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Synthesis and properties of *p*-benzoquinone-fused hexadehydro[18]annulenes

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Abstract—A series of hexadehydro[18]annulenes fused with different numbers of *p*-benzoquinone, **4**-**6**, were synthesized by stepwise transformation of the *p*-dimethoxybenzene moiety of the precursor dehydroannulene **3** fused with three 3,6-dimethoxy-4,5-dimethylbenzene units at 1,2-positions into *p*-benzoquinone using ceric ammonium nitrate. The UV–vis spectra of compounds **4** and **5**, which have both electron-donating *p*-dimethoxybenzene unit(s) and electron-accepting *p*-benzoquinone unit(s) in the π-systems, showed the maximum absorption bands bathochromically shifted in comparison with **3** having only *p*-dimethoxybenzene units and 6 having only *p*-benzoquinone units. However, the solvatochromism expected for **4** and **5** was found to be quite weak possibly because the HOMO and LUMO (B3LYP/6-31G(d)) are not localized but rather delocalized over the whole π-systems.

1. Introduction

There is considerable interest in macrocyclic dehydroannulenes[1] from various viewpoints. For example, the cyclic π-systems containing triple bonds have been shown to be useful precursors for a variety of carbon rich polymeric compounds.[1a,2] Possible application of the macrocycles toward photonic devices has also been studied owing to the unique optical properties of π-conjugated systems.[3,4] In addition, fundamental physical properties such as tropicity of the macrocyclic rings[5] have also been the subject of continued discussion in the dehydroannulene chemistry. In the previous studies, we synthesized a series of dehydroannulenes fused with electron-donating systems such as bicyclo[2.2.2]octene[6] and 1,4-dimethoxynaphthalene (at 2,3-positions),[7] as well as electron-withdrawing system such as tetrafluorobenzene.[8] The electronic effects of these subunits have been shown to significantly affect the properties of the macrocycles as exemplified by the formation of stable complex with Ag(I) ion at the central cavity of tetradehydro[16]annulene when fused with the electron-donating bicyclo[2.2.2]octene systems[6b] and by reduction of the solid-state reactivity of highly strained tetradehydro[12]annulene when fused with electron-withdrawing perfluorobenzene.[8]

As a good π-electron acceptor, *p*-benzoquinone is known to have characteristic electronic properties, and the fusion of such an electron-accepting group to the highly conjugated dehydroannulenes is of interest, since such compounds would constitute a new type of push–pull π-systems when electron-donating moieties are introduced on other site(s) of the macrocyle. In 1993, Youngs and co-workers reported the transformation of *p*-dimethoxybenezene units fused to tridehydro[12]annulene into *p*-benzoquinone using ceric ammonium nitrate (CAN), and they found that only one of three *p*-dimethoxybenezene units in the precursor tridehydro[12]annulene **1** can be transformed into *p*-benzoquinone to give π-conjugated system **2**.[9] However, although the synthesis and NMR, IR, and MS spectral data of **2** were reported, no discussion has been made as to the structural and electronic properties of **2** and/or related compounds. In the present paper, we report the synthesis of hexadehydro[18]annulene fused with 3,6-dimethoxy-4,5-dimethylbenzene units at 1,2-positions **3** and its stepwise transformation into *p*-benzoquinone-fused dehydroannulenes **4**-**6**. Also their electronic properties investigated by means of ^{1}H NMR, electronic spectra, and cyclic voltammetry will be described together with the results of theoretical calculations.

2. Results and discussion

2.1. Synthesis of hexadehydro[18]annulenes 3-6

For the synthesis of dehydroannulene **3** fused with three 3,6-dimethoxy-4,5-dimethylbenzene units at 1,2-positions, which is the precursor of a series of *p*-benzoquinone-fused dehydroannulene **4-6**, the simple copper-mediated coupling

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Keywords: Dehydroannulenes; Benzoquinones; Absorption spectra; Redox potential; DFT calculation.

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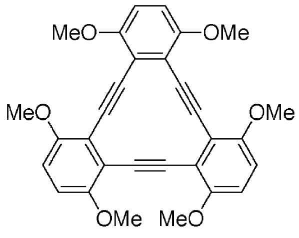

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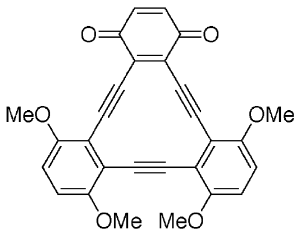

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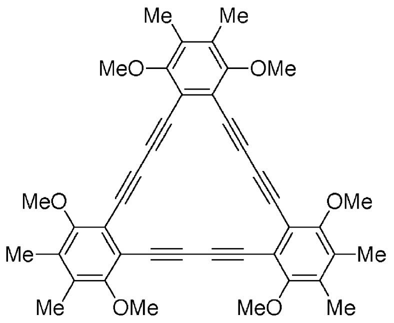

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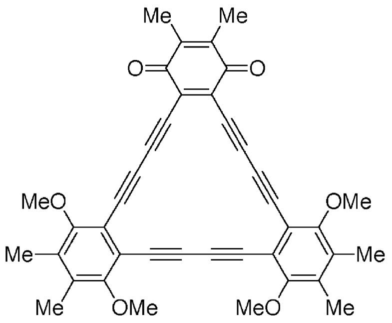

