

Synthesis and Properties of [2.2](3,5)- and
[2.2.2.2](3,3',5,5')-Diphenoquinonophanes

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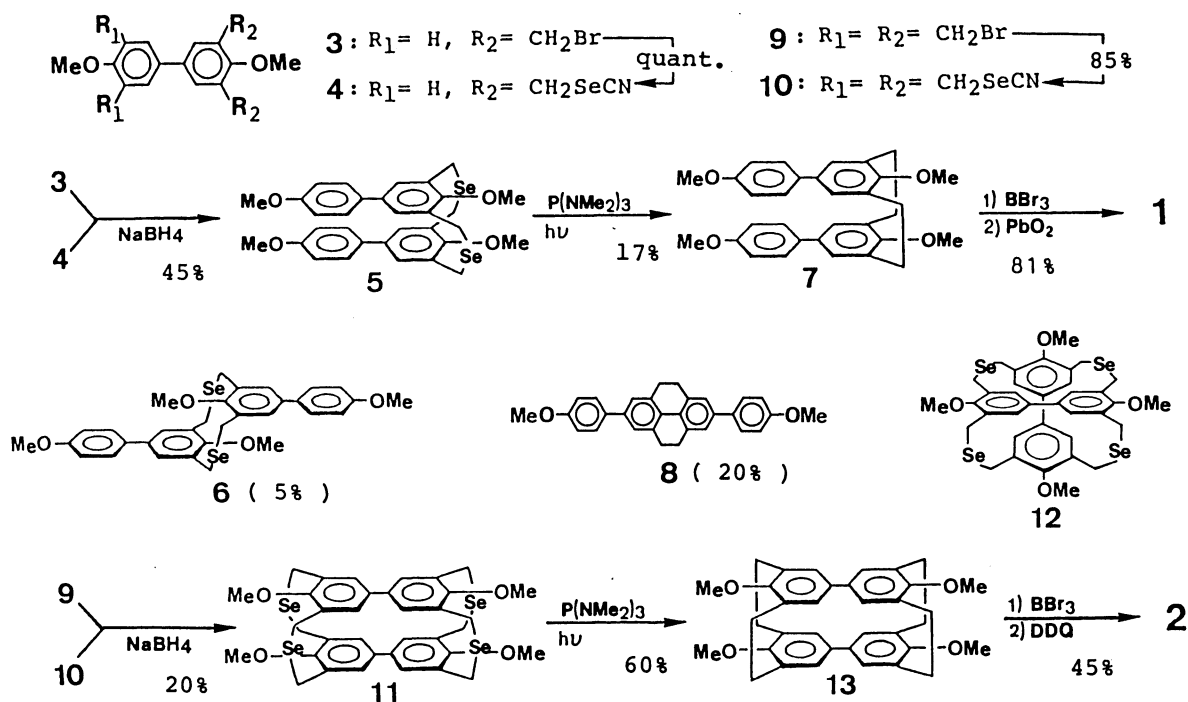
The first synthesis and the physical properties of diphenoquinonophanes is reported along with their spectral evidences.

There have been synthesized a wide variety of benzoquinonophanes not only for the systematic study of their chemical and physical properties but also as the useful precursors for the intramolecular quinhydrones to elucidate the charge transfer(CT) mechanism.¹⁾ Little attention, however, has been paid upon the synthesis of quinonophanes bearing the further extended quinone systems such as diphenoquinone, which has the higher reduction potential, i.e., the higher electron acceptability than benzoquinone, probably because of difficulty on the synthesis due to such high electron susceptibilities.²⁾ In connection with the study of transannular properties in quinono- and CT-phanes,³⁾ we wish to report the first synthesis of the stacked diphenoquinonophanes **1** and **2** together with their spectral properties.



