

学位論文題名

Development of Selective Method for Substituted
Pentacene Derivatives

(置換基を有するペンタセン誘導体の選択的合成法の開発)

学位論文内容の要旨

Ms. Jia's Ph.D. thesis contents of four chapters.

1. First chapter shows general introduction for development of selective method for substituted pentacene derivatives

Acenes have attracted much attention due to useful property in biological and material sciences. Efforts have been made to their application including the development of synthetic methodology. Diels-Alder reactions of pentacene with various dienophiles occur at the central ring to give the corresponding adducts, and the adducts can be converted to pentacene by heating via simple retro-Diels-Alder reaction. Usually these retro-Diels-Alder reactions require relatively high temperature. In order to develop retro Diels-Alder reaction at lower temperature than 140 °C, Ms. Jia investigated the Diels-Alder reaction of pentacene.

Pentacene derivatives with substituents at 6,13-positions are very important. General method to introduce the substituents is reaction of organometallic compounds with 6,13-pentacenequinone. However, this method has critical limitation. New method is necessary to be developed.

Connecting two or three pentacenes is attractive for developing new material. In this thesis my attempt is discussed for the pentacene dimer or trimer will be demonstrated.

2. Second chapter shows synthesis of second-ring adduct of pentacene

In this chapter, Ms. Jia focused on the synthesis of second-ring adduct of non-substituted pentacene. Ms. Jia's idea is introducing bulky substituents to the central-ring of pentacene. After Diels-Alder reaction. Removal of the bulky groups would give second-ring adduct.

The trimethylsilyl (TMS) group was chosen as the bulky group. Bis-silylated pentacene was successfully synthesized via the zirconium-mediated cyclization and the coupling reactions we developed recently. Dihydropentacene reacted with DDQ and Et₃N to give bis(trimethylsilyl)pentacene in 62% isolated yield.

Diels-Alder reaction of disilylpentacene was proceeded smoothly at the second-ring in high regioselectivity. Silyl groups of the Diels-Alder adducts were removed by treatment with CF₃CO₂H. The desired 2nd-ring adducts of pentacene were obtained. The structures were verified by X-ray analysis.

Similarly, desilylated dihydropentacene was also applicable for the alternative synthesis of the second-ring adducts of non-substituted pentacene. 6,13-Bis(trimethylsilyl)-5,14-dihydropentacene was treated with CF₃CO₂H to give 5,14-dihydropentacene in 85% isolated yield.

Next, dihydropentacene was treated with excess amount of dienophiles under heating. The desired 2nd-ring adduct of 5,14-dihydropentacene was obtained. After aromatization, desired 2nd-ring adduct was obtained. Because the central-ring of anthracene is second-ring of pentacene. And a good pentacene precursor of 2nd-ring adduct was synthesized by this method. Retro Diels-Alder reaction also was examined by heating could give pentacene as blue solid. The conversion temperature is lower than 140 °C.

3. Third chapter shows selective synthesis of alkylsubstituted pentacenes by coupling method

In this chapter, a convenient method was developed for the introduction of substituents by cross-coupling at 6,13-positions of pentacene. The substrate 6,13-diiodo-5,14-dihydropentacene was prepared from 6,13-Bis(trimethylsilyl)-5,14-dihydropentacene by iodination with 2.2 equiv of ICl₁ in high yield.

6,13-Diiodo-5,14-dihydropentacene was used for the further introduction of substituents at 6- and 13-positions by cross-coupling reactions. Alkyl-, aryl-, alkynyl-, and alkenyl groups were

introduced by cross-coupling reactions in the presence of Pd catalyst to give the coupling products in high yields. Fortunately, alkyl group could be introduced to 6,13-positions successfully by this new method. After aromatization, 6,13-dialkylpentacenes were synthesized.

When diiododihydropentacene was treated with 1.2 equiv of $\text{Pd}(\text{PPh}_3)_4$, palladated 5,14-dihydropentacene was obtained in 79% NMR yield. Crystallization of the crude product afforded crystals in 41% yield. The structure was determined by NMR and X-ray analysis after changing PPh_3 to PMe_3 .