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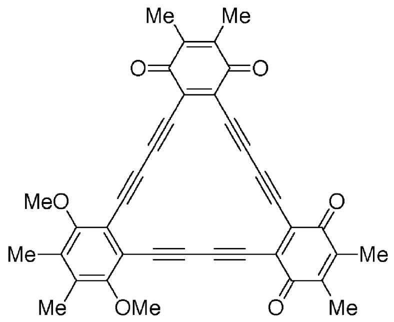

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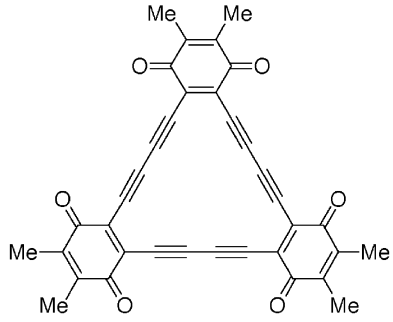

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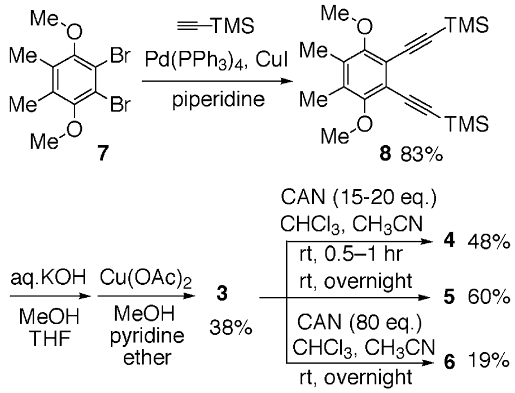
of the corresponding 1,2-diethynylarene was employed. As shown in Scheme 1, the Pd-catalyzed Sonogashira cross-coupling reaction between 1,2-dibromo-3,6-dimethoxy-4,5-dimethylbenzene (**7**)[10] and trimethylsilylacetylene afforded 1,2-bis(trimethylsilylethynyl)-3,6-dimethoxy-4,5-dimethylbenzene (**8**) in 83% yield. After desilylation, the cyclization reaction by the copper-mediated oxidative coupling under Eglinton's condition[11] gave dehydro[18]annulene **3** as yellow solid in 38% yield together with hardly soluble byproducts, which are possibly the higher oligomers.



Scheme 1.

Transformation of the *p*-dimethoxybenzene unit(s) into *p*-benzoquinone unit(s) was conducted by the use of CAN. The reaction was found to proceed stepwise. Thus, when the reaction of **3** was conducted with 15–20 equiv. of CAN in a mixed solvent of $CHCl_3$ and CH_3CN (1:1 by volume) at room temperature for 0.5–1 h, monoquinone **4** was obtained as a main product in 48% yield, while bisquinone **5** was obtained in 60% yield after stirring overnight. For the synthesis of trisquinone **6**, a larger amount, that is, 80 equiv. of CAN was used to complete the reaction by stirring for 24 h at room temperature. For separation of the crude products of annulenes **4-6**, chromatography using either silica gel or alumina was not suitable because of decomposition of the annulenes, and the only applicable method was reprecipitation using chloroform–hexane resulting in rather modest isolated yield (19%) of **6**. All of **4-6** were obtained as red powders.

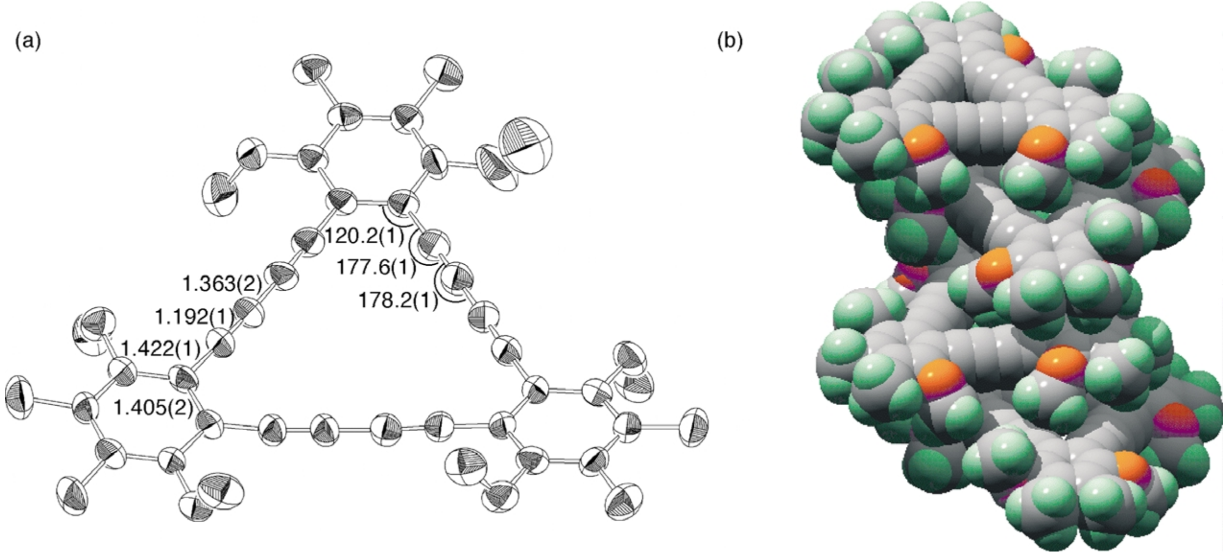


Figure 1. (a) ORTEP drawing (50% probability) showing the X-ray structure of **3** and (b) its crystal packing in a space-filling diagram. The averaged bond lengths (in Å) and angles (in degree) in the [18]annulene core are given with esd's calculated by the following equation; $\sigma(l)=(\sum(1/\sigma_i^2))^{-1/2}$.

