

Unsaturated Strained Cyclophanes Based on Dibenz[*a,j*]anthracene by an Intramolecular McMurry Olefination

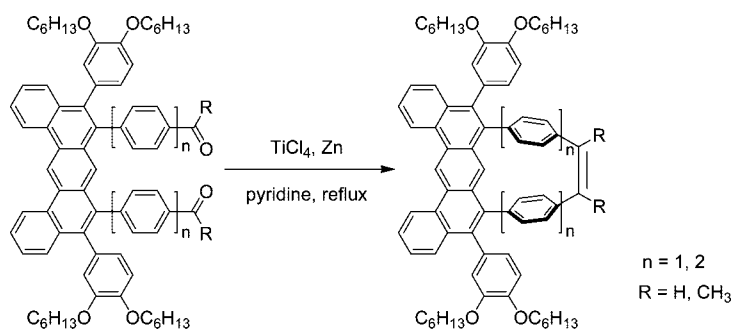
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ABSTRACT



A new type of rigid conjugated unsaturated strained cyclophane derivative containing dibenz[*a,j*]anthracene units was facilely synthesized through an intramolecular McMurry reaction without intermolecular dimerization products in good yields. The photophysical properties of these cyclophane derivatives in dilute solution were investigated, and molecular modeling was employed to study their electronic properties.

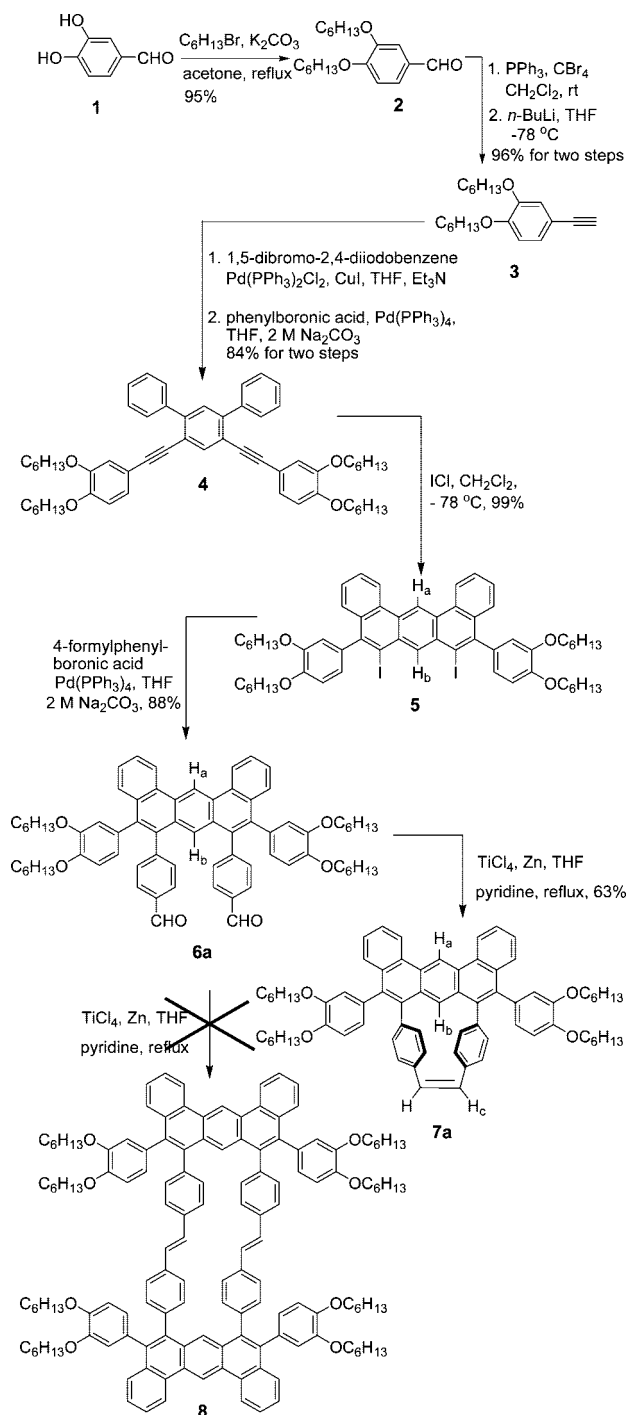
Cyclophanes and assorted cyclic compounds with novel shapes and molecular geometries have attracted considerable attention due to their interesting properties and potential applications in host–guest systems, molecular recognition, information storage, bioscience, and nano devices.¹ Nevertheless, despite the abundance of molecular designs, the efficient synthesis of conjugated unsaturated strained cyclophanes,² whose preparation usually suffered from multiple synthetic steps and overall low yields, is still of great challenge.^{1e,3} Therefore, the design and synthesis of new cyclophanes and assorted cage compounds with novel shapes and supramolecular geometries continue to be topics of current interest. The investigation of the chemical and physical properties of new cyclophanes with novel skeletons also gives insight into the relationship between the rigid structure of cyclophanes and their properties as well as their applications.

