Tetrahedron Letters 51 (2010) 6313–6315

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of functionalized tetracene dicarboxylic imides

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ARTICLE INFO

Article history:
Received 24 July 2010
Revised 6 September 2010
Accepted 24 September 2010
Available online 18 October 2010

Keywords:
Acene
Tetracene
Dicarboxylic imide
Friedel–Crafts reaction
Imidization

ABSTRACT

For the first time, a synthesis of tetracene dicarboxylic imides was established with 1,2,3,4-tetrahydrotetracene (**1**) instead of tetracene as the starting material. Mono-bromination of **1** by $CuBr_2$ followed by a Friedel–Crafts reaction, oxidation, and imidization gave the tetrahydrotetracene carboxylic imides **5a–b**. Subsequent oxidative dehydrogenation of **5a–b** with DDQ afforded the functional tetracene dicarboxylic imide monobromides **6a–b**, which can be further functionalized to provide functional materials such as the 'donor–acceptor' type compounds **7a–b**.

Acenes represent a promising class of molecules with applications in organic electronics.[1] Therefore, a large number of functionalized acenes have been reported and used, for example, for organic light-emitting diodes, field-effect transistors and solar cells.[2] Among derivatives of acene, acene carboximides are attracting increasing interest due to their important roles in the design of new semiconductors and organic dyes. For example, 10 years ago, the smallest acene, naphthalene, was used as a building block for *n*-type semiconductors following the introduction of electron-deficient dicarboxylic imide groups[3] and recently naphthalene carboximides have been widely used for the synthesis of stable semiconducting materials.[4] Anthracene carboximide derivatives have been used as drugs because of their biological activity.[5] In addition, functionalized naphthalene and anthracene dicarboxylic imides (Scheme 1) have been applied to the synthesis of rylene dyes[6] and bisanthryl diimide near infrared (NIR) dyes as shown by us and other groups.[7] Compared with other aryl or alkynyl-substituted acenes, imide substituted acenes usually show high chemical and photostability, which are crucial for practical applications. Moreover, they also exhibit high electron affinity due to the electron-withdrawing character of their carboximide units, and can be used as building blocks for both *n*-type semiconductors and stable NIR dyes. Although naphthalene and anthracene carboximides are now readily available, the synthesis of carboximide substituted higher order acenes such as tetracene and pentacene have not been reported due to synthetic problems. Tetracene as a larger acene is supposed to exhibit superior optoelectronic properties due to its extended π-conjugation and many functionalized tetracene derivatives have been reported.[8] However, no efficient method for the introduction of the electron-deficient carboximide to the tetracene unit has been reported. As imide groups enhance the stabilities and solubilities and also tune the electronic properties of unstable and poorly soluble tetracenes, herein, we report the first synthesis of a series of soluble and stable functional tetracene dicarboxylic imides.

We first attempted to apply chemistry used for the synthesis of anthracene dicarboxylic imides[7] to the tetracene (Scheme 1). However, a direct Friedel–Crafts reaction on tetracene using oxalyl chloride in CS_2 in the presence of $AlCl_3$ gave a complicated mixture and no desired tetracene diketones were observed. Considering the poor solubility of tetracene, the tetracene monobromide[9] which has good solubility in CS_2 was selected as the starting material in a similar reaction under the same conditions. However, again, no desired tetracene diketone was obtained. This indicated that it is not feasible to perform Friedel–Crafts reactions on tetracenes presumably due to their high reactivity. On the other hand, anthracene and its derivatives can undergo Friedel–Crafts reactions to give diketones.[5,7] Therefore, we revised our synthetic strategy by using 1,2,3,4-tetrahydrotetracene as the starting material.

As shown in Scheme 2, mono-bromination of 1,2,3,4-tetrahydrotetracene (**1**)[10] by $CuBr_2$ in CCl_4 gave the mono-bromide **2** in an 86% yield. Compound **2** was then submitted to a Friedel–Crafts reaction with oxalyl chloride in CS_2 and the two diketone isomers **3a** and **3b**, in a molar ratio of 3:1, were obtained as a mixture in a 76% yield. This mixture was used directly for the next step, oxidation by H_2O_2 in dioxane, without further purification due to their poor solubility and similar polarity, and the two carboxylic