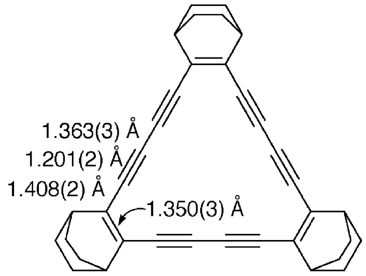


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Figure 2. Structure of **9**. The averaged bond lengths in the [18]annulene core are given with esd's calculated by the following equation; $\sigma(l)=(\sum(1/\sigma_i^2))^{-1/2}$.

2.2. Structures and diatropicity of hexadehydro[18]-annulenes 3-6

Among the newly synthesized four hexadehydro[18]-annulenes **3**-**6**, a single crystal suitable for X-ray structural analysis was obtained only for **3**, and the result is shown in Figure 1. As expected from the structures reported for analogous benzodehydro[18]annulenes,[3] the central 18-membered ring in **3** is essentially planar and the bending of butadiyne moiety is quite small since the averaged angle of C(sp^2)–C(sp^2)–C(sp) (120.2°) is nearly ideal for the formation of the [18]annulene hexagon. In the packing structure (Fig. 1(b)), the nearest intermolecular contact was observed between a hydrogen atom of one of the methoxy groups and an sp carbon (the distance between C(MeO) and C(sp), 3.26 Å) rather than between the sp carbons of the central annulene rings (3.61 Å). Thus, no π stacking structure was observed. Rather, the CH/π interaction between the methoxyl protons and the butadiyne π-system in the central ring is likely to operate in the solid state.

The crystal structure with no π stacking mode of **3** suggests less reactivity and enhanced thermal stability of the hexadehydro[18]annulene π-system in **3** in the solid state. In this respect, for example, unsubstituted hexadehydro[18]annulene turns black at 75 °C and explodes at 85 °C,[12] and the corresponding tribenzo-[13] and tris(tetrafluorobenzo)-[8] derivatives start to decompose at 210 and 193 °C, respectively. A series of other benzodehydro[18]-annulenes with various substituents also undergo exothermic polymerization at the temperature range of 164–240 °C.[3] Among the benzodehydro[18]annulenes so far reported, **3** was found to be most stable against heating: it only turned black at 272 °C. On the other hand, the thermal decomposition took place for **4-6** (**4**; 237 °C, **5**; 220 °C, **6**; 208 °C) at the similar decomposing temperatures observed in the other benzodehydro[18]annulenes.

As concerns the bond-length alternation in the [18]annulene

Table 1. Calculated bond lengths (Å)[a] of the [18]annulene core and NICS(1) values (ppm)[b] for **3**-**6**

Compound	Bond length				NICS(1)		
	C(sp^2)–C(sp^2)	C(sp^2)–C(sp)	C(sp)≡C(sp)	C(sp)–C(sp)	[18]Annulene	Benzene	Quinone
3	1.425	1.414	1.223	1.356	0.43	−11.4	—
4	1.384, 1.426	1.401, 1.411, 1.413	1.223, 1.224, 1.225	1.351, 1.355	−0.1	−11.5	0.5
5	1.387, 1.429	1.398, 1.398, 1.408	1.227, 1.227, 1.226	1.346, 1.348	−1.0	−12.0	0.5
6	1.387	1.398	1.227	1.346	−2.6	—	1.0

[a] B3LYP/6-31G(d).

[b] GIAO/HF/6-31+G(d)//B3LYP/6-31G(d).

core, which is one of the indicators for aromaticity, the averaged length (1.422(1) Å) of C(sp^2)–C(sp) single bonds in **3** is slightly longer than that (1.408(2) Å) in the [18]annulene **9** fused with bicyclo[2.2.2]octene units[6a] (Fig. 2), while the C(sp)≡C(sp) triple bond (1.192(1) Å) in **3** is shorter than that (1.201(2) Å) in **9**. Thus, the bond alternation in **3** is larger than that in **9** and, hence, the aromaticity of **3** is considered to be lower than that of **9**. The presence of diamagnetic ring current in **9** has already been proven based on an upfield shift of the bridgehead protons of the bicyclic framework (δ 3.41) in comparison with that (δ 2.72) of 2,3-diethynylbicyclo[2.2.2]octene.[6a] Apparently, the local ring current in the fused benzene rings of **3** reduces the aromaticity of the central 18-membered ring.

