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A New Antiaromatic Compound: 1,4-Biphenylenequinone Synthesis and Trapping Reactions

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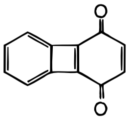
Cyclobutadiene[1−3] and its derivatives are pivotal molecules in the understanding of the antiaromaticity concept. Even more interesting molecules are those containing both [4*n*] and [4*n* + 2] π-electron systems called annulenoannulenes,[4] because they incorporate individual and/or peripheral circuits that may make opposing (e.g., stabilizing and destabilizing) contributions to delocalization energy. A prototype molecule in this area is benzocyclobutadiene,[5] in which the antiaromatic cyclobutadiene is juxtaposed to the aromatic ring of benzene. In order to determine the extent that a quinone unit attached to benzocyclobutadiene can stabilize the cyclobutadiene unit, we were interested in the synthesis of target compound **1**.



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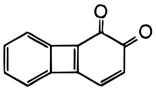

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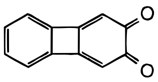

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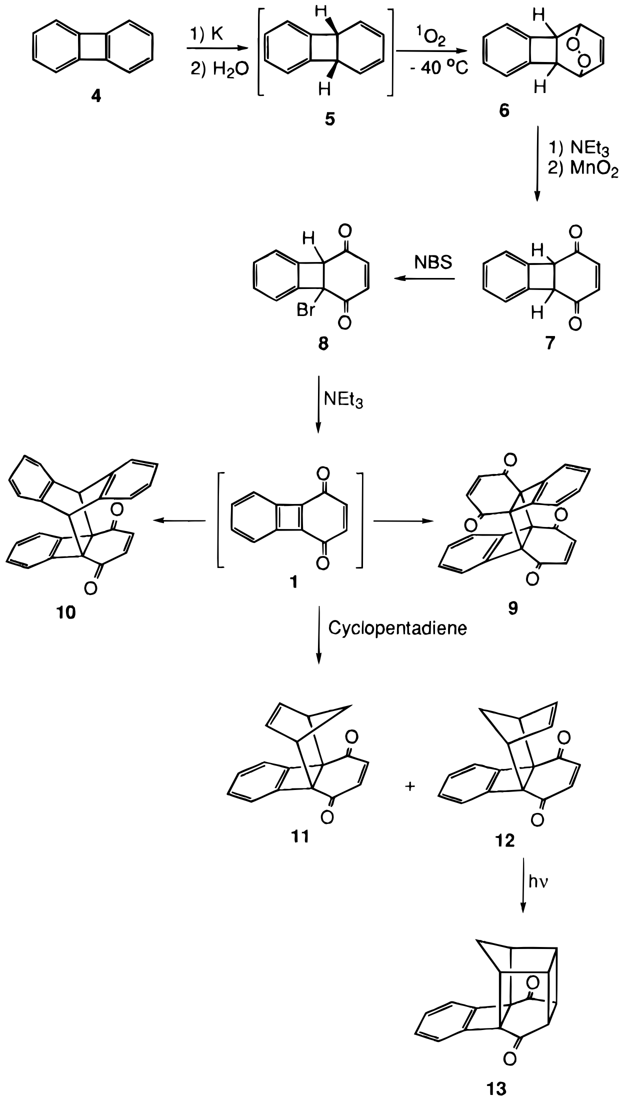
There are six isomeric structures for biphenylenequinones, and three of them (**1**−**3**) contain one intact benzene ring.[1] Only the isomer **3** containing a dimethylenecyclobutene group has been synthesized and characterized.[6] However, isomers **1** and **2** have cyclobutadiene units and are suspected to be less stable than **3**. Theoretical studies[7] have shown that 1,4-biphenylenequinone (**1**) is expected to be highly reactive. Unfortunately, there is no experimental report concerning the synthesis of 1,4-biphenylenequinone, and its antiaromatic character has not been verified experimentally. We report herein the first generation of 1,4-biphenylenequinone (**1**) and a study of its reactions.

