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A new antiaromatic compound: 1,4-biphenylenequinone synthesis and trapping reactions: can a quinone unit stabilize the cyclobutadiene?

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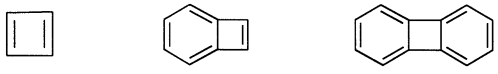
Abstract—The photooxygenation of 4a,8b-dihydrobiphenylene affords an endoperoxide. NEt_3-catalyzed rearrangement of this endoperoxide gave the corresponding hydroxy enone, while the CoTPP-catalyzed rearrangement afforded a bisepoxide. MnO_2 oxidation of hydroxy enol leads to 4a,8b-dihydrobiphenylene-1,4-dione. The NBS bromination of this dione produces mono- and dibromides. NEt_3-supported elimination of monobromide and zinc elimination of dibromide afforded the target compound, 1,4-biphenylenequinone, which was trapped as the dimer and cycloadducts with cyclopentadiene and anthracene, respectively. Furthermore, 1,4-biphenylenequinone was generated upon oxidation of biphenylene-1,4-diol with bis(trifluoroacetoxy)iodobenzene (PIFA). The stability and reactivity of the title compound is discussed.

1. Introduction

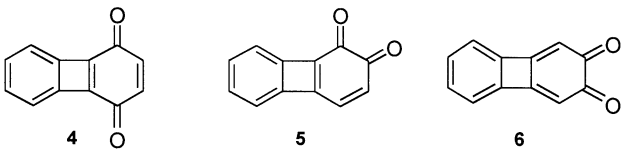
Cyclobutadiene (**1**) and related compounds containing four-membered rings have, over a span of many years, attracted the attention of workers in many areas, including theoretical, carbocyclic, aromatic and organometallic chemistry.[1–7] Cyclobutadiene is a highly reactive molecule and is clearly recognized as an antiaromatic Hückel 4n π-electron system. As such, **1** can only be subjected to spectroscopic studies at low temperature, with the aid of matrix isolation techniques.[8] According to theoretical and experimental evidence, cyclobutadiene (**1**) has a planar rectangular equilibrium with D_{2h} symmetry; the optimized square structure (D_{4h}) represents a transition state joining two equivalent minima on the potential energy surface.[1b]

Various experimental approaches have been devised in attempts to stabilize the reactive π-electron system of **1**. The successful ones include the introduction of bulky[9] or 'push–pull'[10] substituents, the coordination of the π-system to a transition metal group[5,7] and the technique of annelation of the four-membered ring to an aromatic or potentially aromatic π-electron systems.[1,4] With regard to the last mentioned approach, while benzocyclobutene (**2**) is still extremely reactive[11] biphenylene (**3**) is a stable compound,[1,12] although the unique electronic and steric characteristic of the four-membered ring impart a considerable amount of π-bond fixation, in the direction shown in Kekule structure **3**, on the molecule.



1 **2** **3**

A further extension of the annelation approach is to replace one of the benzenoid rings of biphenylene (**3**) by another π-electron system. In case of the quinone unit three such compounds are possible: 1,4- (**4**), 1,2- (**5**) and 2,3-biphenylenequinones (**6**). Inspection of these structures reveals that while **6** may be regarded as a derivative of dimethylenecyclobutene known to be stable,[12] **4** and **5** are derived by formal annelation of benzocyclobutene (**2**) to the quinone unit. The question, thus arises whether **4** will be reactive and short-lived species like **2** or whether there is sufficient π-electron delocalization through contribution of a quinone unit to stabilize this system, and permit its isolation. In order to determine the extent that a quinone unit attached to benzocyclobutadiene (**2**) can stabilize the cyclobutadiene, we were interested in the synthesis of the target compound **4**.[13]



4 **5** **6**

Only the isomer **6** containing a dimethylenecyclobutene

Keywords: biphenylenequinone; cyclobutadiene; singlet oxygen; Diels–Alder reactions; nucleus-independent chemical shifts values.

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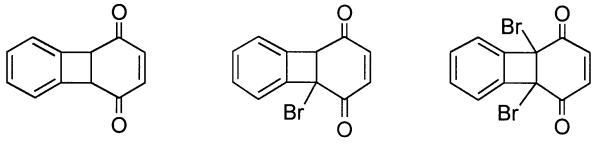
group has been synthesized and characterized so far.[14] The observed chemical reactivity of **6** is completely in agreement with a decreased antiaromatic character of the cyclobutadiene ring.[15,16] Unfortunately, there is no experimental report concerning the synthesis of **4**, and its antiaromatic character has not been verified experimentally. We report herein the first generation of **4** and a study of its reactions. Part of our results have already been briefly reported.[13]

2. Results and discussion

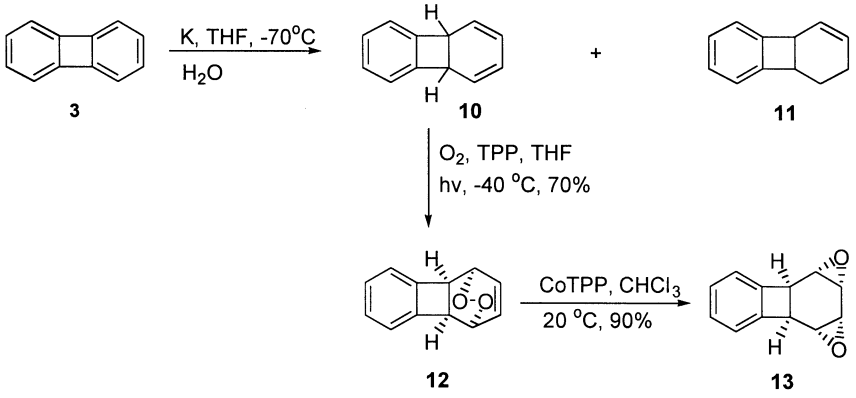
Direct oxidation of biphenylene with various oxidizing reagents results in formation of **6**.[14] Recently we have also showed that **6** can be generated by the reaction of **4** with hydrogen peroxide in the presence of a catalytic amount of methyltrioxorhenium in high yield.[17] Thus, we had to develop an efficient route(s) to **4**, which would permit introduction of the necessary oxygen functional groups at the 1,4-positions of **3**. We selected **7**, **8** and **9** as our initial targets since we expected these molecules to be suitable precursors for **4**.