From the same reason, the bond alternation in the [18]annulene core of benzoquinone-fused systems **4-6** is expected to become smaller with the increase in the number of the quinone unit because the aromatic character of the [18]annulene should be enhanced when the dimethoxybenzene units are transformed into non-aromatic benzoquinone units. This supposition is supported by the comparison of the optimized structures for **3-6** at the B3LYP/6-31G(d) level. As shown in Table 1, the C(sp)≡C(sp) triple bond becomes very slightly longer and C(sp^2)–C(sp) and C(sp)–C(sp) single bonds become shorter as the number of the fused-quinone ring increases. The aromaticity for the quinone-fused [18]annulene core is also experimentally supported by the gradual downfield shift of the ^{1}H NMR signals for methoxy and methyl groups in **3**, **4**, **5**, and **6** as shown in Figure 3, reflecting the increasing diamagnetic ring current in this order. In accord with this, the NICS values[14] (HF/6-31+G(d)//B3LYP/6-31G(d)) calculated for a dummy atom at 1 Å above the center of the ring (NICS(1)) in the central core of the [18]annulenes indicate that the diamagnetic ring current become larger, albeit in a minute degree, with increasing number of the quinone units in **4-6**, as shown in Table 1.

The successful transformation of all the three *p*-dimethoxybenzene units in **3** into *p*-benzoquinone units in **6**, albeit in a rather modest yield, may be attributed to the enhanced aromaticity in the dehydro[18]annulene system. This result is in contrast to the case of dehydro[12]annulene **1**, in which only one *p*-dimethoxybenzene unit could be transformed into *p*-benzoquinone[9] possibly due to the antiaromaticity resulting in the dehydro[12]annulene system fused with larger numbers of *p*-benzoquinone units.

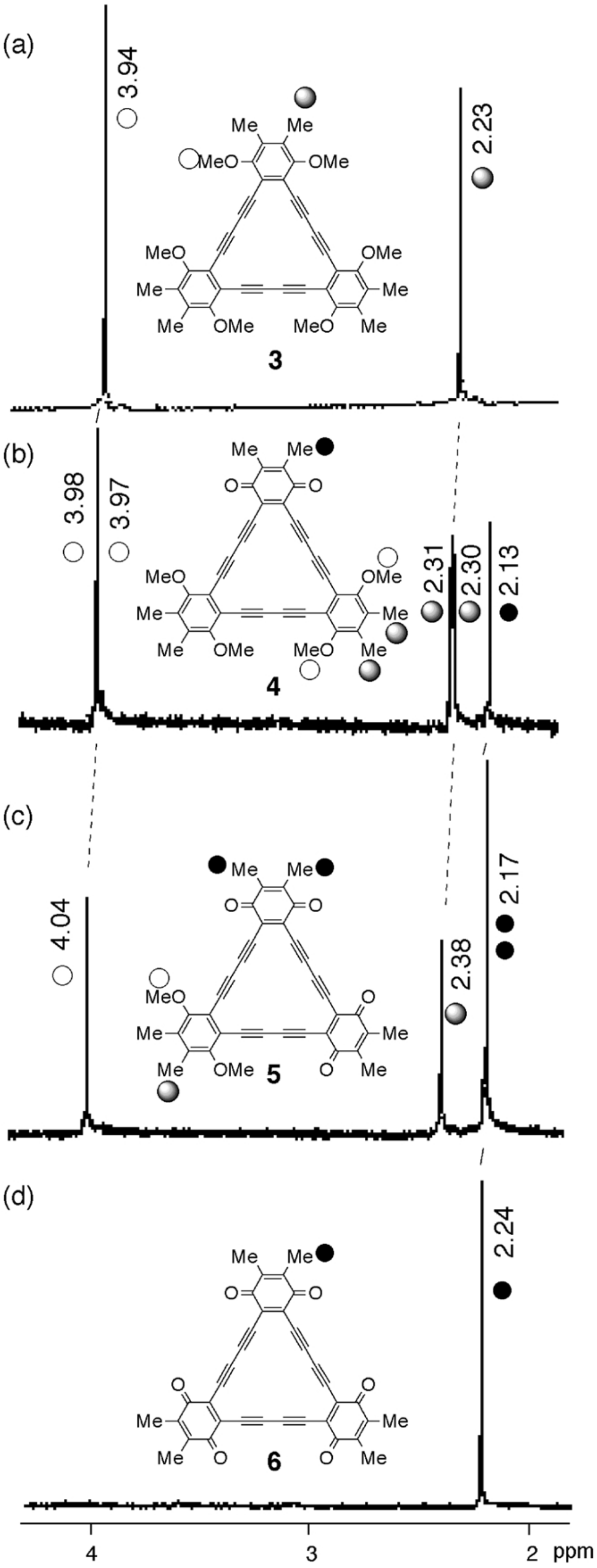

Figure 3. ^{1}H NMR spectra of **3**, **4**, **5**, and **6** in $CDCl_3$.