Direct oxidation of biphenylene[6] with various oxidizing reagents results in the formation of 2,3-biphenylenequinone (**3**). Thus, we had to develop an efficient route to **1**, which permits the introduction of the necessary oxygen functional groups at the 1,4-positions of biphenylene. Birch reduction of biphenylene[8] gives 4a,8b-dihydrobiphenylene (**5**), which converts to its valence isomer benzocyclooctatetraene when heated.

Scheme 1



Tetraphenylporphyrin-sensitized photooxygenation of 1,3-cyclohexadiene unit of **5** in tetrahydrofuran at −40 °C resulted in the formation of the bicyclic endoperoxide **6** (Scheme 1). After chromatography on silica gel, endoperoxide **6** was isolated as the sole product in 70% yield. The structural assignment of **6** follows predominantly from its 200 MHz ^{1}H-NMR and 50 MHz ^{13}C-NMR spectra. Aromatic protons resonate, as required by the molecule symmetry, as an AA′BB′ system at 7.09 and 7.32 ppm where the other protons (bridgehead at 5.06 ppm and double bonds 6.21 ppm) also give rise to another AA′BB′ system in which the high-field part is further coupled to neighboring cyclobutene protons. The ^{13}C-NMR spectrum consisting of four sp^2 carbon and two sp^3 carbon signals is completely in agreement with the proposed structure. Although the regiochemistry of endoperoxide formation was not determined, we assume that singlet oxygen approaches the diene unit from the sterically less crowded face of the molecule to form the

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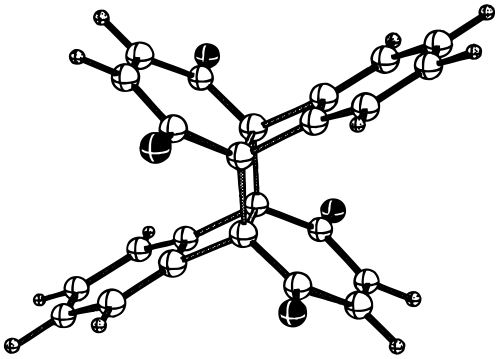


Figure 1. AM1-optimized geometry for the head-to-tail isomer **9**.

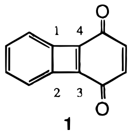
anti-adduct. For the synthesis of the target compound, the correct configuration of this endoperoxide was not important.

Endoperoxide **6** was converted into the corresponding diketone **7** by the known methods described in the literature.[9] Base-catalyzed rearrangement of the endoperoxide followed by MnO_2 oxidation provided diketone **7** in high yield.[10] An attempt to introduce the missing double bond into six-membered ring by oxidation with DDQ failed. Next, diketone **7** was subjected to radical bromination reaction with 1 equiv of *N*-bromosuccinimide to give monobromide **8**. HBr elimination[11] from **8** with NEt_3 or SiO_2 at room temperature in chloroform gave dimer **9**[10] instead of 1,4-biphenylenequinone (**1**), giving a satisfactory high-resolution mass measurement *M* 364.073 17 corresponding to $C_{24}H_{12}O_4$ (calcd mass = 364.073 55. The ^{1}H and ^{13}C NMR spectra surprisingly revealed the formation of only one isomer. The ^{13}C NMR spectrum gave the expected 3 sp^2 CH, the quarternery aromatic and the carbonyl carbon as well as a single sp^3 carbon signal. On the basis of the spectral data and NOE experiments, we were not able to assign the correct configuration of **9**. However, the AM1 calculations[12] indicate that the head-to-tail isomer **9** has 4.6 kcal/mol lower heat of formation (105.8 kcal/mol) than the head-to-head dimer (110.4 kcal/mol). We assume that there is a similar energy difference between the two transition states, which is sufficient to lead to the exclusive formation of the head-to-tail dimer **9** (Figure 1).