The McMurry reaction, an effective way to form a C=C bond under moderate conditions, has been employed to form strained unsaturated conjugated cyclophanes in a few cases.⁴ In this contribution, we report on the design, synthesis, and characterization of a new family of unsaturated conjugated shape-persistent cyclophane derivatives based on a dibenz[*a,j*]anthracene unit through the McMurry reaction. The McMurry reaction, in our case, leads to the reductive coupling of two carbonyl groups to form intramolecular cyclization products without intermolecular dimerization to macrocycles. Our results show that at suitable distances strained double bonds can be formed effectively using the classic McMurry coupling reaction, providing a new strategy in the construction of conjugated unsaturated strained cyclophanes. These conjugated cyclophanes possess strained conformation owing to the unsaturated linkage as well as the rigid dibenz[*a,j*]anthracene unit, which shows strong blue emission in dilute solution. These new members of the

cyclophane family may have potential applications in theoretical chemistry, guest–host systems, and optoelectronics.

Scheme 1 illustrates the synthetic approaches to the cyclophane **7a**. The alkylation of the commercially available material, 3,4-dihydroxy-benzaldehyde, followed by the

Scheme 1. Synthesis of Cyclophane **7a**



Corey–Fuchs reaction afforded alkyne **3** in 91% yield. A Sonogashira coupling reaction between **3** and 1,5-dibromo-

2,4-diiodobenzene with catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ followed by a Suzuki coupling reaction with phenylboronic acid gave compound **4** in 84% yield. Dibenz[*a,j*]anthracene iodide **5** was prepared in almost quantitative yield following the classical procedure via ICl induced intramolecular cyclization of **4**.⁵ Dicarbonyl **6a** was synthesized through another Suzuki coupling reaction between dibenz[*a,j*]anthracene iodide **5** and 4-formylphenylboronic acid in 88% yield. Finally, the McMurry reaction was employed for the coupling of aldehyde groups of **6a**. It is quite worth noting that the intramolecular coupling product **7a** was observed without any intermolecular dimerization side product. This result was in sharp contrast to our recently reported results on the synthesis of another type of macromolecule, indicating the importance of distances between the reacting groups in the McMurry reaction.⁶

The intramolecular coupling was unambiguously confirmed by ^1H NMR spectra and MALDI-TOF MS. The ^1H NMR spectra in CDCl_3 showed the evident change of the proton signal from molecule **6a** to cyclophane **7a**, as was shown in Figure 1. After the Suzuki reaction, the signal assigned to H_b in **5** at a chemical shift of 9.85 ppm (see the Supporting Information) shifted to δ 7.25 ppm in compound **6a**. Such a shift resulted from the shielding effect from the benzene rings connected to the dibenz[*a,j*]anthracene unit. This signal further shifted upfield at an unusual chemical shift δ of 5.91 ppm after the intramolecular McMurry olefination, which was due to the additional shielding effect