2.3. Electronic properties of hexadehydro[18]annulenes 3-6

To compare the electronic properties of **3-6**, UV–vis spectral measurements and cyclic voltammetry (CV) were carried out. As shown in Figure 4, the longest-wavelength absorptions of **4** and **5** showed bathochromic shift in comparison with **3** and **6**, suggesting that the HOMO-LUMO gaps of **4** and **5** are reduced due to the presence of both electron-donating *p*-dimethoxybenzene unit(s) and electron-withdrawing *p*-benzoquinone unit(s) in the same π-conjugated system. On the other hand, the cyclic voltammetry of **4-6** in benzonitrile showed multi-step reversible reduction waves at −0.69 and −1.21 V vs Fc/

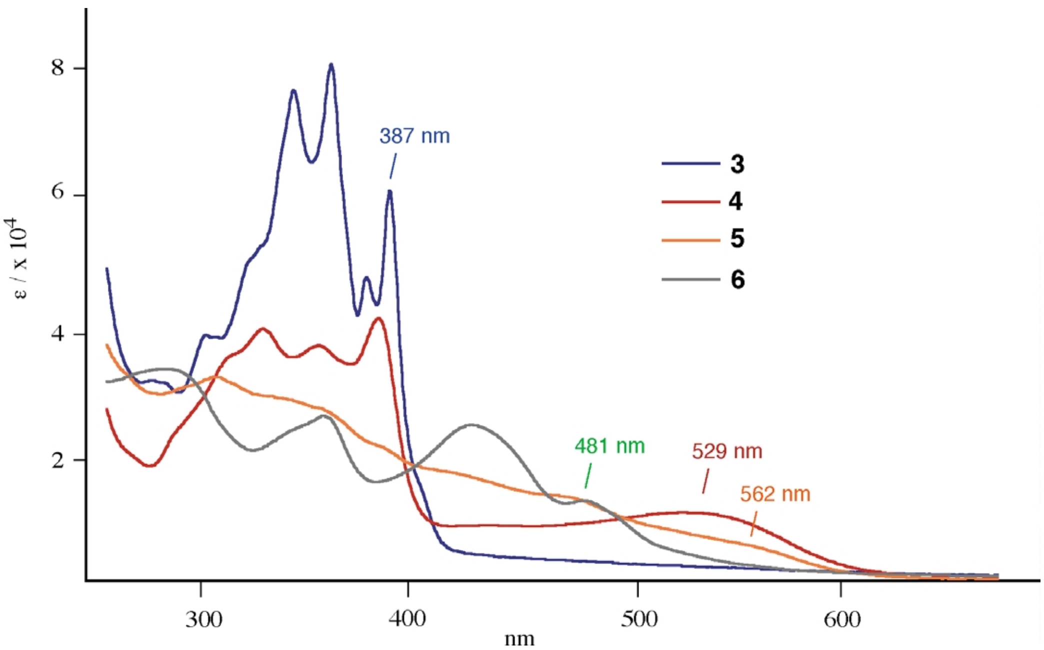

Figure 4. UV–vis spectra of **3**, **4**, **5**, and **6** in $CHCl_3$.

Fc$^+$ for **4**, −0.60, −0.82, and −1.41 V for **5**, and −0.58, −0.75, −0.97, and −1.50 V for **6**. Each wave corresponded to the transfer of one electron and no further reduction wave was observed for these compounds in the potential range lower than −2.0 V. In contrast, no redox wave was observed in a range from +1.2 to −2.2 V for **3**. Thus, the LUMO levels of **4**-**6** are shown to be significantly lowered as compared with **3** due to the presence of *p*-benzoquinone unit(s). The negative charge generated upon one-electron reduction is considered not to localize on the *p*-benzoquinone moiety but to delocalize over the whole π-system since the one-electron reduction was found to take place stepwise reflecting the effective electronic interaction between the multiple *p*-benzoquinone units in **5** and **6**. Thus, no more than three electrons are accommodated in **5** and no more than four electrons in **6** under the present experimental conditions.

These experimental observations are in qualitative agreement with the results of DFT calculations (B3LYP/6-31G(d)). As shown in Table 2, the calculated HOMO-LUMO gaps for **4** and **5** are smaller than those of **3** and **6**, causing the bathochromic shifts in **4** and **5** in comparison with **3** and **6**. Also the calculated LUMO level is lowered as the number of quinone unit increases, which is consistent with the gradual lowering of the first reduction potential with increasing number of the quinone unit.

Table 2. The longest-wavelength UV–vis absorptions, first reduction potentials, and Kohn-Sham (KS) HOMO and LUMO levels of **3-6** calculated at B3LYP/6-31G(d)

Compound	λ_{max}[a] (nm)	$E_{1/2}$[b] (V)	HOMO (eV)	LUMO (eV)	Δ[c] (eV)
3	387	—[d]	−5.31	−1.90	3.41
4	529	−0.69	−5.53	−3.31	2.22
5	562	−0.60	−5.82	−3.68	2.14
6	481	−0.58	−6.41	−3.93	2.48

[a] Measured in $CHCl_3$.
[b] Measured in benzonitrile. Electrolyte; 0.1 M TBAP. V vs Fc/Fc$^+$.
[c] $\Delta = E_{LUMO} - E_{HOMO}$.
[d] No redox wave was observed at the range from +1.2 to −2.2 V.