As shown in Scheme 1, synthesis of the title diphenoquinonophanes **1** and **2** was undertaken by way of stable key intermediates, methoxybiphenylophanes **5** and **11**. Coupling of dibromide **3** with selenocyanate **4**, through our conventional synthetic method for selenacyclophanes,⁴⁾ gave an isomeric mixture of syn- and anti-diselenacyclophanes **5** and **6** in 50% yield with a preferential formation of the syn-isomer **5** in a ratio of 9:1. This suggests that the template effect shown in Fig. 1 works very well between sodium cation from

NaBH_4 and two selenium atoms in the bridging chains and two oxygen atoms in the methoxyl functions, leading preferably to the stacked isomer of 5 in spite of the larger π -electronic repulsion. Deselenation of the syn-isomer 5 was carried out with hexamethylphosphorous triamide under irradiation in THF⁵⁾ to afford 7 in 17% yield together with a 20% yield of the transannularly linked tetrahydropyrene derivative 8. Demethylation of 7 with boron tri-bromide in dichloromethane followed by oxidation with an excess of lead dioxide in a mixture of acetone and chloroform(1:1) gave 1[mp $>180^\circ\text{C}(\text{dec.})$ in a sealed tube] as the reddish crystals in 81% yield. Similarly coupling of tetrabromide 9 with the corresponding selenocyanate 10 gave the desired tetraselenacyclopentane 11 in 20% yield. The perpendicularly twisted selenacyclopentane 12, however, was not found at all in the reaction mixture. The molecular model examinations clearly indicate the marked increase of the skeletal strain in 12 as well as its unsuitable structure for the template effect. Despite of the simultaneous extrusion of four selenium atoms, photoreaction of 11 afforded biphenylophane 13 in such an excellent 60% yield, as can be expected in the less flexible selenacyclopentanes like 11.⁶⁾ Demethylation of 13 followed by oxidation with DDQ gave the completely stacked diphenyloquinonophane 2[mp $>300^\circ\text{C}$] in 45% yield as the reddish crystals, too. Diphenyloquinonophanes 1 and 2 are unexpectedly stable to air and halogenated solvents like chloroform, and can be kept unchanged unless they are exposed to light or protic reagents such as primary amines and alcohols.⁷⁾



Scheme 1.

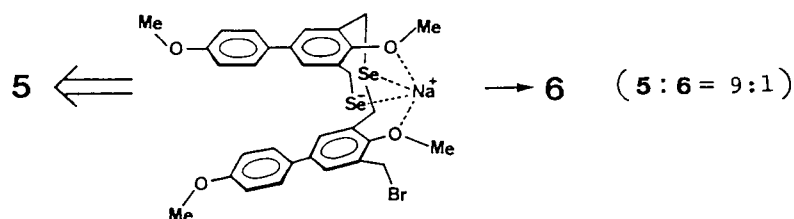


Fig.1. Favorable formation of syn-isomer **5** through template effect.

^1H NMR spectra of **1** and **2** are given in Fig. 2. In the case of bis-bridged cyclophane **1**, Ha [δ 7.27 ppm] protons appear between two sets of doublets owing to Hb [δ 7.75 ppm] and Hc [δ 6.54 ppm] protons similarly to the ring protons in the reference diphenoquinone **14**, and each proton shifts to the up-field by 0.43 for Ha, 0.2 for Hb, and 0.07 ppm for Hc compared with the corresponding protons Ha', Hb', and Hc', respectively. This fact apparently shows that two opposite diphenoquinone rings are fixed with so large dihedral angle that the anisotropic effect from the faced quinone ring is relatively weak for Hc protons. The more intensive up-field shift can be seen for Hd protons [δ 6.94 ppm] in the tetrakis-bridged cyclophane **2**, resulting in the difference of 0.78 ppm from the reference **15**. To our knowledge, the 0.78 ppm up-field shift in **2** from the corresponding component is the largest among all quinonophanes ever reported.

