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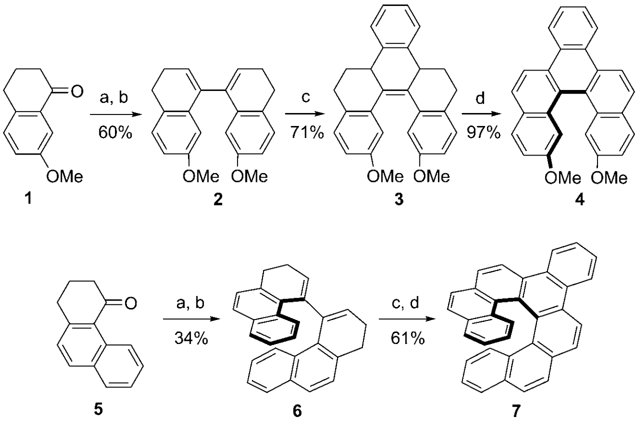
Synthesis and Structures of Multifunctionalized Helicenes and Dehydrohelicenes: An Efficient Route to Construct Cyan Fluorescent Molecules

Jun-Dao Chen,[a, b] Hai-Yan Lu,[b] and Chuan-Feng Chen*[a]

Helicenes, a class of molecules that consist of *ortho*-fused aromatic rings with helical chirality,[1] have attracted great interest owing to their unique structural features and wide potential applications in chiral materials,[2] biomolecular recognition,[3] and asymmetric synthesis.[4] Since Newman and Lednicer reported the first helicene in 1956,[5] various methods for synthesis of helicenes including successive Diels–Alder reactions,[6] cyclotrimerizations of acetylenes,[7] carbenoid couplings,[8] electrophilic aromatic cyclizations,[9] radical cyclizations,[10] olefin metathesis,[11] cycloisomerization,[12] and Friedel–Crafts-type cyclizations[13] have been described. However, in most cases, complicated precursors, expensive and sensitive metallic catalysts or harsh reaction conditions were needed, and the products were usually prepared on a small scale. In particular, functionalized helicenes were obtained by multistep reactions, and the precursors were generally difficult to access.[7,11,14] The direct functionalization of helicenes is undoubtedly the most effective way to prepare the multifunctionalized helicenes, but few of them have been reported to date, which to a certain extent restricts the practical applications of the helicene derivatives.

Dehydrohelicenes[15] are compounds in which the two helical termini of a helicene are connected by a σ bond. As a special class of polycyclic aromatic hydrocarbon (PAH), they could have the wide potential applications in materials science. However, few reports on the cyclodehydrogenation of helicenes were known. Recently, Xue and Scott reported a thermal cyclodehydogenation of [5]helicene by flash vacuum pyrolysis at 1000 °C, but under the same conditions, a significant portion of benzo[5]helicene stayed unchanged.[16] Herein, we report 1) a convenient and efficient synthesis of a dimethoxy-substituted benzo[5]helicene and a benzo[7]helicene, 2) direct bromination of the benzo[5]helicene and synthesis of a series of multifunctionalized [5]helicenes by the Suzuki–Miyaura cross-coupling reactions, and 3) the further oxidative cyclodehydrogenation of the [5]helicene derivatives to afford a series of multifunctionalized dehydro[5]helicene (or naphthoperylene) derivatives with the cyan fluorescent properties and high quantum yields.

Synthesis of the helicenes is depicted in Scheme 1. Starting from the commercially available 7-methoxy-3,4-dihydronaphthalen-1(2*H*)-one **1**, the diene **2** was obtained in 60 % yield for two steps. The Diels–Alder reaction between diene **2** and the benzyne from 2-carboxybenzenediazonium chloride gave the compound **3**, which was then dehydronated by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to afford the benzo[5]helicene **4** in 97 % yield. According to a similar ap-



Scheme 1. Preparation of benzo[5]helicene **4** and benzo[7]helicene **7**: a) Al (1 equiv), $HgCl_2$, toluene, ethanol, reflux; b) CH_3CO_2H, $(CH_3CO_2)_2O$, reflux; c) 2-carboxybenzene-diazonium chloride (2 equiv), CH_2ClCH_2Cl, 2-methyloxirane, reflux; d) DDQ (10 equiv), xylene, reflux.