In many π-conjugated systems containing both donor- and acceptor-substituents, the intramolecular charge-transfer (CT) interaction, which is recognized as an important factor for second-order nonlinear optical properties,[15] has been observed, and such interaction has been proven by observation of the solvatochromism. In the case of **4** and **5**, however, only a small extent of solvatochromism was

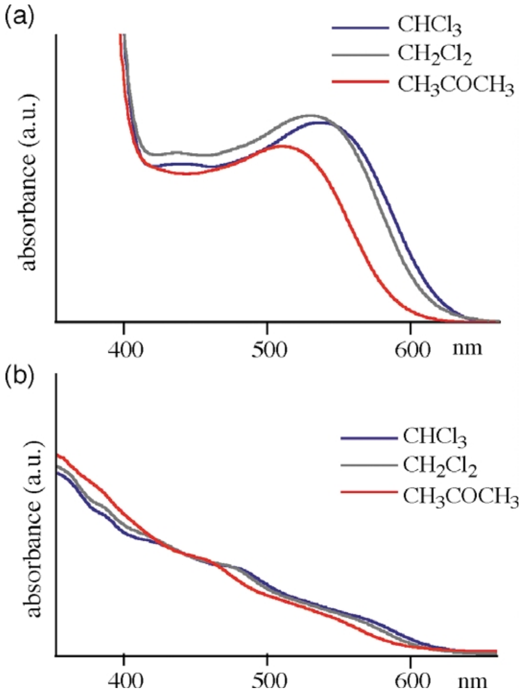

Figure 5. Solvent effects upon the longest-wavelength absorptions of (a) **4** and (b) **5**.

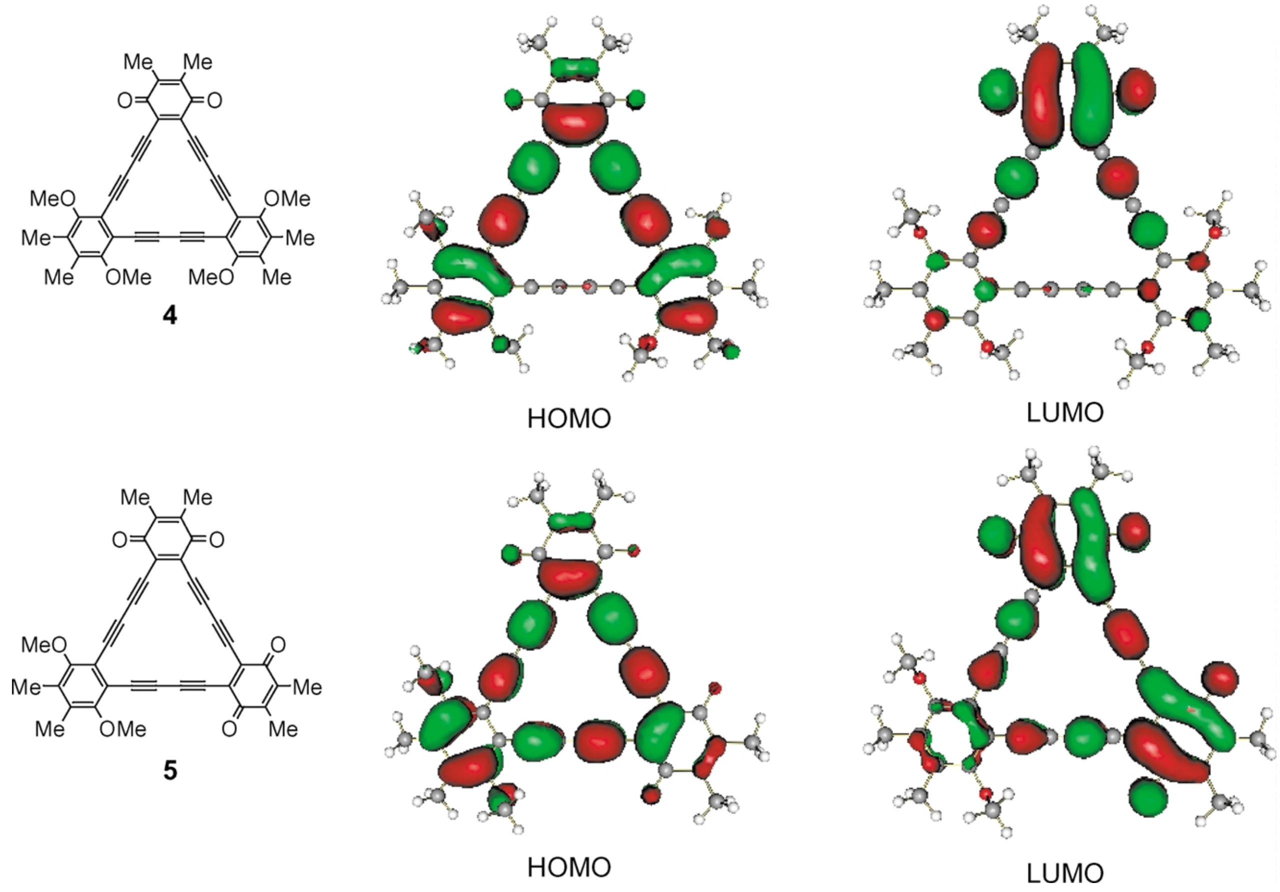

Figure 6. KS HOMOs and LUMOs of **4** and **5** calculated at the B3LYP/6-31G(d) level.

observed, although the examined solvents were quite limited due to the solubility problem (Fig. 5). This result may be rationalized as follows. According to ZINDO calculations, the longest absorption for **4** and **5** can be assigned to the HOMO→LUMO transition (**4**; 531 nm (coefficient 0.66, oscillator strength 0.254), **5**; 562 nm (coefficient 0.61, oscillator strength 0.089)). The HOMO and LUMO are not localized only on the electron donating or accepting moieties, that is, *p*-dimethoxybenzene or *p*-benzoquinone units, but rather delocalized extensively over the whole π-system as shown in Figure 6. Therefore, there would result only a small change in charge distribution, or polarity, upon the HOMO→LUMO transition in the dehydro[18]annulene molecules of **4** and **5**, and hence the extent of solvatochromic shifts becomes small.