Similarly, a series of 6,13-disubstituted-5,14-dihydropentacene were synthesized by cross-coupling from palladated-5,14-dihydropentacene. The yields became higher.

It is well known that tautomerizations of isotoluene, methylenehydronaphthalene, and methylenehydroanthracene give toluene, methylnaphthalene and methylanthracene, respectively. However, when the compound has more than five rings, such as methylpentacene. The situation is different. In NATURE in 1949, Clar and co-workers reported the attempt of preparation of 6-methylpentacene. They carried out the reaction of pentaceneketone with MeMgI , and they claimed 6-methylpentacene was formed, but they did not isolate it.

Our group reported the isolation of 6,13-dipropylpentacene as the first example of alkyl 6,13-disubstituted pentacene. However, this method can not be used for preparation of 6-methylpentacene. Here I tried to develop new method to synthesize 6-methylpentacene. Diiododihydropentacene was treated with catalytic amount of Cp_2TiCl_2 and 3.0 equiv of $n\text{-BuMgCl}$ to give monoiododihydropentacene in 63% yield. After that, 6-methyl-5,14-dihydropentacene was obtained by Negishi cross-coupling reaction in high yield. Aromatization by DDQ and triethylamine gave 6-methylpentacene in 42% isolated yield. 6-Methylpentacene was characterized by ^1H , ^{13}C , UV spectrum, and HMRS. Surprisingly, 6-methylpentacene was very stable at room temperature under nitrogen.

4. Fourth chapter shows synthesis of pentacene side oligomer by coupling method

In this chapter, the 1,2,3,4,8,9,10,11-octaalkylpentacenes was successfully synthesized from diynes by our homologation method. The zirconiummediated cyclization of diynes with 4-octyne or 5-decyne proceeded in the presence of $\text{NiBr}_2(\text{PPh}_3)_2$ to give tetrahydropentacene derivatives in 43% and 46% yields, respectively. And I also examined the dehydro side coupling reaction of 1,2,3,4,8,9,10,11-octaalkylpentacenes.

Tetrahydropentacenes reacted with an excess of DDQ (3 equiv) at room temperature to give their Diels-Alder adducts in quantitative yield. The reaction mixtures were treated with 50 equiv of γ -terpinene at 80 °C in the presence of triethylamine to induce the retro-Diels-Alder reaction. Finally, 1,2,3,4,8,9,10,11-octaalkylpentacenes were obtained as stable purple solids under nitrogen in 78 and 82% yields, respectively.

Interestingly, the dehydro side-coupling of pentacene derivatives occurred by heating in the presence of DDQ (0.5 equiv) and a catalytic amount of (\pm)-10-camphorsulfonic acid (CSA) to give the corresponding 6,6'-dipentacenyl derivatives in high yields. The side dimers were stable blue solids under nitrogen, and it has much lower solubility than the corresponding pentacene derivatives in common organic solvents. The structure of side dimer was confirmed by X-ray analysis.

The side-coupling product also could be directly synthesized from tetrahydropentacenes by 2.5 equiv of DDQ in mesitylene at 120 °C for 6 h in 82% and 76% yields instead of pentacenes respectively. This result indicated that the hydroquinone derivative DDQ- H_2 , which was formed in situ from DDQ, played the same role as the acid in the dehydro side-coupling reaction of pentacenes. Without addition of a catalytic amount of CSA, pentacene derivative was treated with 0.5 equiv of DDQ in mesitylene at 120 °C for 6 h. Only its DDQ adduct was formed in 49% yield along with the recovery of unreacted 4a in 51% yield. Side-coupling product was not observed. Without the presence of DDQ (0.5 equiv), pentacene derivative was heated with 0.1 equiv of CSA under the same conditions. The side-coupling product was also not obtained, but further reaction products were detected.

As shown above Ms. Jia's Ph.D. thesis has high quality and enough discussions and it is suitable for Ph.D. degree.