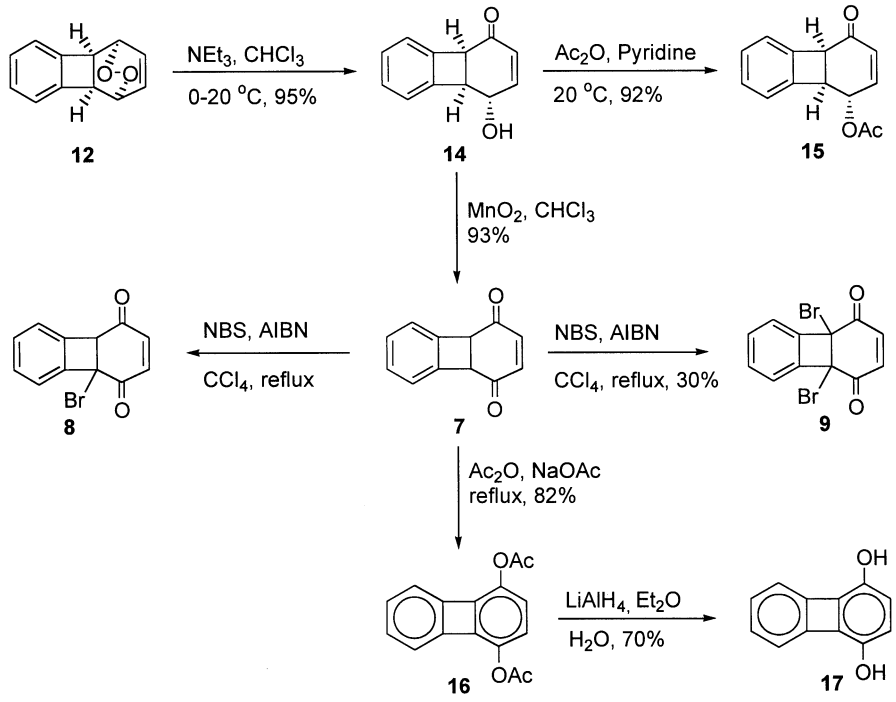
To this end, **3** was submitted to Birch reduction,[18,19] which gives 4a,8b-dihydrobiphenylene (**10**) converting to its valence isomer benzocyclooctatetraene when heated,[20] and tetrahydrobiphenylene **11**. Tetraphenylporphyrin-sensitized photooxygenation of the 1,3-diene unit of **10** in tetrahydrofuran at −40°C resulted in the formation of bicyclic endoperoxide **12** (Scheme 1). Chromatography on silica gel with hexane gave tetrahydrobiphenylene **11** and unreacted starting material **3**, respectively, then eluting with chloroform–hexane yielded endoperoxide **12** in 70% yield (based on the reacted **3**).

The 200 MHz ^{1}H NMR spectrum of **11** displayed an unsymmetrical aromatic region (7.38–7.00 ppm), a vinyl absorption of two separate multiplets (centered at 6.15 and 5.90 ppm), the cyclobutane protons as two separate multiplets (centered at 3.96 and 3.86 ppm) and a fairly complex aliphatic region (2.15–1.61 ppm). The ^{13}C NMR spectrum of **11** gave the expected eight sp^2 and four sp^3 carbon signals, good agreement with the structure. The structural assignment of bicyclic endoperoxide **12** follows predominantly from its 200 MHz ^{1}H NMR and 50 MHz ^{13}C NMR spectra. Aromatic protons resonate, as required by the molecular symmetry, as an AA′BB′ system at 7.32 and 7.09 ppm where the other protons (bridgehead at 5.06 ppm and double bond 6.21 ppm) also give rise to an AA′XX′ system in which the high-field part is further coupled to neighboring cyclobutane 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. After successful isolation of endoperoxide **12**, we turned our attention to determination of the exact configuration of **12**. The peroxide linkage is highly susceptible to cleavage by several reagents. One of the common reactions of the unsaturated bicyclic endoperoxide is the cleavage of the oxygen–oxygen bond followed by addition of the oxygen radicals to the adjacent double bond to give bisepoxide with *syn*-configuration.[21] To corroborate the structure chemically, endoperoxide was treated with cobalt(II) tetraphenylporphyrin (CoTPP) to afford exclusively the desired bisepoxide **13**. The structural assignment of the bisepoxide is secured on the basis of physical behavior. Thus the elemental analysis confirmed the molecular formula $C_{12}H_{10}O_2$. The ^{1}H NMR spectral data were particularly decisive. Thus aromatic protons and epoxide protons form two separate AA′BB′ systems, while the benzocyclobutane protons constitute a singlet at 3.78 ppm. Six signals in ^{13}C NMR spectrum is good agreement with the structure. Assuming that the addition of singlet oxygen to 1,3-diene unit in **10** has occurred from the sterically less hindered face (from the side of protons) of the molecule, then the cyclobutane protons and the adjacent epoxide protons in **13** must have the *trans*-configuration. Inspection of the *Dreiding* models indicates clearly, that the dihedral angle between those protons in the *trans*-configuration of **13** is nearly 90°, thereby accounting for no coupling. The fact, that no measurable coupling between the cyclobutane and the adjacent epoxide protons in **13** has been observed, supports strongly the suggested configuration of **13**. These results confirm that singlet oxygen adds to the diene unit in **10** from the less-hindered side to give **12** with the *anti*-configuration.