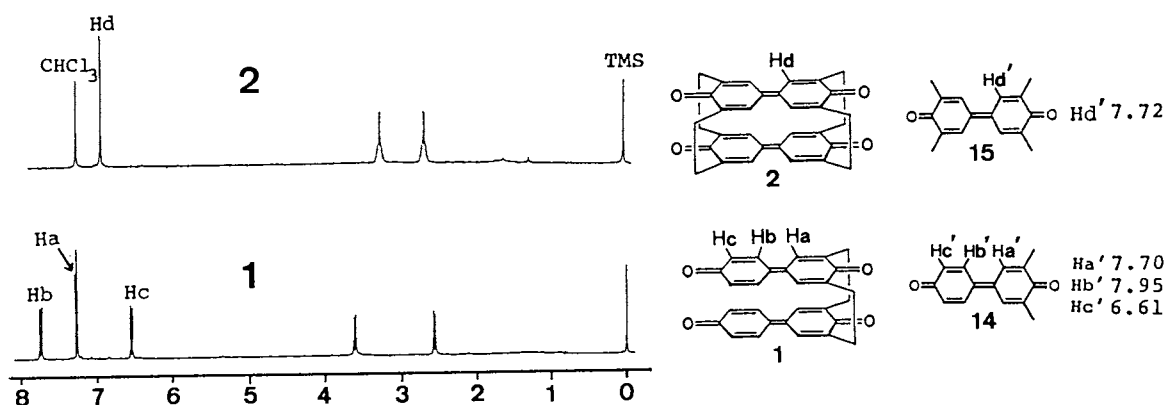


Fig.2. ^1H NMR spectra of stacked diphenoquinonophanes **1** and **2** (360 MHz, CDCl_3).

The electronic spectra of diphenoquinonophanes **1** and **2** and their references **14** and **15** are shown in Figs. 3 and 4. The main absorption bands of diphenoquinonophanes appear at the longer wavelength by around 100 nm than benzoquinonophanes, in accordance with the higher half-wave reduction potential of diphenoquinone [$E_{1/2}^1$ -0.24 V]⁸⁾ than benzoquinone [$E_{1/2}^1$ -0.51 V].⁸⁾ The completely stacked diphenoquinonophane **2** shows about 15 nm bathochromic shift of the longest wavelength absorption band compared with that of tetramethyl diphenoquinone **15**, though very similar absorption curve to the reference, as has been observed in the case of benzoquinonophanes.¹⁾ On the other hand, the spectrum of the partially opened diphenoquinonophane **1** exhibits a clear

splitting of the main band of the reference 14[λ_{max} 405 nm] into two broad bands[λ_{max} 378 nm and 450(sh) nm]. This may be ascribed to the large difference of the exciton band energies arising from the characteristic π -electronic interaction in the cyclophane molecules, although the relationship between the dihedral angle of the stacked diphenoquinone planes and the exciton splitting in their spectrum is obscure at present.

To study the relationship of the stacking mode of diphenoquinones with the electronic interaction between them in detail, synthesis of a series of bis- and tris-bridged diphenoquinonophanes is now in progress.

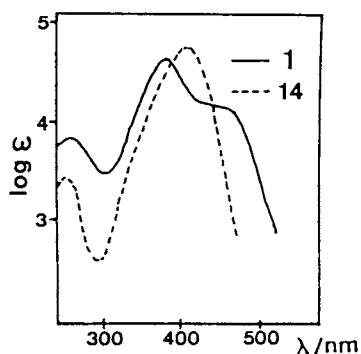


Fig.3. Electronic spectrum of 1 in CHCl_3 .

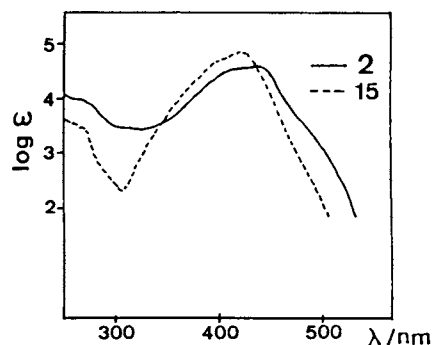


Fig.4. Electronic spectrum of 2 in CHCl_3 .

The authors wish to express their thanks to Material Analytical Center, ISIR, Osaka University for spectral measurements.

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(Received June 6, 1991)