2.974 Å
Selected angles	
C1–P–C2	105.14(17)°
C2–P–C3	100.27(16)°
C1–P–C3	112.58(17)°
Selected dihedral angles	
C10–C12–C8–C6	14.46°
C6–C8–C4–C2	32.17°
C2–C4–C5'–C2'	25.51°
C2'–C5'–C9'–C7'	28.17°
C7'–C9'–C13'–C11'	11.60°

Selected bond lengths	
C2–C4	1.412(5) Å
C2–C5	1.408(5) Å
C4'–C5	1.439(5) Å
Selected angles	
C4–C2–C5	124.7(3)°
C2–C4–C5'	113.9(3)°
C2–C5–C4'	115.6(3)°
Selected dihedral angles	
C4–C2–C5'–C2'	157.06°
C4–C2–C5'–C5	156.93°
C2–C5'–C5–C2'	179.84°

Figure 3. ORTEP drawing of (*M*,*M*′)-**1**. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity.

The distorted structure of the central benzene ring along with the surrounding atoms is shown in Figure 4. The bond lengths are elongated by 0.01–0.04 Å compared to those of the solid-state structure of benzene (1.39 Å).[12] The hexagon is slightly expanded toward each phosphorus atom (Figure 4a,b). The tetrahedral phosphorus atoms uphold the C2 atoms. The helical conformation causes the C5 and C9 atoms to be above, and the C4 and C8 atoms to be below the optimum plane (Figure 4c). Because of the oppositely directed torsion strains introduced by the two independent helicenes, the central benzene ring has a large bending angle (23.0°, Figure 4d) which is comparable to that of [1.1]paracyclophane (24.9°).[3b]

Density functional theory (DFT) calculations[13] of **1** show an efficient π-conjugation spread over the whole molecule, despite the curved structure. The HOMO and LUMO of **1** delocalize over the entire molecular surface (Figure 5a). The HOMO–LUMO gap of **1** (2.96 eV) is comparable to that of tetracene (2.78 eV). The aromaticities of the six-membered rings in **1** were evaluated by performing a nucleus-independent chemical shift (NICS) analysis (Figure 5b).[13] The relatively small NICS(0) value of −4.3 for the central benzene ring suggests a decrease in aromaticity as a result of the torsion (for the sake of comparison, the

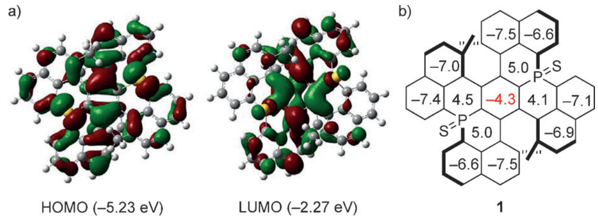
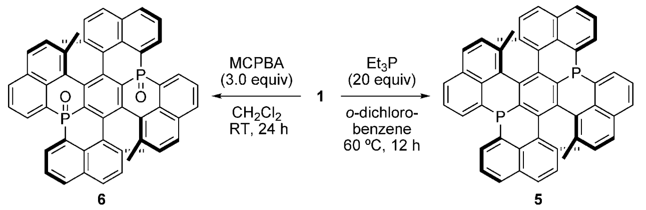


Figure 5. a) Kohn–Sham molecular orbitals (MOs) of **1** calculated at the B3LYP/6-31G(d) level. b) NICS(0) values for the six-membered rings calculated at the GIAO/B3LYP/6-311+G(d,p) level based on the X-ray structure.

value of planar benzene ring of $C_6(PSH_2)_2(CH_3)_4$ is −8.4).[14] In addition, the Harmonic oscillator model of aromaticity (HOMA) values (**1**: 0.687 versus $C_6(PSH_2)_2(CH_3)_4$: 0.872) also suggest the decrease in aromaticity.[14] Albeit with the reduced aromaticity of the central benzene ring, decomposition of **1** was not observed even at 600 K under air atmosphere, probably because of its rigid framework.

Desulfurization of **1** with triethylphosphine gave the corresponding bis(phosphine) **5** in 89 % yield (Scheme 2).



6
75% yield

5
89% yield

Scheme 2. Synthesis of **5** and **6**.

Since the double helical structure was maintained under the reducing conditions, **5** may be considered as a useful C_2-symmetric ligand for bimetallic complexes upon optical resolution. Oxidation of **1** with *m*-chloroperoxybenzoic acid (MCPBA) selectively gave the corresponding bisphosphine oxide **6** in 75 % yield, and oxidation of the central benzene ring was not observed.