The endoperoxide **12** was converted into the corresponding diketone **7** by the known methods described in the

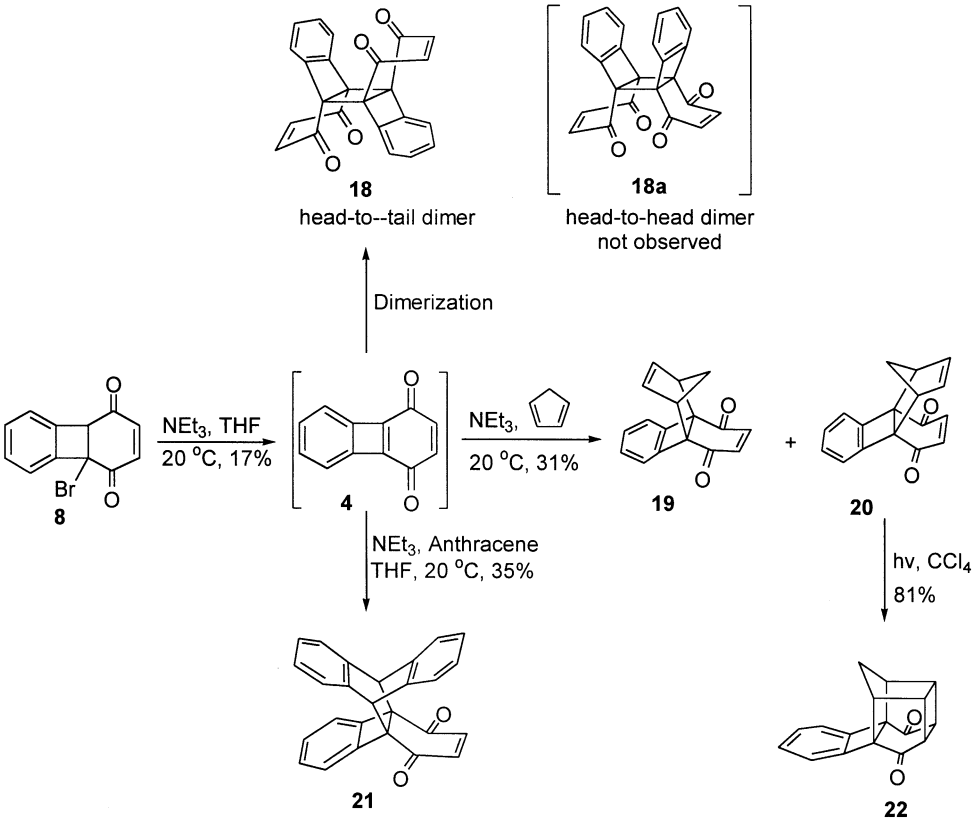


Scheme 1.



Scheme 2.

literature.[22] Base-catalyzed rearrangement of **12** yielded hydroxy ketone **14** (Scheme 2). The IR, ^{1}H and ^{13}C NMR spectral data substantiate the structure assignment. The IR exhibited the characteristic hydroxyl band at 3380 cm^{-1} and enone band at 1650 cm^{-1}. The ^{1}H NMR spectrum displayed an AB system for the olefinic protons as required by the α,β-unsaturated carbonyl derivatives. Aromatic protons comprised a multiplet, and cyclobutane protons gave rise to two separate multiplets. The fact that the ^{13}C NMR spectrum gave nine sp^2 carbon and three sp^3 carbon resonances



Scheme 3.

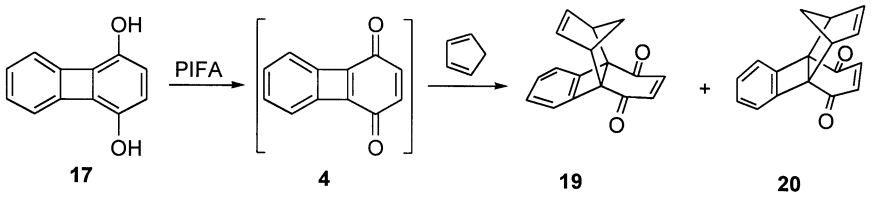
implied an unsymmetrical molecule. Since only the oxygen–oxygen bond breaks in this reaction, it preserves the configuration at all carbon atoms. For further structural proof, **14** was converted to the corresponding acetate **15** which has been fully characterized. In the next step, ketone **7** was readily obtained by oxidation of **14** with MnO_2[23] in chloroform at room temperature, which was characterized by spectroscopic methods. The ^1H and ^{13}C NMR spectra of **7** were highly symmetrical according to the symmetry in the molecule.