3. Conclusion

A series of hexadehydro[18]annulenes **4-6** fused with one, two, and three *p*-benzoquinone unit(s) were synthesized by the stepwise oxidation of *p*-dimethoxybenzene units of tris(3,6-dimethoxy-1,2-benzo)-dehydro[18]annulene **3**. In these annulenes, the diatropicity of the central 18-membered ring was shown to gradually increase with the increasing number of *p*-benzoquinone unit(s) due to the enhanced double bond character at the fused position(s). Although **4** and **5** have both the π-electron donating and accepting groups and can be regarded as novel push–pull type π-systems, the extent of intramolecular charge-transfer is very small, due to the delocalization of both HOMO and LUMO over the whole dehydro[18]annulene π-systems.

4. Experimental

4.1. General

Melting points were measured on a Yanaco MP-500D apparatus and are uncorrected. Elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 or a JEOL JNM-GX 400 spectrometer. The chemical shifts of NMR are expressed in ppm from TMS as determined with reference to the internal $CHCl_3$ and $CDCl_3$ (δ 7.26 in ^{1}H and δ 77.0 in ^{13}C NMR). UV–vis spectra were taken on a SHIMADZU UV-2100PC spectrometer. Mass spectra were taken on a JEOL JMS 700 spectrometer for EI method and on a Finigan TSQ7000 for APCI method. Preparative gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns.

Ether and THF were distilled from sodium benzophenone ketyl. Methanol was distilled from sodium methoxide. Piperidine, pyridine, chloroform, and acetonitrile were distilled over CaH_2. All other solvents and reagents were used as purchased. Theoretical calculations were performed using the Gaussian 98 program.[16]

4.1.1. 1,2-Bis(trimethylsilylethynyl)-3,6-dimethoxy-4,5-dimethylbenzene (8). To a degassed solution of 1,2-dibromo-3,6-dimethoxy-4,5-dimethylbenzene (**7**)[10] (671 mg, 2.07 mmol), $Pd(PPh_3)_4$ (106 mg, 0.092 mmol), and CuI (37 mg, 0.19 mmol) in dry piperidine (70 mL) was added trimethylsilylacetylene (1.0 mL, 0.70 g, 7.1 mmol), and the reaction mixture was stirred at 100 °C for 13 h under an Ar atmosphere in a sealed tube. After the reaction was quenched with water, the mixture was extracted with ether, and the ethereal solution washed with aqueous NaCl, and dried over $MgSO_4$. After the removal of the solvent and the volatile under reduced pressure, the product was purified by chromatography over silica gel (hexane–EtOAc (20:1)) to give **8** (615 mg, 1.72 mmol, 83%) as a colorless solid: mp 112.7–113.0 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 6H), 2.16 (s, 6H), 0.28 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.8, 132.4, 117.7, 102.1, 99.5, 60.4, 12.8, 0.0. Anal. Calcd for $C_{20}H_{30}O_2Si_2$: C, 66.98; H, 8.43%. Found: C, 66.70; H, 8.47%.

4.1.2. tris(3,6-Dimethoxy-4,5-dimethyl-1,2-benzo)hexadehydro[18]annulene (3). A solution of KOH (ca. 0.5 g) in distilled water (2 mL) was added in one portion to a solution of **8** (1.39 g, 3.86 mmol) in a mixed solvent of methanol (40 mL) and THF (9 mL). The reaction mixture was vigorously stirred at room temperature for 15 min, diluted quickly with water (10 mL), extracted with ether, and the ethereal solution dried over $MgSO_4$. The volatiles were removed in vacuo and the crude product was separated by flash chromatography over silica gel eluted with hexane–AcOEt (20:1) to give crude 1,2-diethynyl-3,6-dimethoxy-4,5-dimethylbenzene (0.791 g, 3,69 mmol, 95%) as a colorless solid; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 6H), 3.50 (s, 2H), 2.19 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.2, 133.1, 117.1, 84.4, 78.3, 60.8, 12.9. The crude diyne was used for the next step without further purification.

To a solution of $Cu(OAc)_2$ (1.38 g, 7.59 mmol) in a mixed solvent of pyridine (50 mL), methanol (50 mL), and ether (10 mL) was added a solution of 1,2-diethynyl-3,6-dimethoxy-4,5-dimethylbenzene (434 mg, 2.03 mmol) in a mixed solvent of pyridine (20 mL) and methanol (20 mL) over a period of 2 h. The mixture was stirred at 60 °C for 0.5 h and overnight at room temperature under air. The reaction was quenched by 30% aqueous H_2SO_4, and the aqueous layer was extracted with $CHCl_3$. The combined organic solution was washed with 50% aqueous H_2SO_4 and with aqueous $NaHCO_3$, and dried over $MgSO_4$. The organic solution was evaporated and the crude mixture was separated by preparative GPC to give crude **3** (163 mg, 0.256 mmol, 38%). The crude product was recrystallized from $CHCl_3$ to give single crystals of **3** suitable for X-ray analysis.

