



# Construction of new fluorophores by Diels–Alder reaction of diacenaphthothiophenes



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## ABSTRACT

The Diels–Alder (DA) reaction of diacenaphtho[1,2-*b*;1',2'-*d*]thiophene (**1a**) with benzyne affords 1:1 and 1:2 adducts, **7** and **8**, in 47 and 11% yields. An X-ray crystallographic analysis reveals that **8** possesses a dibenzobarrelene structure involving a rigid di(1-naphthyl)ethene moiety. Thus, the second DA reaction occurs at the central benzene ring of **7** selectively. The 1:2 adduct **8** emits intense blue fluorescence in CH<sub>2</sub>Cl<sub>2</sub>. Moreover, we examined the DA reactions of **1a** and tetra-*t*-butyl derivative **1b** with *p*-benzoquinone to afford acenaphtho[1,2-*j*]fluoranthene **10a**, and its tetra-*t*-butyl derivative **10b** and a quinone **11b**, respectively. Novel fragmentation reaction should occur to produce the acenaphtho-fluoranthene frameworks of **10**. An X-ray crystallographic analysis reveals a rather planar structure of **11b**. The central benzene ring of **11b** shows large bond alternation by the Mills–Nixon effect. The compounds **10a** and **10b** emit sky blue fluorescence with moderate  $\phi_{SN}$  values. The electronic properties of new compounds are well consistent with the theoretical predictions.

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## 1. Introduction

Thiophene is one of heterocyclic compounds with high aromatic stability. Therefore, the reactivity of thiophene as a diene part of Diels–Alder (DA) reaction is considerably low. On the other hand, diacenaphtho[1,2-*b*;1',2'-*d*]thiophene (**1a**) readily prepared by heating acenaphthene with sulfur can be served as a DA diene. Actually, Clapp reported the DA reaction of **1a** with maleic anhydride to afford acenaphtho[1,2-*j*]fluoranthene-4,5-dicarboxylic anhydride (**2**).<sup>1</sup> The result indicates that fusion of two acenaphthylene ring systems enhances reactivity of the thiophene ring of **1a** probably due to increasing molecular strain. Upon the early works, several studies of **1a** relating to chemical reactions,<sup>2</sup> derivatization,<sup>3</sup> molecular structures,<sup>4</sup> and solid state properties<sup>5</sup> have been performed to date; however, the DA reaction of **1a** has not been explored well. In 2000, Kilwey and coworkers reported as one exception that the DA reaction of tetra-*t*-butyl derivative **1b** with *p*-benzoquinone provides an anthraquinone derivative **3** (Fig. 1).<sup>6</sup>

Recently, we synthesized *N*-octyl acenaphtho[1,2-*j*]fluoranthene-4,5-dicarboxylic imides **4** from **2**.<sup>7</sup> At the same time, we examined direct synthesis of **4** using the DA reaction of **1a** with *N*-octyl maleinimide **5**. Unexpectedly, the reaction provides a 1:2 adduct **6** as a major product (Scheme 1). Because **6** displays intense blue fluorescence [quantum yield ( $\phi$ ) = 98% in CH<sub>2</sub>Cl<sub>2</sub>], the compound can be regarded as a new fluorophore based on a rigid 1,2-di(1-naphthyl)ethene moiety. Thus, **1a** and **1b** would be versatile synthetic building blocks for polycyclic conjugated systems with excellent fluorescence properties. In the course of the study, we examined the DA reaction of **1a** with benzyne. The reaction affords a 1:2 adduct **8** possessing a rigid dibenzobicyclo[2.2.2]octatriene (dibenzobarrelene **9**) structure<sup>8</sup> together with a 1:1 adduct **7**<sup>9</sup> (Fig. 2). We also examined the DA reaction of **1a** and its tetra-*t*-butyl derivative **1b** with *p*-benzoquinone; **1a** afforded acenaphtho[1,2-*j*]fluoranthene derivative **10a**, on the other hand **1b** provided **10b** and its *p*-benzoquinone-fused compound **11b**. Although **10a** is a known compound,<sup>10</sup> our synthesis is rather simple and effective, and its electronic properties has not been explored as far. We report here electronic and optical properties of **7**, **8**, **10a**, **10b** and **11b**, as well as the molecular structures of **8** and **11b**.

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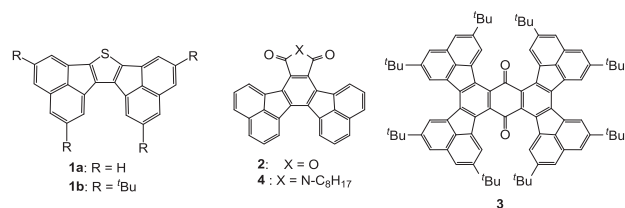


Fig. 1. Molecular structures of 1–4.

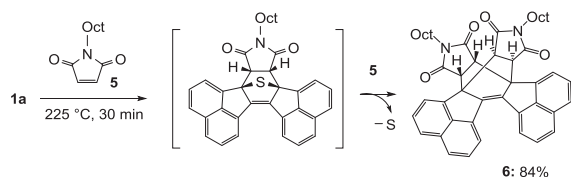
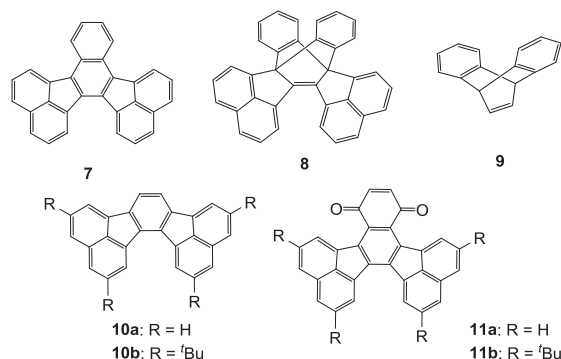
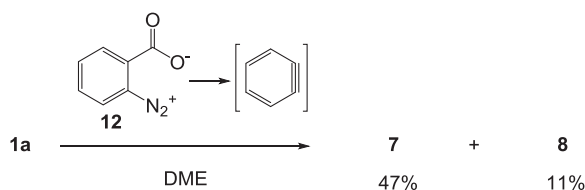
Scheme 1. DA reaction of **1a** and *N*-octylmaleinimide **5**.