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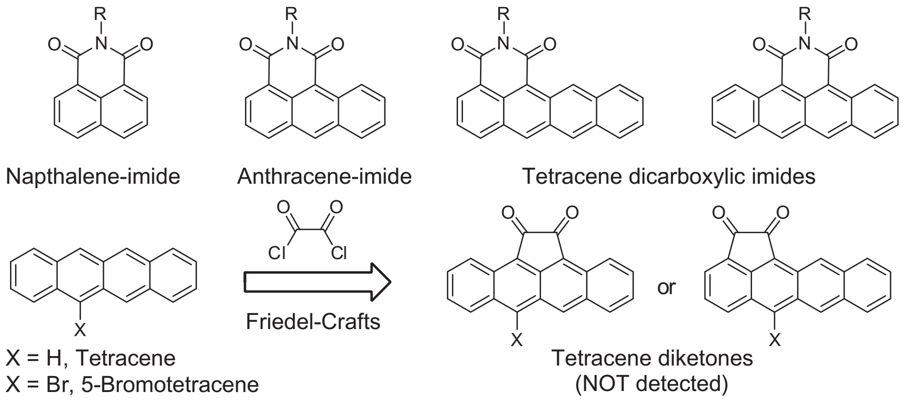
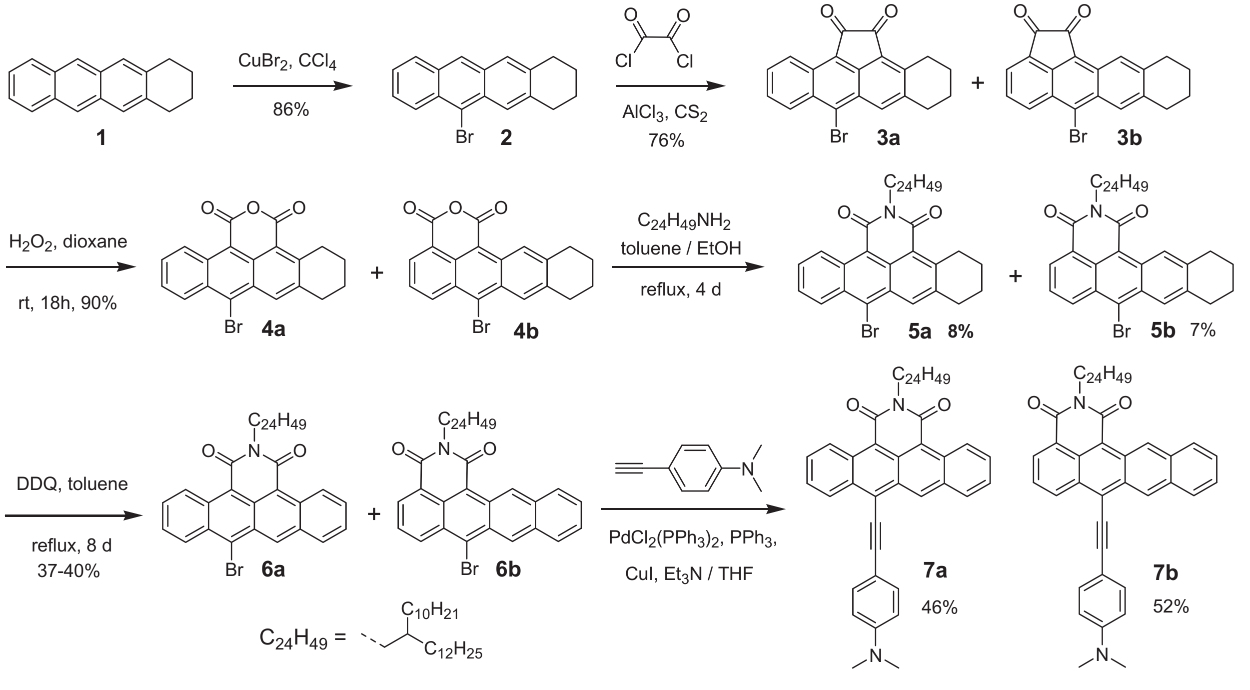
doi:10.1016/j.tetlet.2010.09.116



Scheme 1. Structures of some acene dicarboxylic imides and attempted synthesis of tetracene diketones.

anhydride isomers **4a** and **4b** were obtained in a total yield of 90%. Again, the poorly soluble anhydrides were used directly for the subsequent imidization reaction. A mixture of **4a**, **4b** and 2-decyltetradecan-1-amine[11] in anhydrous toluene and ethanol was refluxed for four days and the tetrahydrotetracene dicarboxylic imides **5a** and **5b** were separated in 8% and 7% yields, respectively. In view of the low yields, other reaction conditions were used[4a] and solvents such as NMP, DMF, or propanoic acid. However, the results indicated that the current solvent system is the only one that can give the desired carboximides. This is surprising since, in many cases, imidization of naphthacene and anthracene carboxylic anhydrides can be achieved in high yields. The reason for such low yields is still not clear but may be due to the electronic and steric effects of the additional 1,4-tetramethylene unit. Finally, oxidative dehydrogenation of **5a** and **5b** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing toluene gave the tetracene dicarboxylic imides **6a** and **6b**, respectively, both in 37–40% yields. Obviously, the bromine group in **6a** and **6b** gives opportunities for the synthesis of functional tetracene dicarboxylic imides with tunable properties. As a preliminary test, Sonogashira coupling reactions of **6a** and **6b** with 4-ethynyl-*N*,*N*-dimethylaniline were conducted and compounds **7a** and **7b**, with a 'donor–acceptor' type structure, were obtained in 46% and 52% yields, respectively (Scheme 2).