An attempt was then made to introduce a second double bond into the six-membered ring in **7**. Unfortunately, after the oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ),[24] the starting material **7** was recovered. In assessing potential routes to **4**, we chose to prepare monobromide **8** since the presence of the bromine atom at α-position of carbonyl group in this molecule should permit introduction of the missing double bond at 4a,8b-positon via elimination. The diketone **7** was therefore subjected to radical bromination with *N*-bromosuccinimide (NBS). All attempts to purify **8** completely by chromatography on silica gel failed since it underwent dehydrobromination during the column chromatography leading to polymeric material. Structural assignment of **8** was made on the basis of spectroscopic data. The ^1H NMR spectrum displays unsymmetrical region for aromatic protons. Olefinic protons resonate as an AB system and the cyclobutane proton gives rise to singlet. The high-resolution mass spectrum of **8** confirmed the molecular formula ($C_{12}H_7O_2Br$). For our approach to **4**, we treated **8** with triethylamine at room temperature and obtained the dimer **18** in 17% yield instead of **4** (Scheme 3). The structure of the dimer **18** follows from its analytic and spectroscopic properties. Thus, a satisfactory high-resolution mass measurement confirmed molecular formula $C_{24}H_{12}O_4$ (calcd=364.07355, found=364.07317). The ^{13}C NMR spectrum shows six carbons atoms as a consequence of the plane of symmetry present in **18**. To our surprise all spectroscopic data revealed the formation of only one isomer. Furthermore the spectral data and NOE experiments did not allow us to determine the correct configuration of **18**. However, AM1 calculations[25] indicate that the head-to-tail isomer **18** has 4.6 kcal mol^{-1} lower heat of formation (105.8 kcal mol^{-1}) than the head-to-head dimer **18a** (110.4 kcal mol^{-1}). We therefore conclude that 1,4-biphenylenequinone (**4**) is formed and trapped as the dimer **18** in this reaction. We assume that dimer **18** is formed from [2+2] cycloaddition of **4** to **4**. In terms of orbital symmetry considerations, thermal [2+2] cycloaddition is a 'forbidden' reaction, since the predicted suprafacial mode of four-membered ring formation is impossible, due to geometric constraint imposed by the four-membered ring. Dewar has suggested that the forbidden reaction still takes place in a concerted fashion, rather than via diradical intermediate in some cases.[26]

It may of course be argued whether **4** can be detected by spectroscopic methods at low temperatures. In order to monitor the formation of **4**, dehydrobromination experiments of **8** with NEt_3 were carried out in THF-d_8 at −70°C and at different concentrations in the cavity of an NMR instrument. In all cases we observed only signals belonging to dimer **18**, together with polymeric materials.

In order to trap **4** with other dienes, the elimination reaction was carried out in the presence of trapping agents such as cyclopentadiene and anthracene. Dehydrobromination in the presence of cyclopentadiene gave the two compounds **19** and **20** in a ratio of 3:2, which could not be separated chromatographically. Thus, exposure of this isomeric mixture to sunlight or projector lamp in carbon tetrachloride converted the isomer **20** to the cage molecule **22** where the other isomer **19** remained unchanged. The resulting mixture was easily separated by silica gel column to give **19** and **22**. All spectral data including the high-resolution mass spectrum of these compounds support the proposed structures. However, dehydrobromination of **8** in the presence of anthracene as a trapping reagent gave only one isomer **21** as expected. The structural assignment of **21** has been elucidated on the basis of its 200 MHz ^1H and 50 MHz ^{13}C NMR spectra. The ^1H NMR spectrum displays two AA′BB′ systems and one singlet belonging to aromatic protons, and two separate singlet at 6.35 and 5.11 ppm, showing double bond and bridgehead protons, respectively. In particular, the observation of 13 signals ^{13}C NMR spectrum, as required by the symmetry in the molecule, is good agreement with the structure.

For our next approach to **4**, we examined whether dibromide **9** and hydroquinone **17** could serve as potential precursors for the target molecule **4**. The diketone **7** was submitted to NBS bromination for seven days, which provided dibromide **9** in a yield of 30% (Scheme 2). The dibromide **9** was purified by means of column chromatography on silica gel, and the structure is assigned on the basis of spectroscopic evidence. That ^1H NMR spectrum shows an AA′BB′ system in aromatic region and, a singlet at 6.87 ppm, and five sp^2 and one sp^3 carbon signals in the ^{13}C NMR spectrum confirm the structure. Then, we submitted it to debromination with zinc in refluxing dimethylformamide (DMF) in the presence of anthracene with the expectation to trap 1,4-biphenylenequinone (**4**) to give **21**. Indeed, after usual work-up and chromatography on silica gel, we obtained the expected trapping product **21** and hydroquinone **17** as side product, which is formed from **9** via reductive elimination under the conditions. The structural assignment of **17** was supported by spectral data. In the 200 MHz ^1H NMR spectrum, aromatic protons clearly experience shielding as do the analogous protons of biphenylene (**3**).[27] This implies that in **17** there is appreciable paramagnetic contribution from the four-membered ring. The ^{13}C NMR spectrum also confirmed the structure **17**. As an alternative approach to **4**, we were naturally intrigued by the possibility of oxidation of **17**, having a close structural relationship to the target molecule **4**. Thus we tried to develop an efficient route(s) to **17** starting from the diketone **7**. Base-catalyzed isomerization of **7** with triethylamine and potassium *tert*-butoxide or heating at high temperature (170°C) caused low yield of **17**. However, treatment of **7** in boiling acetic anhydride in the presence of sodium acetate gave cleanly acetate derivative **16** in high yield (Scheme 2). In the ^1H NMR spectrum of the acetate **16**, the four-membered ring sustains a paramagnetic ring current, which results in highfield shifts of the benzene protons. We submitted **16** to $LiAlH_4$ reduction in diethyl ether to provide the hydroquinone **17** in high yield, which is a stable compound and does not show tendency to tautomerization. Treatment of **17** with



Scheme 4.

bis(trifluoroacetoxy)iodobenzene (PIFA)[28] in the presence of cyclopentadiene gave the cycloadducts **19** and **20** (Scheme 4).