Compound **3**: mp >300 °C (the color turned to black at 272 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 3.94 (s, 18H), 2.23 (s, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.8, 133.6, 117.2, 81.5, 77.7, 61.4, 13.1; IR (KBr) 2210 ($C\equiv C$) cm^{-1}. HRMS (EI) calcd for $C_{42}H_{36}O_6$ 636.2512, found 636.2514.

4.1.3. Transformation of 3 to *p*-benzoquinone-fused dehydro[18]annulenes 4-6. To a stirred solution of **3** (15 mg, 0.023 mmol) in a mixed solvent of CH_3CN (6 mL) and $CHCl_3$ (6 mL) was added dropwise a solution of ceric ammonium nitrate (CAN) (190 mg, 0.35 mmol) in distilled water (0.8 mL) over 5 min. After 25 min of stirring, the reaction was quenched by adding water (ca. 10 mL). The aqueous layer was extracted with $CHCl_3$. The combined organic solution was dried over $MgSO_4$ and evaporated to give a crude mixture containing the mono-benzoquinone derivative **4** as a major component. The mixture was dissolved in $CHCl_3$ (ca. 10 mL), and 10 mL of hexane was slowly diffused into the solution to give pure **4** (7.0 mg, 0.011 mmol, 48%) as a red powder.

Compound **4**: mp >300 °C (the color turned to black at 237 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 3.98 (s, 6H), 3.97 (s, 6H), 2.31 (s, 6H), 2.30 (s, 6H), 2.13 (s, 6H); IR (KBr) 2192, 2172, and 2129 ($C\equiv C$), 1656 ($C=O$) cm^{-1}. HRMS (FAB) calcd for $C_{40}H_{30}O_6$ 606.2042, found 606.2029. The poor solubility of **4** hampered the ^{13}C NMR measurement.

In the same way, the reaction of **3** (11 mg, 0.017 mmol) with CAN (200 mg, 0.36 mmol) was conducted by stirring at room temperature overnight. The reaction mixture was treated in exactly the same way as above. Reprecipitation with $CHCl_3$–hexane gave bis-benzoquinone derivative **5** (5.7 mg, 0.10 mmol, 60%) as a red powder.

Compound **5**: mp >300 °C (the color turned to black at 220 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (s, 6H), 2.38 (s, 6H), 2.17 (s, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 181.9, 181.7, 157.6, 142.7, 142.5, 135.6, 133.1, 130.8, 116.3, 94.2, 92.5, 91.1, 85.4, 82.5, 81.9, 78.1, 62.0, 13.5, 13.1; IR (KBr) 2189 ($C\equiv C$), 1650 and 1628 ($C=O$) cm^{-1}; MS (APCI) *m/z* 576 (M^+).

In the same way, the reaction of **3** (25 mg, 0.039 mmol) with CAN (1.86 g, 3.39 mmol) was conducted in a mixed solvent of CH_3CN (10 mL) and $CHCl_3$ (10 mL) at room temperature overnight. The post treatment as described above and the similar reprecipitation afforded tris-benzoquinone derivative **6** (4 mg, 0.007 mmol, 19%) as a red powder.

Compound **6**: mp >300 °C (the color turned to black at 208 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 2.24(s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 181.5, 143.2, 132.0, 92.5, 83.5, 13.2; IR (KBr) 2178 and 2126 ($C\equiv C$), 1655 ($C=O$) cm^{-1}; MS (APCI) *m/z* 546 (M^+).

4.2. Cyclic voltammetry

Cyclic voltammetry (CV) was performed on a BAS-50W electrochemical analyzer. The CV cell consisted of a glassy carbon working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out for 1.0 mM solutions of each sample with tetrabutylammonium perchlorate as a supporting electrolyte (0.1 M) in benzonitrile, and the values for oxidation potentials were calibrated with ferrocene as an internal standard.

4.3. X-ray structural determination

Crystal data for **3**: $(C_{42}H_{36}O_6)\cdot CHCl_3$, FW=1392.79, triclinic; space group P-1; a=11.755(5) Å, b=17.474(7) Å, c=20.099(8) Å, α=66.685(9)°, β=84.648(11)°, γ=78.572(9)°, V=3716(3) Å^3, Z=4, D_{calc}=2.488 mg/m^3. Intensity data were collected at 123 K on a Bruker SMART APEX diffractometer with Mo K$_\alpha$ radiation (λ=0.71073 Å) and graphite monochromater. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10 s per frame. A total of 21075 reflections were measured and 14161 were independent. The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares on F^2 (SHELXL-93). The presence of a disordered solvent molecule in the lattice was evident, and the SQUEEZE[17] data processed with the program implemented in PLATON-96[18] were used for the further refinement. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically and the refinement converged to R_1=0.0667, wR_2=0.1739 ($I>2\sigma(I)$), and GOF=0.948. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 229724. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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