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Synthesis and properties of polycyclic quinones condensed with 1,6-methano[10]annulene

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Abstract

Two types of polycyclic quinones condensed with 1,6-methano[10]annulenes as type A: 1,6-methanonaphtho[2,3-*c*][10]annulene-7,12-dione **5a**, and type B: 1,6-methanonaphtho[2,3-*c*][10]annulene-5,14-dione **18**, bis(1,6-methano[10]annuleno[3,4-*b*; 3,4-*g*])anthracene-10,21-dione **20**, 1,6-methanoanthraceno[2,3-*c*][10]annulene-5,16-dione **22**, 1,6-methanotetraceno[2,3-*c*][10]annulene-6,17-dione **23**, and 1,6-methano phenanthreno[2,3-*c*][10]annulene-5,6-dione **24** have been synthesized. The acene derivative **6** corresponding to that of **5a** was synthesized by the reduction of quinone **5a**. The physical, spectral, and chemical properties of these new compounds have been investigated.

Keywords: Bridged [10]annulene; Poly condensed quinone; Condensed acene; Rearrangement; Fluorescence; Reduction potentials

1. Introduction

Polycyclic quinones and quinodimethanes (**D**), known as electron acceptors [1], are of interest in their utility of dichroic dyes [2], dyes as textile colorants [3], paints [4], organic transistors [5] and so on. For example, the acenes (**E**), especially pentacene, are mostly used in organic thin film transistors [6]. Anthracene derivatives were also used in blue light emitting materials [7]. These utilities deeply related with their structure and electronic states. We have studied the relation between structure and electronic states in π-conjugated polycyclic compounds such as quinones and related acenes containing 1,6-methano[10]annulene (bridged annulene). This is because bridged annulenes, an isoelectronic isomer of naphthalene, are expected to be good electron current compounds than naphthalene by delocalization of electron over the ring for the use of organic materials, and ^{1}H NMR chemical shifts of the methylene protons of bridged annulenes are good indicators for the estimation of the ring current related with electronic states. We synthesized such new polycyclic quinone compounds containing bridged annulene types **A**, **B**, and acene **C** as shown in Fig. 1 and examined their properties by spectral measurements. Details of the results are described as follows.

2. Synthesis and identification of quinone type A and acene

2.1. Synthesis and identification of quinone 5a; type A

The synthesis of quinone **5a** [8] as type **A** has previously been reported in our paper; however, the detailed properties were not described, and the yield was not satisfactory. Although the synthetic key compound of dione **4** has been known, the yield was low (25%) [9]. We developed a new synthetic method and improved the yield as follows. The reaction of **1** [8] with morpholine in the presence of a three molar excess of $TiCl_4$ and a 12 molar excess of NEt_3 in

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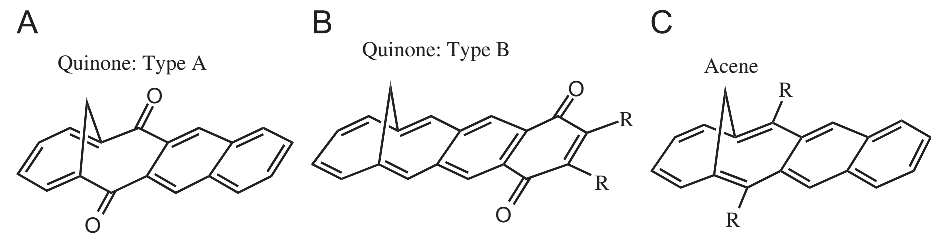
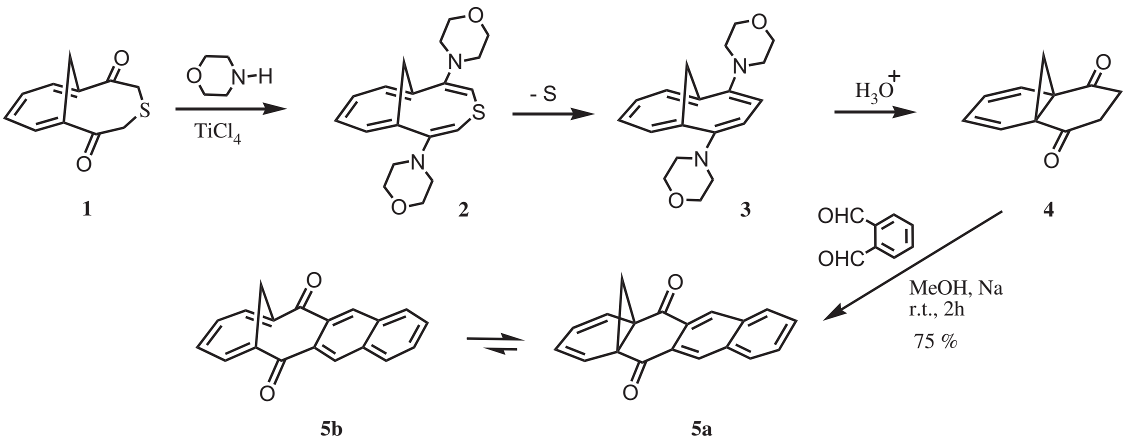