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[a] J.-D. Chen, Prof. C.-F. Chen
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratory of Molecular Recognition and Function
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100190 (P.R. China)
Fax: (+86) 10-62554449
E-mail: cchen@iccas.ac.cn

[b] J.-D. Chen, Prof. H.-Y. Lu
Graduate School, Chinese Academy of Sciences
Beijing 100049 (P.R. China)

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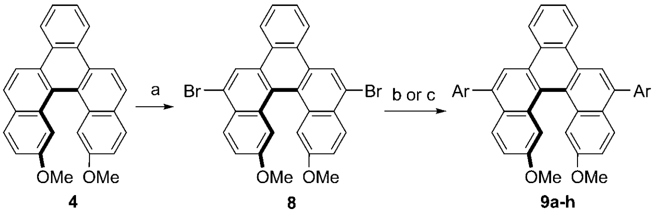
proach, the benzo[7]helicene **7** was conveniently synthesized in four steps in 21 % total yield starting from 2,3-dihydrophenanthren-4(1*H*)-one **5** (Scheme 1).

It was known that halide-substituted aromatic compounds can be used as important precursors for the further functionalization by, for example, Suzuki–Miyaura cross-coupling reactions.[17] Thus, we carried out the bromination of the benzo[5]helicene **4** with *N*-bromosuccinimide (NBS) in dichloromethane, which provided the dibromo-substituted **8** in quantitative yield (Scheme 2). The bromination selectively took place at the 5- and 12-positions of the [5]helicene, which was proved by its single-crystal structure (Figure 1).[18] It was found that the dihedral angle of the two twisted phenyl rings is 30.68°, which is smaller than that of its analogue [5]helicene (35.6°) without the methoxy groups.[19] Moreover, the distance between the two oxygen atoms is 4.80 Å, and no intramolecular hydrogen-bonding interactions were found in the molecule. With the [5]helicene derivative **8** in hand, we then examined its Suzuki–Miyaura cross-coupling reactions in two systems with [Pd(PPh$_3$)$_4$] as catalyst and K$_2$CO$_3$ as base, which provided a series of 5,12-disubstituted [5]helicene derivatives **9a**–**h** in middle or good yield (Table 1). Moreover, the results showed that the reactions in toluene/water/ethanol gave higher yields than those in DME/water solvent mixtures, which is probably caused by the favorable solubility of the PAH substrates in toluene.



Scheme 2. Bromination of benzo[5]helicene **4** and the Suzuki–Miyaura cross-coupling reactions of **8** with various arylboronic acids: a) NBS (2.2 equiv), CH$_2$Cl$_2$, RT; b) Pd(PPh$_3$)$_4$, arylboronic acid (3 equiv), DME, H$_2$O, K$_2$CO$_3$, reflux; c) Pd(PPh$_3$)$_4$, arylboronic acid (3 equiv), toluene, ethanol, H$_2$O, K$_2$CO$_3$, reflux.

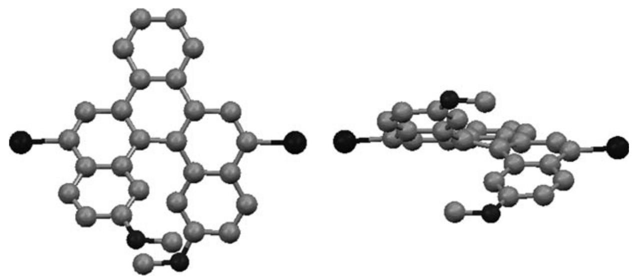


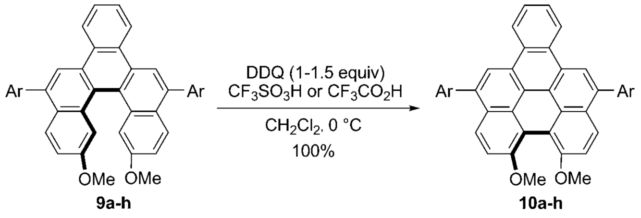
Figure 1. Top view (left) and side view (right) of crystal structure of **8**. Hydrogen atoms are omitted for clarity.

Table 1. Suzuki–Miyaura cross-coupling of **8** with various arylboronic acids.

Entry	Product	Ar	Yield [%]	
			Method 1[a]	Method 2[b]
1	**9a**	phenyl	72	83
2	**9b**	4-methoxy-phenyl	46	79
3	**9c**	4-chloro-phenyl	62	70
4	**9d**	4-carboxyl-phenyl	75	78
5	**9e**	4-amino-phenyl	51	76
6	**9f**	4-formyl-phenyl	66	73
7	**9g**	4-cyano-phenyl	53	75
8	**9h**	3-thienyl	49	56

[a] Solvent: DME, H$_2$O. [b] Solvent: toluene, ethanol, H$_2$O.