In order to trap **1** with other dienes, the elimination reaction was carried out in the presence of trapping reagents such as cyclopentadiene and anthracene. Dehydrobromination of **8** in the presence of cyclopentadiene gave the two compounds **11** and **12** in a ratio of 3:2, which could not be separated chromatographically. Exposure of these isomeric mixture to sunlight or projector lamp converted the isomer **12** to the corresponding cage molecule **13** where the other isomer **11**[10] remained unchanged. The formed mixture could be separated easily to give **11** and **13**. All the spectral data including the high-resolution mass spectrum of these compounds support the proposed structures. However, dehydrobromination of **8** in the presence of anthracene provided only one isomer (**10**, 35% yield) as expected.

The experiments summarized above clearly demonstrate that 1,4-biphenylenequinone (**1**) undergoes dimerization and other intermolecular reactions with extraordinary ease. **1** is apparently stable with respect to decomposition or rearrangement. On the other hand, it can be noticed **1** is not as stable as biphenylene; the quinone unit does not stabilize the cyclobutadiene unit as well as a benzene ring.

AM1 calculations[12] indicate that **3** (ΔH_f = 64.995 kcal/mol) is more stable than **1** (ΔH_f = 83.463 kcal/mol) by 18.5 kcal/mol. The structural parameters obtained from these semiempirical calculations show that the deformation of the cyclobutadiene unit from the square structure in **1** is more pronounced than in **3**. The $C_3{-}C_4$ bond (1.381 Å) is 0.1 Å shorter than $C_1{-}C_2$ (1.473 Å) and $C_2{-}C_3$ (1.493 Å) bonds. On the other hand, the $C_3{-}C_4$ bond in **1** is 0.13 Å shorter than those in **3**. According to AM1 calculations, **1** has a rectangular equilibrium geometry.



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Clearly, a decision regarding the antiaromatic character of 1,4-biphenylenequinone awaits matrix isolation and spectroscopic studies of **1**, which will be reported in the future. Detailed calculations on **1**−**3** are currently in progress.

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Supporting Information Available: Experimental procedures and spectral data for compounds **5**−**13** including ^{1}H- and ^{13}C-NMR spectra of compounds **6**, **7**, **9**, **10**, **11**, and **13** (10 pages).

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[10] Selected physical data for **7**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.26−7.29 (AA′BB′-system, aromatic, 4H), 6.66 (s, olefinic, 2H), 4.57 (s, cyclobutene, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 195.9, 142.8, 140.6, 129.7, 123.4, 52.00. Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.01; H, 4.46. **9**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.32−7.45 (AA′BB′-system, aromatic, 4H), 6.41 (s, olefinic, 2H), 4.46; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 194.7, 143.7, 142.6, 133.0, 126.6, 64.1. **10**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.91−7.31 (AA′BB′-systems, aromatic, 12H), 6.35 (s, olefinic, 2H), 5.11 (s, bridgehead, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.09, 143.86, 141.17, 140.06, 139.73, 129.39, 127.31, 126.87, 125.81, 125.61, 122.84, 65.03, 50.90. **11**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.04−7.26 (AA′BB′-system, aromatic, 4H), 6.72 (s, olefinic, 2H), 5.89 (m, olefinic, 2H) 3.45 (m, bridgehead, 2H) 1.71−2.02 (AB-system, methylenic, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.7, 146.6, 141.4, 135.0, 128.9, 123.3, 64.5, 53.75, 47.6); HRMS *m*/*z* (M^+) calcd for $C_{17}H_{12}O_2$ 248.0836, obsd 248.0837.

[11] Dehydrobromination experiments were also carried out using THF-d_8 at −70 °C and at different concentrations in the cavity of an NMR instrument in order to monitor the formation of **1**. In all cases we observed only signals belonging to the dimer **9**. It should be noted that the majority of dimer **9** was precipitated with polymeric materials.

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