Fig. 1. Newly synthesized polycyclic quinone compounds containing bridged annulene types **A**, **B**, and acene **C**.



Scheme 1.

toluene at 40 °C for 2 h gave 2,6-morpholino-1,7-methano-4-thio[11]annulene **2** as an unstable compound under air moisture with 76% yield. Desulfurization of **2** easily occurred at over 40 °C to give 2,5-morpholino-1,6-methano[11]annulene **3** as stable compound with 95% yield. The hydrolysis of **3** in acidic media gave key intermediate **4** in over 78% yield. The reaction of **4** with *o*-phthalaldehyde in the presence of NaOMe in dry MeOH at 40 °C for 4 h gave condensed compound **5a** with 67% yield. The identification of **5a** was done as follows. The IR spectrum of **5a** showed that the strongest absorption band appearing at 1680 cm^{-1} was assigned as carbonyl groups of a typical quinone compound. The ^{1}H NMR signals at δ 8.65, 8.05, and 7.68 ppm were assigned as protons on the naphthalene moiety, and the signals at δ 7.06 and 6.19 ppm were assigned as protons of the bridged annulene moiety. The signals at δ 2.62 and 0.92 ppm were assigned as bridged methylene protons. The coupling constants ($J = 4.4$ Hz) of methylene protons and ^{13}C chemical shift of the methylene carbon (δ 24.4 ppm) indicate that the bridged annulene moiety of **5a** is a norcaradiene form rather than a cycloheptatriene form **5b**. The mass spectrum of **5a** shows that the parent peak appeared at m/z 272 corresponding to the assigned structure (Scheme 1).

2.2. Synthesis of acene derivative 6 by reduction of 5a

Acene **6** corresponding to quinone **5a** was synthesized by the reductive acetyloxylation of **5a** as follows. As expected from its reduction potentials, 0.61 and 1.10 eV measured by the cyclic voltammetry (CV) method, reduction of **5a** with Zn in acetic anhydride at reflux for 1 h gave acene derivative **6** and its rearranged compound **7**, in 33% and 32% yields, respectively, as shown in Scheme 2. The structures of these compounds were confirmed by the physical and spectral data as described in the next section.

2.3. Structure of acene derivatives 6 and 7

The structure of the new acene **6** was confirmed by the spectral data. The IR spectrum of **6** showed that the strong absorption band at 1750 cm^{-1} was assigned to acetate as typical ester groups. The structure of **6** was identified by the ^{1}H-, ^{13}C-NMR spectra, which were assigned by the ^{1}H–^{1}H, ^{1}H–^{13}C, two-dimensional methods, HMBC, HMQC methods, etc. The ^{1}H-NMR spectrum of acene type compound **6** is shown in Fig. 2 and the signals observed at δ 1.71 ppm ($J = 8$ Hz, 1H) and 1.39 ($J = 8$ Hz, 1H) are assigned as bridged methylene protons. They are lower fields than those of parent 1,6-methano[10]annulene **7** [10] and also benzannelated 1,6-methano[10]annulene **8** [11] rather similar to those of thiophen-condensed 1,6-methano[10]annulene **9** [12]. This suggests that the contribution of the conjugation in the bridged annulene moiety is quinodimethane form **5a** rather than 18π electron peripheral conjugation as **5b**. This phenomenon may depend on the number of condensed rings as mentioned