In summary, we have successfully constructed a highly distorted benzene ring in the P-fused double helicene by a tandem intramolecular phospha-Friedel–Crafts reaction. Notably, the procedure only required four steps. Thus, the simple and practical strategy proposed here can be considered a useful method for the synthesis of a diverse range of distorted molecules. Despite its reduced aromaticity, the distorted double helicene shows thermal and chemical stability. These are important features which make these compounds attractive for applications as new C_2-symmetric bis(phosphine) ligands. The optical resolution of the proposed compound and its applications are currently under investigation in our laboratory.

Received: August 20, 2014

Keywords: aromaticity · density functional calculations · helical structures · ligand design · structure elucidation

[1] a) J. F. Liebman, A. Greenberg, *Chem. Rev.* **1976**, *76*, 311–365; b) H. Bock, K. Ruppert, C. Näther, Z. Havlas, H.-F. Herrmann, C. Arad, I. Göbel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel, B. Solouki, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 550–581; *Angew. Chem.* **1992**, *104*, 564–595; c) M. D. Levin, P. Kaszynski, J. Michl, *Chem. Rev.* **2000**, *100*, 169–234; d) I. Hisaki, M. Sonoda, Y. Tobe, *Eur. J. Org. Chem.* **2006**, 833–847; e) A. Boudhar, M. Charpenay, G. Blond, J. Suffert, *Angew. Chem. Int. Ed.* **2013**, *52*, 12786–12798; *Angew. Chem.* **2013**, *125*, 13020–13032.

[2] a) F. Bickelhaupt, W. H. d. Wolf, *J. Phys. Org. Chem.* **1998**, *11*, 362–376; b) F. Feixas, E. Matito, J. Poater, M. Solà, *J. Phys. Chem. A* **2007**, *111*, 4513–4521; c) R. A. Pascal, Jr., *Chem. Rev.* **2006**, *106*, 4809–4819; d) R. Gleiter, B. Esser, S. C. Kornmayer, *Acc. Chem. Res.* **2009**, *42*, 1108–1116; e) D. Eisenberg, R. Shenhar, M. Rabinovitz, *Chem. Soc. Rev.* **2010**, *39*, 2879–2890.

[3] a) T. Tsuji, M. Ohkita, S. Nishida, *J. Am. Chem. Soc.* **1993**, *115*, 5284–5285; b) H. Kawai, T. Suzuki, M. Ohkita, T. Tsuji, *Angew. Chem. Int. Ed.* **1998**, *37*, 817–819; *Angew. Chem.* **1998**, *110*, 827–829; c) M. A. Dobrowolski, M. K. Cyranski, B. L. Merner, G. J. Bodwell, J. I. Wu, P. v. R. Schleyer, *J. Org. Chem.* **2008**, *73*, 8001–8009; d) Y. Koyama, S. Hiroto, H. Shinokubo, *Angew. Chem. Int. Ed.* **2013**, *52*, 5740–5743; *Angew. Chem.* **2013**, *125*, 5852–5855; e) G. Ohlendorf, C. W. Mahler, S.-S. Jester, G. Schnakenburg, S. Grimme, S. Höger, *Angew. Chem. Int. Ed.* **2013**, *52*, 12086–12090; *Angew. Chem.* **2013**, *125*, 12308–12312.

[4] a) H. Sakurai, K. Ebata, C. Kabuto, A. Sekiguchi, *J. Am. Chem. Soc.* **1990**, *112*, 1799–1803; b) W. Clegg, A. J. Edwards, H. C. E. McFarlane, W. McFarlane, *Polyhedron* **1998**, *17*, 3515–3518; c) J. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml, R. A. Pascal, Jr., *J. Am. Chem. Soc.* **2004**, *126*, 11168–11169.

[5] The details of the bending angle calculation are shown in the Supporting Information.

[6] T. Hatakeyama, S. Hashimoto, M. Nakamura, *Org. Lett.* **2011**, *13*, 2130–2133.

[7] $NEt(iPr)_2$ is not necessary for this reaction because of the absence of acidic side product.

[8] a) K. Shiraishi, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**, *127*, 9312–9313; b) Z. Wang, J. Shi, J. Wang, C. Li, Z. Tian, Y. Cheng, H. Wang, *Org. Lett.* **2010**, *12*, 456–459.

[9] CCDC 1020103 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] The contact distance is defined as a distance between a methyl carbon and a plane defined by the three carbon atoms in the nearest nonbonded benzene ring (C14 and C9′-C13′-C7′, C15 and C8-C12-C6, respectively).

[11] H. M. Doesburg, *Cryst. Struct. Commun.* **1980**, *9*, 137–142.

[12] G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, *Proc. R. Soc. London Ser. A* **1987**, *414*, 47–57.

[13] Computational details are given in the Supporting Information.

[14] NICS and HOMA values of **1** are calculated for the X-ray structure and the comparison was made with the values of related compounds. Please see the Supporting Information for details.