Furthermore, the oxidative cyclodehydrogenation reactions of the helicenes were carried out under the established Scholl reaction conditions.[20] As shown in Scheme 3, the [5]helicene derivatives **9a**–**h** could be selectively cyclodehydrogenated by DDQ to give the dehydro[5]helicenes **10a**–**h** in quantitative yields in both trifluoroacetic acid and trifluoromethanesulfonic acid systems. Moreover, it was found that the dehydrogenation only took 5–30 min; however, longer reaction time and more oxidant (up to 1.5 equiv DDQ) were needed for the [5]helicene derivatives with electron-withdrawing groups in the substituted aromatic subunits. Under the same conditions, we also found that the oxidative cyclodehydrogenation of [7]helicene **7** did not take place, mainly due to the overlapped steric situation of the molecule. Furthermore, a single crystal of **10a** suitable for X-ray diffraction was obtained by slow evaporation of a solution of **10a** in chloroform and cyclohexane. The crystal structure[18] (Figure 2a and b) showed that the molecule **10a** was nonplanar because of the two close methoxy groups, and the dihedral angle of the two twisted phenyl rings is 31.76°. It was also found that the two substituted phenyl groups are noncoplanar, and each of them shows a 62.91° dihedral angle to its adjacent phenyl ring in the [5]helicene. Moreover, the packing pattern of **10a** includes both edge-to-face and face-to-face arrangements (Figure 2c), in which one molecule faces another while it forms a T-shape with the edges of two other molecules. The face-to-face arrangement consists of a pair of enantiomers; the interplanar distance is 3.37 Å and π–π and C–H···π interactions are present. The face-to-edge arrangement shows a 70.12° dihedral angle between the two adjacent molecules, which results in a herringbone-like packing (Figure 2c).



Scheme 3. Synthesis of dehydro[5]helicene derivatives **10a**–**h**.

All dehydro[5]helicene (or naphthoperylene) derivatives showed good solubility in common organic solvents, such as

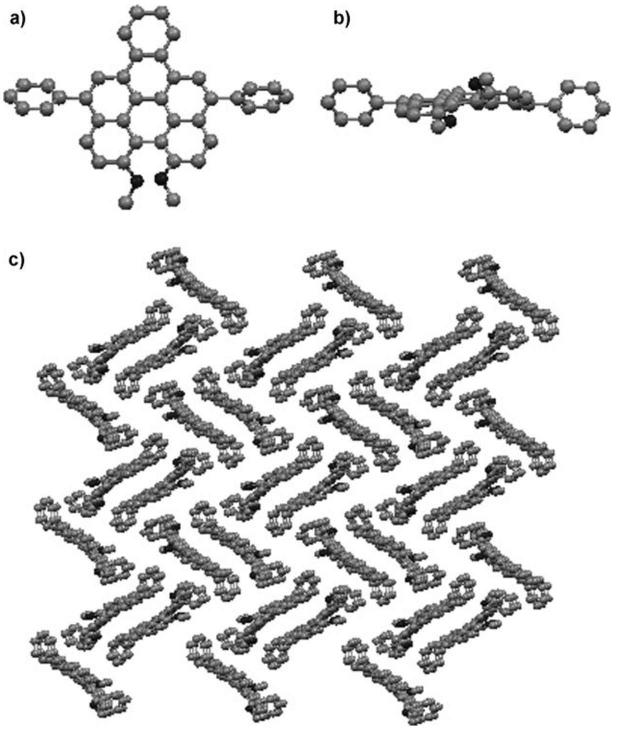


Figure 2. a) Top view and b) side view of crystal structure of **10a**. c) Herringbone-like packing of **10a** viewed along the *a* axis.

cyclohexane, CH_2Cl_2, $CHCl_3$, toluene, and so forth. As shown in Figure 3, the UV/Vis spectrum of dehydro[5]helicene **10a** in cyclohexane exhibited the maximum absorption

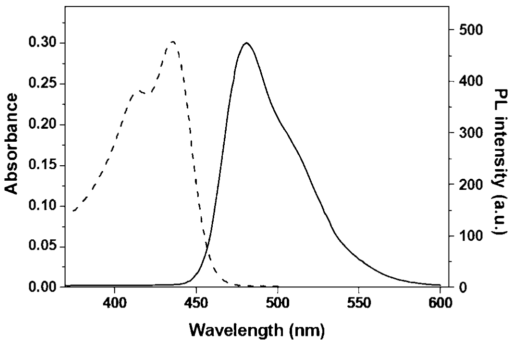


Figure 3. UV/Vis (dashed line) and emission (solid line) spectra of **10a** in cyclohexane at room temperature. $[\mathbf{10a}] = 1 \times 10^{-6}$ M.