We therefore conclude that 1,4-biphenylenequinone (**4**) is formed and trapped as the [4+2] cycloadducts. When the trapping reagent cyclopentadiene was omitted from the reaction, the majority of products are polymeric material with a small quantity of the dimer **18**.

The experiments summarized above clearly demonstrate that 1,4-biphenylenequinone (**4**) is easily formed and undergoes dimerization and other intramoleculer reactions with extraordinary ease. On the other hand, it can be noticed **4** is not as stable as biphenylene; the quinone unit cannot stabilize the cyclobutadiene unit as well as a benzene ring.

This was also confirmed by our recent calculations.[15] Schleyer et al.[29] have proposed the use of absolute magnetic shielding, computed at *ring centers* with available quantum mechanical programs as a new aromaticity/antiaromaticity criterion. Nucleus-independent chemical shifts (NICS) values, which are the negative of the absolute magnetic shielding constants calculated at the ring centers have proven to be simple and efficient probes of aromaticity. Negative NICS values denote aromaticity (benzene, −11.5, naphthalene, −11.4) and positive NICS values antiaromaticity (cyclobutadiene, 28.8) (Table 1).

NICS values of the compounds **4** and **5** indicate strong antiaromatic character for cyclobutadiene units. However, **6** shows negative NICS values where the quinonoid system reduces the antiaromaticity significantly by forcing this system to possess a dimethylene structure (Table 1). These calculations are well in agreement with our experimental results.

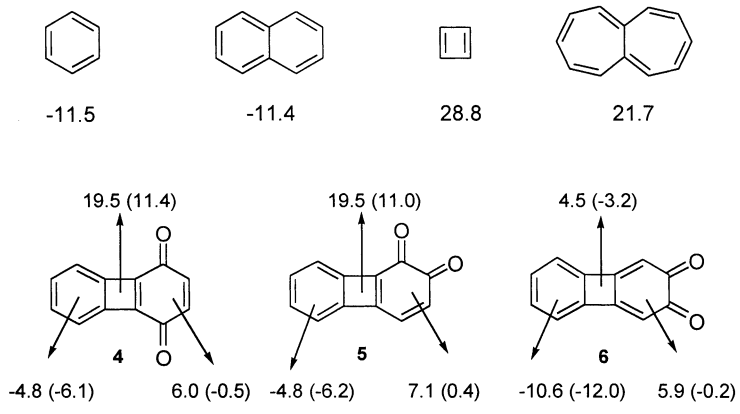
3. Experimental

3.1. General

Biphenylene was synthesized according to the literature.[30] Reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Solvents were concentrated at reduced pressure (ca. 20°C, 20 Torr). Infrared spectra were obtained on KBr pellets by employing a Matson apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a 200 (50) MHz spectrometer. All column and Thin Layer chromatography were performed on silica gel.

3.1.1. 4a,8b-Dihydrobiphenylene (10). A solution of biphenylene (5.0 g, 32.5 mmol) in 100 mL THF were placed in 250 mL three-necked round-bottomed flask equipped with a magnetic stirbar and nitrogen inlet. The flask was cooled to −70°C and freshly cut potassium (5 g, 0.13 mol) was added slowly under nitrogen. After addition was completed the temperature was raised slowly to −10°C. The resulting mixture was stirred for 6 h at −10°C until red-brown color appeared. Then, the reaction mixture was cooled to −70°C and hydrolyzed carefully with 15 mL of cold H_2O–THF (1:1). The yellow colored solution was filtered quickly through 15 g silica gel to remove inorganic salts. Silica gel was washed with 50 mL of cold THF (−40°C) and ca. 150 mL solution of 4a,8b-dihydrobiphenylene was kept at −40°C for the next reaction.

Table 1. GIAO-SCF calculated NICS values at the ring center.[15] Values in parentheses give the NICS values at 1 Å above the ring



3.1.2. 11,12-Dioxatetracyclo[8.2.2.0^{2,9}.0^{3,8}]tetradeca-3,5,7,13-tetraene (12). A 150 mL solution of 4a,8b-dihydrobiphenylene (**10**) prepared according to the above procedure, was placed into a 250 mL three-necked round-bottomed flask equipped with a thermometer, cooling bath and magnetic stirbar. Singlet oxygen, photochemically generated by means of a tungsten 150 W lamp using TPP as a sensitizer, was passed through the solution for 8 h at −40°C while the progress of the reaction was monitored by 200 MHz ^{1}H NMR spectrometer. The solution mixture was allowed to come to room temperature and extracted with diethyl ether (3×50 mL). The etheral layer was washed with cold, saturated NH_4Cl and water, then dried over $MgSO_4$. After removal of the solvent, the mixture (5.2 g) was chromatographed over silica gel (120 g) column by elution with hexane to afford 20 mg of pure **11**, and 1.5 g of a mixture consisting of unreacted biphenylene (**3**) and **11** in a ratio of 93:7 (determined by 200 MHz ^{1}H NMR spectroscopy) and TPP. Further elution with chloroform–hexane (1:3) gave 3.0 g (16.1 mmol) of endoperoxide **12** in 70% yield (relative to converted material, conversion. ca. 70%). Recrystallization from hexane–carbon tetrachloride afforded colorless crystals: mp 106–108°C: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00–7.26 (AA′BB′ system, aromatic protons, 4H), 6.20–6.23 (quasi triplet, A-part of AA′BB′XX′ system, olefinic protons, 2H), 5.03–5.09 (m, B-part of AA′BB′XX′ system, bridgehead protons 2H), 3.98–4.00 (m, X-part of AA′BB′XX′ system, cyclobutane protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.13, 128.76, 128.40, 122.96, 75.16, 39.56; IR (KBr, cm^{-1}) 3070, 2960, 1457, 1374, 1200, 910, 890. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.23; H, 5.24. **For 11**. Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.00–7.28 (m, aromatic protons, 4H), 6.17 (ddd, *J*=13.0, 5.4, 2.0 Hz, olefinic proton, 1H),) 5.84–5.93(m, olefinic proton, 1H), 3.98 (bt, *J*=5.0 Hz, cyclobutane proton, 1H), 3.86 (m, cyclobutane proton, 1H), 1.55–2.15 (m, aliphatic protons, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ147.90, 147.77, 129.85, 128.72, 128.07, 127.16, 122.55, 121.64, 42.45, 41.92, 26.05, 21.83; IR (CCl_4, cm^{-1}) 2978, 2922, 2898, 2856, 1446, 1246.