While the pure tetracene and 5-bromotetracene are air and light sensitive materials with an orange-yellow color in solution, the tetracene dicarboxylic imides **6a** and **6b** showed violet colors in chloroform and exhibited very good stability on exposure to ambient light and air. A detailed photostability test disclosed that the half life-times of solutions of tetracene, 5-bromotetracene and **6a** on irradiation with a 100 W white light bulb were 15, 16 and 660 min, respectively. That is, the introduction of the electron-withdrawing imide groups into the tetracene improved its photostability significantly. Compounds **6a–b** exhibited similar UV–vis absorption and fluorescence spectra in dichloromethane (CH_2Cl_2) although they are structural isomers. A sharp absorption band centered at 292 nm and a broad band from 450 to 670 nm were observed for both (Fig. 1a). The optical band gaps were estimated to be 1.87 eV (670 nm) and 1.88 eV (661 nm) for **6a** and **6b**, respectively. For comparison, tetracene and 5-bromotetracene in CH_2Cl_2 have optical band gaps of 2.49 eV (498 nm) and 2.39 eV (518 nm), respectively (Fig. 1a). Accordingly, the fluorescence



Scheme 2. Synthesis of functionalized tetracene dicarboxylic imides.

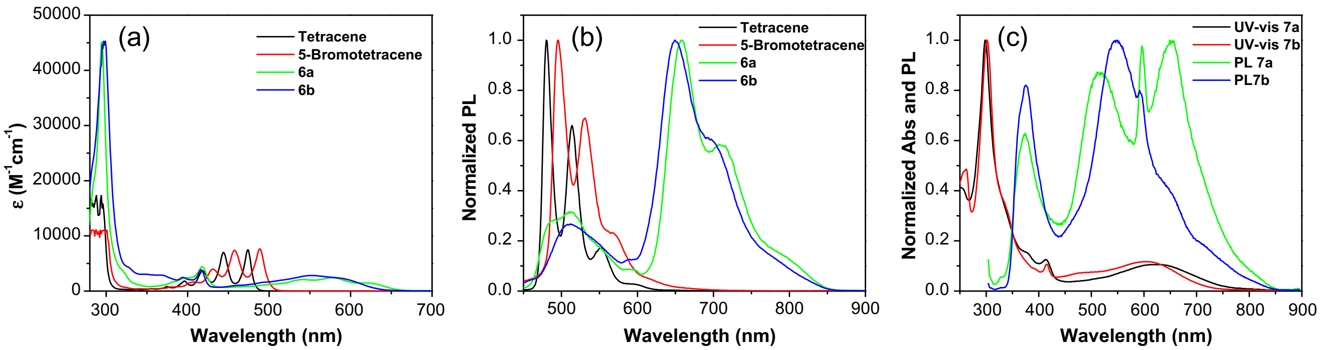


Figure 1. (a) UV–vis absorption spectra of compounds tetracene, 5-bromotetracene, **6a** and **6b** in CH_2Cl_2 (1×10^{-5} M). (b) Normalized fluorescence spectra of compounds tetracene, 5-bromotetracene, **6a** and **6b** in CH_2Cl_2 (1×10^{-6} M). (c) Normalized UV–vis absorption and fluorescence spectra of compounds **7a** and **7b** in CH_2Cl_2 (the concentration of solutions for absorption and emission spectra is 1×10^{-5} and 1×10^{-6} M, respectively, and the excitation wavelength is 294 nm).

spectra of **6a** and **6b** exhibited significant red-shifts with respect to tetracene and 5-bromotetracene (Fig. 1b). Such a convergence in band gap and red-shift of the absorption/emission spectra can be explained by the intramolecular donor–acceptor interaction induced by the electron-rich tetracene (donor) and electron-deficient dicarboxylic imide group (acceptor). The fluorescence quantum yields for tetracene, 5-bromotetracene, **6a** and **6b** in CH_2Cl_2 were determined to be 0.118, 0.007, 0.077 and 0.075, respectively. After introduction of the strongly electron-donating 4-dimethylaminophenylethynyl unit, compounds **7a** and **7b** had appeared a deep blue color in CH_2Cl_2 and displayed significant further red-shifts in absorption spectra in comparison to **6a** and **6b**, with optical band gaps being 1.56 eV (794 nm) and 1.58 eV (784 nm), respectively (Fig. 1c). These changes can be ascribed to the extended π-conjugation and enhanced intramolecular donor–acceptor interactions in **7a** and **7b**. Compounds **7a** and **7b** showed quite different fluorescence spectra from **6a–b** in solution, which could be related to their different symmetries and dipole moments.

In conclusion, stable and functionalizable tetracene dicarboxylic imides such as **6a** and **6b** were synthesized for the first time by using 1,2,3,4-tetrahydrotetracene as the starting material. This will allow further functionalization on the tetracene dicarboxylic imides in order to prepare soluble and stable tetracene carboximide-based semiconductors and NIR dyes with tunable optoelectronic properties. Although the unexpectedly low yield of the imidization step may limit scale-up work, the new synthetic method provides a direction for the synthesis of carboximide derivatives of higher order acenes or other polycyclic aromatics in the future.

Acknowledgment

This work was financially supported by Singapore DSTA DIRP Project (DSTA-NUS-DIRP/2008/03), NRF Competitive Research Program (R-143-000-360-281), and NUS Young Investigator Award (2007).

Supplementary data

Supplementary data associated (detailed synthetic procedure and characterization data for all new compounds) with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.116.

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