Fig. 2. Molecular structures of 7–11.

## 2. Results and discussion

### 2.1. Synthesis

We examined the DA reaction of **1a** with benzyne. Benzyne has been known as a highly reactive intermediate. It can be generated by thermal decomposition of *o*-benzenediazonium carboxylate **12**, which was prepared by the reaction of anthranilic acid with isoamyl nitrite. The DA reaction was carried out in a 1,2-dimethoxyethane (DME) solution to afford 1:1 and 1:2 adducts, **7** and **8**, in 47 and 11% yields, respectively (Scheme 2). The 1:2 adduct should form by the DA reaction of the central benzene ring A of **7** with benzyne. In 1963, Miller and Stiles reported thermal decomposition of **12** in naphthalene to afford dibenzobarrelene **9** in 7% yield.<sup>11</sup> Taking into account that the Miller's experiment was performed under neat conditions, **7** should have a higher reactivity toward benzyne than pristine naphthalene. Although **7** has three naphthalene rings in the molecule, the DA reaction selectively

Scheme 2. DA reaction of **1a** with benzyne.

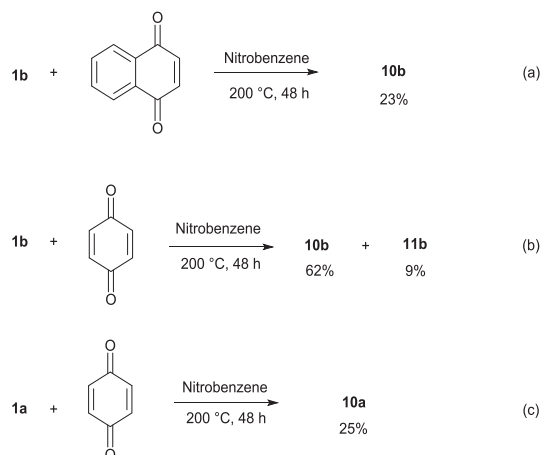
occurs at the central benzene ring A of **7**, probably due to inherent ring strain of the benzene ring by two outside naphthalene rings.

We examined the DA reaction of **1b** with 1,4-naphthoquinone in nitrobenzene at 200 °C for 2 days. To our surprise, the reaction furnished tetra-*t*-butylacenaphtho[1,2-*j*]fluoranthene **10b** as pale yellow crystals in 23% yield (Scheme 3a). Then, we also reinvestigated the DA reaction of **1b** with *p*-benzoquinone under the same conditions to produce **10b** in 62% yield together with naphthoquinone derivative **11b** as orange needles in 9% yield (Scheme 3b). Under these conditions, the anthraquinones **13b**<sup>9</sup> (the structure is shown in Scheme 4) and **3b**<sup>6</sup> were not obtained. The DA reaction of **1a** with *p*-benzoquinone also provided parent **10a** as pale yellow crystals in 25% yield (Scheme 3c). The low yield is estimated to be due to low solubility of **10a** in common organic solvents. The compounds **10a** and **10b** display intense sky blue fluorescence. The molecular structures are confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra as well as high resolution mass spectra (HRMS). We also examined that **1b** was heated at 200 °C in nitrobenzene in the absence of the quinones, and **11b** was heated at 200 °C in nitrobenzene in the absence of **1b**. In both cases, no reaction occurred. Thus, novel fragmentation reactions from reaction intermediates **14** to produce **10a** and **10b**, where the quinones act as an acetylene equivalent, should preferentially occur under the high temperature conditions (Scheme 4). The dehydrogenative aromatization from **14** to produce **11b** and **13b** would be unfavorable processes under the conditions. The known synthesis of **10a** can be achieved via three steps from acenaphthene-1-one.<sup>10b</sup> Our synthesis is more simple and effective than the known procedure.

### 2.2. Crystallographic analysis

A good single crystal of **8** suitable for X-ray analysis was obtained from an *n*-hexane/toluene solution. ORTEP drawings of **8** are shown in Fig. 3. The crystallographic analysis confirms the rigid dibenzobarrelene structure of **8**. A 1,2-di(1-naphthyl)ethene moiety of **8** has a highly planar structure; the dihedral angle of C(1)–C(2)–C(3)–C(4) is –1.2(5)° (for the numbering of **8**, see Fig. 3a). Mean angles between the di(1-naphthyl)ethene and two benzene ring planes are 57.36 and 58.72°, respectively (Fig. 3b). In the molecular packing, the molecules form a head-to-tail dimer structure, in which the di(1-naphthyl)ethene planes are stacked with 3.273 Å of the closest contact. The molecules does not have a columnar structure (Fig. 3c).

A needle single crystal of **11b** suitable for the analysis was obtained from a toluene solution. The compound crystallizes in the monoclinic space group *C2/c*. Crystal structures and selected bond

Scheme 3. DA reactions of **1a** or **1b** with quinones.

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