3.1.3. *syn*-1a,1b,2a,2b,6b,6c-Hexahydrooxireno[2′,3′:3,4]biphenyleno[1,2-*b*]oxirene (13). To a stirred solution of **12** (100 mg, 0.54 mmol) in 10 mL of dry chloroform was added a solution of CoTPP (7 mg, 0.01 mmol) in 2 mL of chloroform. The resulting mixture was stirred at room temperature for 30 min while the reaction progress was monitored by TLC and peroxide test (KI/AcOH). Evaporation of the solvent gave a crystalline residue, which was chromatographed over silica gel (25 g), eluting with chloroform–hexane (1:10). As the first eluate TPP was collected. As the second fraction **13** (90 mg, 0.48 mmol, 90%) was isolated. Recrystallization from hexane gave colorless crystals: mp 179–180°C: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.97–7.13 (AA′BB′ system, aromatic protons, 4H), 3.78 (s, cyclobutane protons, 2H), 3.12–3.26 (AA′BB′ system, epoxide protons, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.01, 130.09, 124.62, 51.66, 50.29 41.79; IR (KBr, cm^{-1}) 3010, 2980, 1450, 1415, 1290, 1270, 940, 850. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.31; H, 5.27.

3.1.4. 4-Hydroxy-4a,8b-dihydrobiphenylen-1(4*H*)-one (14). A solution of triethylamine (270 mg, 2.68 mmol) in 25 mL chloroform was added dropwise over 15 min to a stirred solution of **12** (1.0 g, 5.37 mmol) in 50 mL chloroform at 0°C. The solution was stirred at 0°C for 1 h, allowed to warm to room temperature and stirred further for 7 h. After evaporation of the solvent, hydroxyketone **14** was recrystallized from carbon tetrachloride to give colorless crystals: 0.98 g (5.26 mmol; 95%), mp 127–128°C: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31–7.13 (m, aromatic protons, 4H), 6.81 (ddd, *J*=10.2, 5.2, 1,4 Hz, A-part of AB system, olefinic proton, 1H), 6.00 (d, *J*=10.2 Hz, B-part of AB system, olefinic proton, 1H), 4.70 (bd, *J*=5.4 Hz, allylic proton, 1H), 4.32 (bd, *J*=4.8 Hz, cyclobutane proton, 1H), 4.19 (bd, *J*=4.4 Hz, cyclobutane proton, 1H), 3.25 (bs, hydroxyl proton, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.07, 145.66, 145.57, 143.37, 129.62, 128.99, 128.91, 123.39, 122.77, 65.21, 51.66, 49.08; IR (KBr, cm^{-1}) 3380, 3050, 1650, 1025. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.69; H, 5.38.

3.1.5. 4-Oxo-1,4,4a,8b-tetrahydrobiphenylen-1-yl acetate (15). To a stirred solution of **14** (100 mg, 0.53 mmol) in 5 mL pyridine was added 100 mg (0.8 mmol) of acetic anhydride at room temperature. The resulting mixture was stirred for 2 h while the reaction progress was monitored by TLC. After completion of the reaction, the mixture was poured into cold, saturated $NaHCO_3$ solution and extracted with diethyl ether (2×25 mL). The etheral layer was washed with 25 mL of cold 0.1N HCl and water, then dried over $MgSO_4$. Removal of the solvent under reduced presure gave 110 mg of **15** (0.48 mmol; 92%). Mp 104–105°C from hexane; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29–7.15 (m, aromatic protons, 4H), 6.71 (ddd, *J*=10.2, 5.2, 1.4 Hz, A-part of AB system, olefinic proton, 1H), 6.09 (d, *J*=10.2 Hz, B-part of AB system, olefinis proton, 1H), 5.72 (dm, *J*=5.4 Hz, allylic proton, 1H), 4.33 (bd, *J*=4.4 Hz, cyclobutane proton, 1H), 4.11 (bd, *J*=4.4 Hz, cyclobutane proton, 1H), 2.12 (s, acetate protons, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.30, 172.17, 146.21, 144.84, 142.65, 133.14, 130.78, 130.61, 124.81, 124.57, 68.55, 52.89, 47.74, 22.97; IR (KBr, cm^{-1}) 3060, 1750, 1660, 1360, 1240, 1020. Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.54; H, 5.19.

3.1.6. 4a,8b-Dihydrobiphenylene-1,4-dione (7). A suspension of hydroxyketone **14** (1.0 g, 5.37 mmol) and MnO_2 (4.62 g, 53.7 mmol) in 50 mL chloroform was stirred overnight at room temperature. After filtration and evaporation of the solvent, the residue was recrystallized from ethanol to give **7** (0.92 g, 5 mmol; 93%); yellow crystals, mp 87–89°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26–7.29 (AA′BB′ system, aromatic protons, 4H), 6.66 (s, olefinic protons, 2H), 4.57 (s, cyclobutane protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.92, 142.82, 140.64, 129.66, 123.40, 52.04; IR (KBr, cm^{-1}) 3050, 2920, 1680, 1590, 1450, 1385, 1130. Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.01; H, 4.46.