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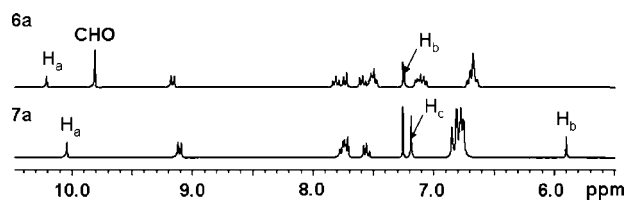
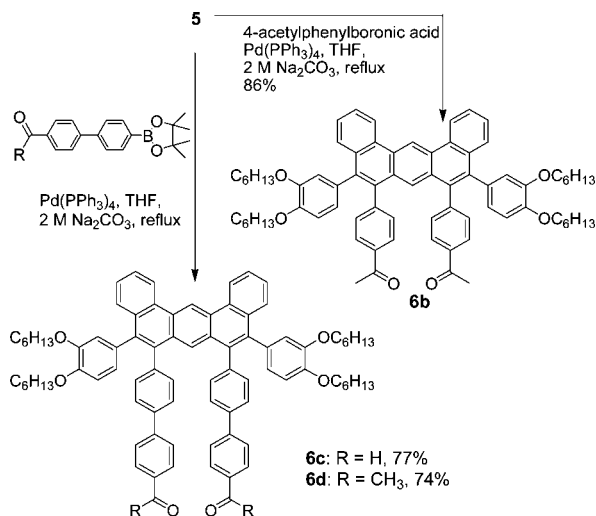


Figure 1. ^1H NMR spectra of dicarbonyl compound **6a** and cyclophane **7a** in CDCl_3 at the aromatic range.

from the $\text{C}=\text{C}$ double bond. MALDI-TOF MS analysis of **7a** (see the Supporting Information) further confirmed the intramolecular cyclization structure. It is assumed that the rigid scaffold offers a proper distance between two carbonyl groups to form the strained double bond in the key step.

With the above results in hand, it is very important to understand the effect of structural rigidity and hindrance in this intramolecular cyclization. As shown in Scheme 2, three

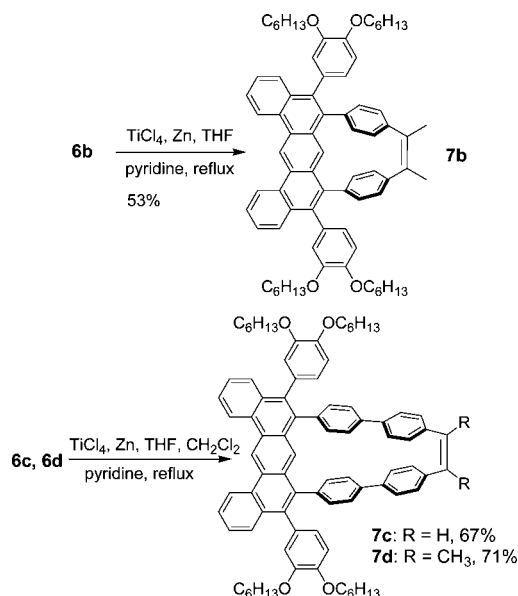
Scheme 2. Synthesis of Dicarbonyl Compounds **6b–6d**



dicarbonyl compounds **6b–d** were synthesized through the similar Suzuki coupling procedures between **5** and various boronic acids in 74–86% yields. Herein, due to the poor solubility of **6c** and **6d** in THF, the McMurry reaction of **6c** and **6d** was processed in a mixed solvent of CH_2Cl_2 and THF. Cyclophane **7b** was obtained in a moderate yield of 53%. With the increase in length of the “arm”, cyclophanes **7c** and **7d** were prepared in relatively high yields of 67% and 71%, respectively (as shown in Scheme 3), which might come from the decrease of the torsion angles in the desired products. The structures and the purity of all new cyclophanes were confirmed by ^1H and ^{13}C NMR spectra, MALDI-TOF MS, and elemental analysis (see the Supporting Information). Again, no intermolecular olefination products were observed.