band at 436 nm, a bathochromic shift of 51 nm compared to benzo[*g*,*h*,*i*]perylene,[21] which is probably due to the larger conjugated π system and the electron-donating effect of methoxy groups in **10a**. In the fluorescent spectrum, the maximum emission wavelength of **10a** was observed at 478 nm, which was consistent with cyan fluorescence. Under the same conditions, the photophysical properties of the other dehydro[5]helicenes were also investigated, and the results were summarized in Table 2. Similar to **10a**, dehydrohelicenes **10b–h** all showed the strong dazzling cyan fluorescence in cyclohexane. Because of the nonplanarity of the substituted aromatic rings with the dehydro[5]helicene core, only small emission wavelength shifts in the spectra were observed with the changes of the substitution groups. However, it was found that the quantum yields of the dehydrohelicenes differ significantly (Table 2), in which electron-withdrawing groups generally gave low Φ values, while electron-donating groups gave high Φ values.

Table 2. The photophysical properties of dehydrohelicenes **10** in cyclohexane.[a]

	Abs [nm]	Em [nm]	Φ[b]
10a	436	478	0.51
10b	436	479	0.78
10c	435	480	0.45
10d	432	480	0.33
10e	436	478	0.58
10f	433	479	0.40
10g	433	480	0.47
10h	438	481	0.75

[a] $[\mathbf{10}] = 1 \times 10^{-6}$ M. [b] Perylene as the standard (cyclohexane, 0.98).

In conclusion, we have shown a convenient and efficient synthesis of a dimethoxy-substituted benzo[5]helicene and a benzo[7]helicene. By direct bromination of the benzo[5]helicene and then Suzuki–Miyaura cross-coupling reactions, we have also synthesized a series of multifunctionalized benzo[5]helicene derivatives. Moreover, we found that the convenient oxidative cyclodehydrogenation of the [5]helicenes by DDQ in trifluoroacetic acid or trifluoromethanesulfonic acid quantitatively provided the corresponding dehydro[5]-helicene (or naphthoperylene) derivatives, which showed the cyan fluorescent properties and high quantum yields. We believe that these easily available, multifunctionalized helicenes and dehydro[5]helicene derivatives will find wide applications in materials science and supramolecular chemistry; further investigations along these lines are in progress in our laboratory.

Experimental Section

Full experimental details and characterization data are given in the Supporting Information.

Synthesis of compound 3: A mixture of diene **2** (10 g, 31 mmol) and 2-carboxybenzenediazonium chloride (11.6 g, 62 mmol) in 1,2-dichloroethane (250 mL) and propylene oxide (20 mL) was refluxed for 6 h. The reaction mixture was concentrated under reduced pressure, and the residue was recrystallized from ethyl acetate to give pure product **3** (8.7 g, 71 %) as white powder.

Synthesis of the benzo[5]helicene 4: Compound **3** (1.10 g, 2.79 mmol) and DDQ (6.3 g, 27.9 mmol) were added to dried xylene (50 mL). After being refluxed for 16 h, the reaction mixture was cooled to room temperature, filtered, and then washed with CH_2Cl_2 (10 mL×3). The solvent was removed from the dark red filtrate under reduced pressure. The residue was subjected to flash column chromatography with CH_2Cl_2:petroleum ether (3:1) as eluent to afford **4** (1.05 g, 97 %) as pale yellow solid.

General procedure for oxidative dehydrogenation of the [5]helicene derivatives 9: Trifluoroacetic acid or trifluoromethanesulfonic acid (1 mL) was added by a syringe to a mixture of the [5]helicene **9** (0.096 mmol) and DDQ (0.096 mmol for **9a**, **9b**, **9e** and **9h**; 0.144 mmol for **9c**, **9d**, **9f** and **9g**) in dry CH_2Cl_2 (10 mL) at 0 °C under argon atmosphere. The mixture was then stirred and monitored by TLC. After the reaction was completed, the mixture was quenched by saturated $NaHCO_3$ solution (20 mL), and then extracted with CH_2Cl_2 (20 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to column chromatography to give the desired dehydro[5]helicene **10** as greenish yellow powder.

Acknowledgements

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Keywords: fluorescence · functionalization · helicenes · helical structures · synthetic methods

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[18] CCDC-780282 (**8**) and 779937 (**10a**) contain 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.

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