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Title(English)	
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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	化学 系 化学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 理学 ）
学生氏名： Student's Name	植田泰之	指導教員（主）： Academic Supervisor(main)	大森 建
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This thesis, entitled "Study on the Synthesis and Chemical Transformation of Optically Active Asymmetric Cyclophanes", consists of an introduction, 4 chapters and a conclusion.

The introduction provides basic structural features of cyclophanes, explains the background of the study, and describes the significance and purpose of this study.

Chapter 1 describes the results of the efficient synthesis of heptaphenylene derivatives in which optically active C_2 symmetric cyclophane derivatives and unsubstituted phenylene groups are alternately linked by a convergent synthesis. The obtained heptaphenylene derivative was chemically stable and soluble in general-purpose organic solvents. It is stated that these characteristics at due to consisting the oligophenylene moiety serving as the main chain is sterically protected by a cross-linked chain of a hydrocarbon. When the UV and CD spectra of this compound were measured, a characteristic cotton effect was observed in the CD spectrum. Further, at various temperatures CD spectrum measurement revealed that these cotton effects have temperature dependence. That is, it was found that when the measurement temperature was reduced, the absorption intensity of each cotton effect increased, and when the temperature was raised, the absorption intensity decreased. It states that when the temperature was reduced, molecular motion was suppressed, the abundance ratio of conformers with energetically stable dihedral angles increased, and strong absorption intensity was observed. In addition, calculations of the conformation of these oligomers showed that the two benzene rings forming each biaryl structure were sterically affected by the bridge chain of the cyclophane and all maintained the same dihedral angle. It suggests that the entire chain is twisted in one direction.

In the second chapter, an efficient method for the synthesis of diboryl anthracene derivatives. [14] (1,5) Anthracenophane derivative was successfully synthesized. The key to was established success for this synthesis is to use a reversible [4 + 2] cycloaddition reaction between anthracene and an alkene to temporarily protect / deprotect the chemically unstable anthracene structure. By using this technique, it became possible to synthesize various anthracenophane derivatives on a gram scale.

In Chapter 3, made use of the structural features of anthracenophane to construct an in-cyclophane structure in a broad sense. Firstly, macrocycles were synthesized based on the [4 + 4] cycloaddition of anthracene derivatives. There for 2,6-dialkylanthracene was irradiated with visible light to induce dimerization. Next, hydrogen bromide was eliminated from the end of the side chain, lead to a tetraene having a double bond at the end of the side chain. Subsequently, the obtained tetraene is reacted with a first-generation Grubbs catalyst to form the corresponding cyclized product, followed by catalytic hydrogenation to give the saturated double cyclized product. Finally, construction of the macrocyclic structure was achieved by microwave irradiation under high temperature conditions. Based on this synthesis method, macrocyclic compounds containing anthracenophane units were synthesized and their UV and CD spectra were measured. The resulting spectrum gave the characteristic Cotton effect due to the optically pure dimer. Furthermore, when tetracyanoethylene was allowed to act on the obtained cyclic compound, the [4+2] reaction proceeded quantitatively, and the 1H NMR spectrum of the obtained adduct was symmetric. When the most stable conformation of the obtained adduct was determined, it was found that the two adducts on the anthracenophane unit had a structure facing inward and filling the inside of a large ring. There is no example of such a simple hydrocarbon chain forming a nested structure, and it is interesting in organic chemistry.

In Chapter 4, to construct a rotaxane structure using the structural characteristics and reactivity of anthracenophane. First, a fumaric acid derivatives with different a protecting groups were introduced to the anthracenophane are bound by a [4 + 2] cycloaddition reaction. Subsequently, the carbon-carbon double bonds at the side chain of the anthracene were reacted with each other by olefin metathesis to form a ring. Finally, the anthracenophane and alkene moieties were cleaved by a retro- [4 + 2] cycloaddition reaction. It

was found that the conpounds obtained differ depending on the structure of the protecting group. First, in the case of trityl-type protecting groups having a large size, as capping groups one of the capping molecules was decomposed and slipped through the anthracenophane, so that both components were obtained separately. On the other hand with a small-sized trityl-type capping group different result were obtained when similar experiments were performed. The results obtained from the mass spectrum and 1H NMR suggest that the rotaxane had been formed.

The conclusion summarizes the major work of this doctoral research and states the significance of the results obtained in this research in the field of synthetic organic chemistry.

In summary, this paper describes the derivatization of optically active cyclophanes and the synthesis and chemical transformation of anthracenophanes. Therefore, this dissertation is considered to be sufficiently valuable as a doctoral dissertation.