The absorption spectra of **7a–7d** in dilute CH_2Cl_2 solutions were recorded. The concentration of all compounds in

Scheme 3. Synthesis of Cyclophanes **7b–7d**



solutions was ca. 10^{-6} M. Figure 2 illustrates the absorption spectra of **7a–7d** in solution. The absorption λ_{max} of **7a–7d** peaked at 312 nm, assignable to the dibenz[*a,j*]anthracene.⁷ Another absorption peak at 270 nm was observed from **7c**

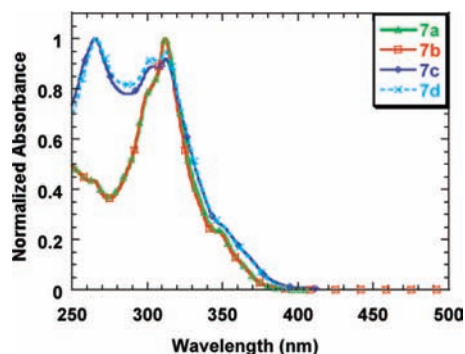


Figure 2. Normalized absorption spectra of **7a–7d** in dilute CH_2Cl_2 solutions.

and **7d**, which was closed to the absorption band of the 1,4-diphenylbenzene section.⁸ Because of the slight increase in effective conjugation length, the onset of the absorption spectra of **7c** and **7d** red-shifted to about 400 nm in comparison to that of **7a** and **7b** (about 390 nm).

Molecular modeling was employed to study the electronic properties of these cyclophanes. We have optimized the structures of cyclophanes using density functional theory (DFT) as implemented in Gaussian 03⁹ software with a 6-31G* basis set for carbon and hydrogen atoms. The features of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LOMO) of the optimized structures of cyclophanes **7a–7d** are shown in

Figure 3. Ethoxy-substituted cyclophanes were employed to

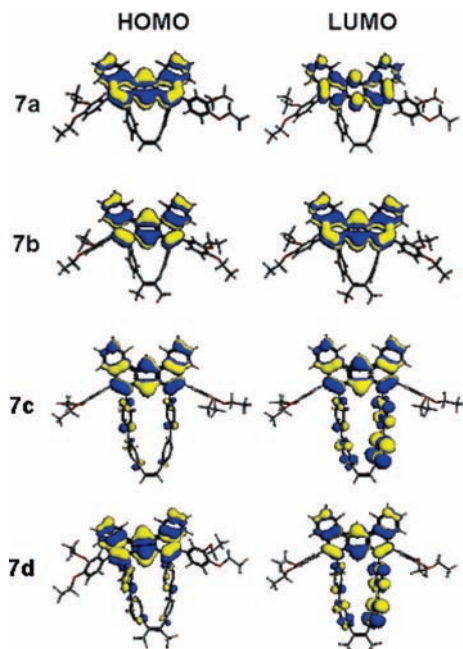


Figure 3. Highest occupied molecular orbitals and lowest unoccupied molecular orbitals of optimized structures of **7a–7d**.

simplify the calculations. The highest occupied molecular orbitals of cyclophane **7a** and **7b** are localized on the dibenz[*a,j*]anthracene section, and so are the lowest unoccupied molecular orbitals. However, for cyclophane **7c** and **7d**, the highest occupied molecular orbitals delocalized over the dibenz[*a,j*]anthracene and benzene groups connected through a Suzuki reaction. The extension in the conjugated system results in a slight red shift in the absorption spectra,

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which was in good agreement with the experimental data above. The slight bend of the C–C single bonds and the benzene rings between dibenz[*a,j*]anthracene and C=C double bonds was observed in the models.

In conclusion, a new class of π -conjugated strained cyclophanes were prepared through an intramolecular McMurry reaction. Such a facile synthetic approach is useful for us to construct novel unsaturated strained cyclophanes with different conjugation lengths, which are suitable building blocks for supramolecular assemblies and optoelectronics. In these molecules, intramolecular coupling reactions occurred in preference to intermolecular dimerization due to the preferable distance between the two carbonyl groups. The strained structure of the cyclophanes and the luminescent dibenz[*a,j*]anthracene section provides potential applications such as organic optoelectronics, and the C=C double bond in the products can be employed for further modifications for more complex structures in future studies. Also, the combination of the number and type of unsaturated linkages in these molecules might create a twisted conformation that imparts helical chirality.

Acknowledgment. This work was supported by the National Basic Research Program (No. 2006CB921602) from the Ministry of Science and Technology and the National Natural Science Foundation of China (NSFC 20425207, 50473016, and 20521202, and 20604001).

Supporting Information Available: Experimental procedures and ^1H and ^{13}C NMR spectra for all new compounds (PDF, 46 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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