3.1.7. 4a-Bromo-4a,8b-dihydrobiphenylene-1,4-dione (8). To a solution of diketone **7** (1.0 g, 5.43 mmol) and *N*-bromosuccinimide (NBS) (1.5 g, 10.86 mmol) in 75 mL carbon tetrachloride was added a small amount of 2-2′-azabisisobutyronitril (AIBN) and the mixture was heated under reflux for two days. Filtration and evaporation of

the solvent gave 1.5 g of brown-coloured oil, which was used directly for further reactions. ^{1}H NMR analysis of the reaction mixture indicated the presence of **8** and **9** in a ratio of 95:5. Attempted purification on any column material was unsuccessful due to the instability of **8**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20–7.45 (m, aromatic protons, 4H), 6.70–6.82 (AB system, J=10.5 Hz, olefinic protons, 2H), 4.79 (s, cyclobutane proton, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.77, 190.49, 143.25, 142.82, 140.66, 140.56, 139.04, 132.60, 131.12, 123.74, 64.74, 55.01. MS m/z (M^+) 262/261 (70%), M−Br 182 (100%), 155 (42), 127 (49), 101 (19).

3.1.8. 4a,8b-Dibromo-4a,8b-dihydrobiphenylene-1,4-dione (9). To a solution of diketone **7** (0.5 g, 2.71 mmol) and *N*-bromosuccinimide (1.92 g, 10.84 mmol) in 75 mL carbon tetrachloride was added a small amount of 2-2′azabisisobutyronitril (AIBN) and the mixture was heated under reflux for seven days. Filtration and evaporation of the solvent gave brown-colored oil, which was chromatographed over silica gel (75 g). Elution with EtOAc–hexane (1:4) gave dibromide **9** (0.27 g, 0.78 mmol; 30%); mp 133–134°C from ethanol; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40–7.54 (AA′BB′ system, aromatic protons, 4H), 6.87 (s, olefinic protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.92, 141.59, 139.14, 144.45, 123.92, 67.36; IR (KBr, cm^{-1}) 3040, 1680, 1330, 1260, 1080. Anal. Calcd for $C_{12}H_6O_2Br_2$: C, 42.15; H, 1.77. Found: C, 41.89; H, 1.67.

3.1.9. 1,4-Biphenylenequinone (4) and synthesis of dimer 18. A solution of 1.0 g crude monobromide **8** in 150 mL THF was placed into a 250 mL flask equipped with nitrogen inlet, and magnetic stirbar. Ten milliliters of a mixture of THF–NEt_3 (95:5) was added dropwise over a period of 15 min at room temperature and stirred additionally for 10 min. After addition of water the mixture was extracted with 50 mL of ethyl acetate and washed with excess of water. The solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was chromatographed on TLC plates, elution with chloroform–hexane (4:1) gave the dimer **18** (130 mg, 0.35 mmol; 17%) as yellow solid. Decomposition at 250°C without melting; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32–7.45 (AA′BB′ system, aromatic protons, 4H), 6.41 (s, olefinic protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.67, 143.69, 142.64, 132.98, 126.56, 64.06; IR (KBr, cm^{-1}) 3020, 2940, 1690, 1670, 1445, 1260, 1050; HRMS m/z (M^+) calcd for $C_{24}H_{12}O_4$; 364.0736, obsd 364.0732.

3.1.10. Trapping of 1,4-biphenylenequinone with anthracene. Formation of 21. Crude monobromide **8** (0.75 g, 2.85 mmol) and anthracene (0.75 g, 4.2 mmol) were dissolved in 50 mL THF and placed into a 100 mL flask equipped with nitrogen inlet and magnetic stirbarr. To the resulting mixture was added 10 mL of a mixture of THF–NEt_3 (95:5) dropwise over a period of 15 min at room temperature and stirred additionally for 10 min. After addition of water the mixture was extracted with (2×25 mL) ethyl acetate and washed with excess of water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel (75 g) chromatography. Elution with hexane–ethyl acetate (4:1) gave excess of anthracene as the first fraction. Trapping product **21** was isolated as the second fraction (360 mg; 35%) as pale yellow crystals. mp 257–260°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.91–7.31 (AA′BB′ system, aromatic protons, 12H), 6.35 (s, olefinic protons, 2H), 5.11 (s, bridgehead protons, 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; IR (KBr, cm^{-1}) 3040, 1700, 1470, 1260, 1100; Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47. Found: C, 86.79; H, 4.23.

3.1.11. Trapping of 1,4-biphenylenequinone with cyclopentadiene. Formation of 19 and 20. Crude monobromid **8** (0.75 g, 2.85 mmol) and freshly cracked cyclopentadiene (0.3 g, 4.5 mmol) were disolved in 50 mL THF and placed into a 100 mL flask equipped with nitrogen inlet and magnetic stirbar. To this resulting mixture was added 10 mL of a mixture of THF–NEt_3 (95:5) dropwise over a period of 15 min at room temperature and stirred additionally for 10 min. After addition of water the mixture was extracted with ethyl acetate (2×25) and washed with excess of water. Then, the solution was dried over $MgSO_4$ and evaporated. The ^{1}H NMR analysis of the residue (220 mg; 31%) showed the existence of **19** and **20** in a ratio of 3:2. All attempts to separate these compound failed.