学位論文審査の要旨

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(置換基を有するペンタセン誘導体の選択的合成法の開発)

ベンゼン環が直線状に縮合している化合物群をアセンといい、その中で5つの環からなるペンタセンは1997年にアモルファスシリコンと同程度またはそれを凌ぐ性能をもった有機半導体であることが見出されてから、ペンタセンに関する有機材料研究が世界中で展開されるようになった。特に有機溶媒に不溶なペンタセンをどのようにして可溶なペンタセンに変換するか、あるいは印刷法でペンタセン薄膜を形成する方法の開発など、多くの課題が存在する。賈志英さんはこのような状況の下、ペンタセンの6位と13位への置換基の導入方法の開発、可溶性ペンタセン前駆体の開発、低温で分解するプラスチック基板用前駆体の開発、ペンタセンオリゴマーの開発などをおこなった。賈志英さんの博士論文は全体で4章からなり、最初の章はイントロダクションとして、これまで開発されてきた置換ペンタセンの合成法の歴史とそれらの問題点、ディールス・アルダー反応によるペンタセン前駆体の合成法について述べている。

第2番目の章から今回の成果について述べられている。まず2番目の章を第1章として、2番目の環でディールス・アルダー反応をおこなわせる方法についての結果がまとめてある。通常ペンタセンは5つの環のうち、中央の環がもっとも反応性が高く、ジエノファイルと反応させると必ず中央の環が反応する。この環化付加体を前駆体としてペンタセン薄膜を形成せざるためには、180℃以上の加熱が必要である。プラスチックを基板とする場合、140℃以上に加熱することはできず、140℃以下で分解してペンタセンを与える前駆体を開発する必要がある。賈志英さんはこの問題において、より不安定な前駆体が合成できれば、低温で分解すると考え、中央での環での環化付加

ペンタセンの2番目の環での環化付加体は知られておらず、新しい開発が必要であると判断した。賈志英さんは2つの方法を開発した。ペンタセンの中央の環にかさ高いトリメチルシリル基を導入して、環化付加反応が中央の環で進行しないようにし、2番目の環で進行させた。そのあと、トリメチルシリル基をはずすという方法であった。2つ目の方法は、ジヒドロペンタセンを合成し、そのアントラセン部分の中央の環、すなわちペンタセンの2番目の環でディールス・アルダー反応を行い、その後残りの環を芳香化させるというものである。この方法を用いて選択的に2番目の環に環化付加反応を起こした付加体を合成した。ジエノファイルとしてアゾジエノファイルを用いたとき、140℃で分解しペンタセンを与えることを見出し低温でペンタセンを与える前駆体を開発することに成功した。

第2章はペンタセンの6位と13位に任意の置換基を導入するための方法について述べている。前章で開発したトリメチルシリルペンタセンから収率良く変換した6、13-ジヨードジヒドロペンタセンが利用価値が高いと判断し、この化合物のクロスカップリングをおこなうことによって、任意の置換基を導入する一般的な手法を開発した。

また1949年に発表されたネーチャーの論文に記載されている6-メチルペンタセンがきちんと同定されていないため、これまでいくつかのグループが合成を試みたが、成功していなかった。そこでこの化合物について賈志英さんは独自に開発した方法を用いてチャレンジを行い、6-メチルペンタセンを安定に単離することに成功した。これによりネーチャーの発表データの中で、室温で不安定であるとされていた6-メチルペンタセンが実は非常に安定であることなど、多くの部分での修正をおこなうことができた。

第3章はペンタセンのオリゴマーの合成にチャレンジした結果が述べられている。アルキル基を持つペンタセン誘導体に酸と酸化剤であるDDQを加えて反応させると、ペンタセンが中央の環で結合した2量体が見出された。これらの2量体の構造はx線構造解析などで明らかにしている。

以上、賈志英さんはペンタセン誘導体の合成の分野で顕著な成果を収め、博士論文としてまとめている。よって著者は、北海道大学博士（生命科学）の学位を授与される資格あるものと認める。