3.1.12. Irradiation of 19 and 20. The mixture consisting of **19** and **20** (150 mg, 0.60 mmol) was dissolved in 75 mL carbon tetrachloroide and exposed to a tungsten lamp (150 W) at room temperature for 4 h while being stirred. After removal of the solvent, the residue was chromatographed on silica gel (50 g), elution with hexane–ethyl acetate (3:1) gave 87 mg unreacted isomer **19** and as the second fraction, the cage compound **22** (50 mg, 81%, based on **20**), respectively.

3.1.13. Pentacyclo[6.4.4.1^{9,12}.0^{1,8}.0^{2,7}]heptadeca-2,4,6,10,14-pentaene-13,16-dione (19). Mp 126–127°C, yellow crystals from methanol; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.04–7.26 (AA′BB′ system, aromatic protons, 4H), 6.72 (s, olefinic protons, 2H), 5.88–5.90 (m, olefinic protons, 2H), 3.43–3.47 (m, bridgehead protons, 2H), 1.71–2.02 (m, methylene protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.72, 146.57, 141.35, 135.00, 128.94, 123.30, 64.54, 53.75, 47.60; IR (KBr, cm^{-1}) 3010, 2980, 1700, 1470, 1250, 1100; HRMS m/z (M^+) calcd for $C_{17}H_{12}O_2$ 248.0836, obsd 248.0837.

3.1.14. Heptacyclo[9.6.0.0^{1,5}.0^{3,9}.0^{4,8}.0^{7,11}.0^{12,17}]heptadeca-12,14,16-triene-2,10-dione (22). Mp 187–188°C, colorless crystals from methanol; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24–7.42 (AA′BB′ system, aromatic protons, 4H), 3.21–3.30 (m, aliphatic protons, 2H), 2.92–3.01 (m, aliphatic protons, 4H), 1.81–2.00 (AB system, methylene protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 211.43, 140.72, 131.64, 126.34, 76.97, 45.86, 45.78, 40.52, 39.53; IR (KBr, cm^{-1}) 3020, 2980, 1750, 1730, 1480, 1250, 1080; Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 81.87; H, 4.54.

3.1.15. Debromination of 9 with zinc. A solution of **9** (200 mg, 0.58 mmol), anthracene (120 mg, 0.6 mmol) and zinc (75 mg, 1.15 mmol) in 30 mL DMF was refluxed for

30 min while the reaction progress being monitored by TLC. Then, the mixture was cooled to room temperature and filtered and, then poured into seperatory funnel and washed with excess of water. The mixture was extracted with ethyl acetate (2×20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was purified on TLC plates, elution with ethyl acetate gave 56 mg (26%) **21** and 35 mg (33%) hydroquinone **17**.

3.1.16. 1,4-Acetyloxybiphenylene. To a stirred solution of **7** (1.0 g, 5.43 mmol) in 20 mL acetic anhydride was added NaOAc (1.1 g, 13.5 mmol) at room temperature. The resulting mixture was refluxed for 6 h while the reaction progress was monitored by TLC. The solution was cooled to room temperature and poured into 100 mL saturated cold solution of $NaHCO_3$ and stirred until gas evulation ceased. Then the mixture was extracted with diethyl ether and washed with water. The solution was dired over $MgSO_4$ and the solvent removed under reduced pressure. The residue was loaded on a silica gel (25 g) column, elution with hexane–chloroform (4:1) afforded 1.2 g (82%) of diacetate **16**; mp 125–126°C, yellow crystals from ethanol; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.54–6.80 (AA′BB′ system, aromatic protons, 4H), 6.46 (s, aromatic protons, 2H), 2.28 (s, acetate protons, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.76, 149.18, 140.39, 137.39, 129.19, 124.11, 119.45, 21.37; IR (KBr, cm^{-1}) 3060, 1750, 1465, 1370, 1205, 1015, 750; Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.28; H, 4.54.

3.1.17. Biphenylene-1,4-diol (17). A solution of **16** (0.75 g, 2.79 mmol) in 50 mL dry diethyl ether was put into 100 mL three-necked round-bottomed flask equipped with a magnetic stirbar and nitrogen inlet. The flask was cooled to 0°C and 220 mg (6.11 mmol) of $LiAlH_4$ was added slowly under nitrogen. The resulting mixture was stirred for 30 min and hydrolyzed with 0.5 mL of water. Then, the solution was filtered out and the residue was washed with 20 mL diethyl ether. The etheral layer was dried over $MgSO_4$ and the solvent was removed. The residue was purified on silica gel (20 g) with methanol to afford 0.36 g (1.95 mmol; 72%) hydroquinone **17**; mp 177–178°C, yellow crystals from methanol–chloroform; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.56–6.66 (AA′BB′ system, aromatic protons, 4H), 6.21 (s, aromatic protons, 2H), 4.87 (s, hydroxyl protons, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.5, 142.59 132.88, 128.25, 123.19, 118.08; IR (KBr, cm^{-1}) 3250, 3042, 1604, 1474, 1198; Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.63; H, 4.22.

3.1.18. Oxidation of biphenylene-1,4-diol (17) with bis(trifluoroacetoxy)iodo benzene (PIFA) (19 and 20). To a stirred solution of hydroquinone **17** (150 mg, 0.81 mmol) and cyclopentadiene (80 mg, 1.21 mmol) in 50 mL THF in a 100 mL flask equipped with magnetic stirbar and nitrogen inlet was added PIFA (520 mg, 1.20 mmol) at room temperature. The resulting mixture was stirred for 10 min while the reaction progress was monitored by TLC. The solvent was removed under reduced pressure and the residue was chromatographed on TLC plates, elution with hexane–ethyl acetate (4:2) gave a mixture of 57 mg (0.22 mmol; 28%) of **19** and **20**.

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