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Synthesis and Electronic Properties of Anthracene Fully Annelated with Bicyclo[2.2.2]octene Frameworks

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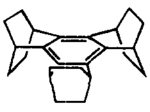
Abstract: Anthracene derivative **4** annelated with four bicyclo[2.2.2]octene (BCO) units was newly synthesized by the Diels–Alder reaction of BCO dimer with *p*-benzoquinone as a key reaction, and its electronic properties were investigated. The remarkable effect of BCO annelation was observed in its redox behavior, and **4** was readily transformed into stable cation radical $\mathbf{4}^{+\bullet}$ and dication $\mathbf{4}^{2+}$.

Among the commonly known polycyclic arenes, anthracene has a relatively low ionization potential.[1,2] It acts as a good π-donor in the formation of charge transfer complexes,[2–4] and can be readily converted to the corresponing cationic species.[2,5,6] The redox behavior of anthracene has therefore been the subject of extensive study.[7] However, compared with the readily available 9- or 9,10-disubstituted derivatives, those having multiple alkyl substituents at 1- to 8-positions seem to be less studied[8] in spite of their possibly enhanced π-donor ability.

In the previous studies, we have synthesized several monocyclic conjugated π-systems annelated with bicyclo[2.2.2]octene (abbreviated as BCO) frameworks such as **1**,[9] **2**,[10] and **3**.[11] It has been found that cation **2**[10] and dication $\mathbf{3}^{2+}$[12] as well as cation radical $\mathbf{1}^{+\bullet}$[9] and $\mathbf{3}^{+\bullet}$[13] are remarkably stabilized by inductive and hyperconjugative effects, in addition to the steric protection, by bicyclic σ-frameworks surrounding the π-systems. The similar stabilization can be expected for the cationic species of polycyclic arenes annelated with BCO units, and the properties of such π-systems are quite intriguing. In this paper, we report the synthesis and properties of anthracene **4**, which is fully annelated with BCO units.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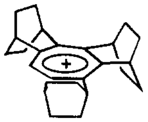

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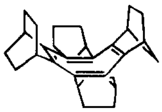
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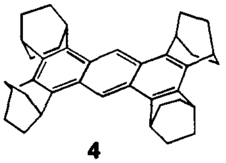
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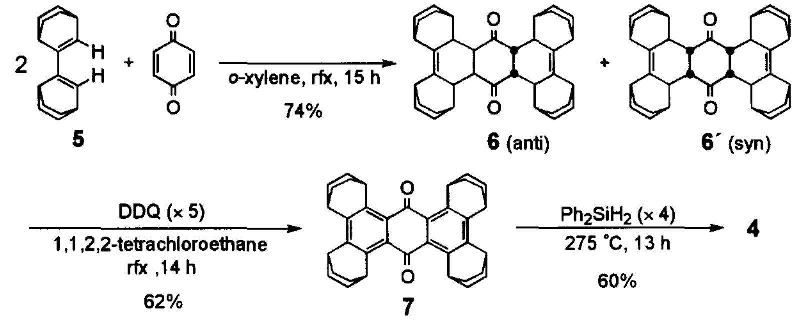
The Diels-Alder reaction of two equivalents of BCO dimer **5**[14] with *p*-benzoquinone in refluxing *o*-xylene afforded a mixture of syn- and anti-isomers of adducts **6** and **6'** as white precipitates. These adducts were dehydrogenated by DDQ to give anthraquinone **7**, which was reduced in boiling diphenylsilane[15] to give desired anthracene **4**[16] as a yellow solid (Scheme 1).

Scheme 1



The X-ray crystallography[17] of **4** (Fig. 1) revealed that the anthracene π-system is planar and that the annelation with four BCO frameworks induces only slight modification to the bond alternation intrinsic to parent anthracene. The averaged bond lengths (Å) are 1.372 (C1–C2), 1.416 (C2–C3), 1.427 (C1–C9a) 1.444 (C9a–C4a), and 1.397 (C9–C9a); whereas the reported values for the corresponding bonds in anthracene are 1.375, 1.418, 1.444, 1.433, and 1.405.[18]

The UV-vis spectrum of **4** exhibited fine structure between 350 and 420 nm. These absorptions are characteristic to anthracene[19], but are bathochromically shifted by 30 to 40 nm, which is attributed to the substantial elevation of the occupied orbitals.

The remarkable effect of BCO annelation upon the HOMO level was observed in the redox behavior. As shown in Fig. 2, anthracene was only irreversibly oxidized at +1.04 V *vs* ferrocene/ferricenium upon cyclic voltammetry in dichloromethane. Even 1,2,3,4,5,6,7,8-octamethylanthracene has been reported to show only one reversible oxidation wave at $E_{1/2}$ = +0.86 V *vs* Ag/AgCl [20] (calibrated to +0.36 V *vs* Fc/Fc$^+$)[21] in the same solvent. In contrast, compound **4** exhibited a well-defined reversible oxidation wave at a low potential such as $E_{1/2}$ = +0.21 V and an irreversible one at +0.87 V. These results indicate that **4** can yield a stable cation radical and a less stable dication upon consecutive oxidation.

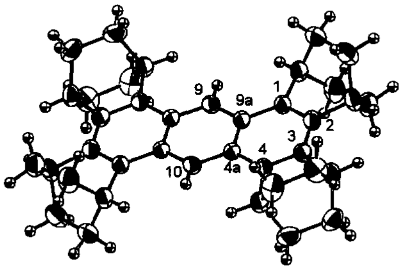


Fig. 1. ORTEP view of the X-ray crystal structure of **4**.

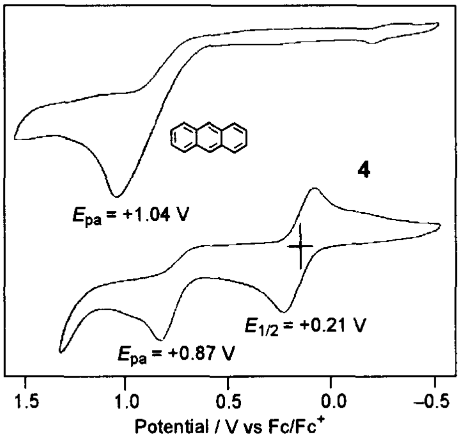


Fig. 2. Cyclic voltammograms of **4** and anthracene in CH_2Cl_2 with Bu_4NClO_4 as a supporting electrolyte; scan rate, 0.1 V s^{-1}.

In fact, oxidation of **4** by one equivalent of $NO^+SbCl_6^-$ in dichloromethane gave a red-violet solution, which exhibited a triplet ESR signal of $\mathbf{4}^{+\bullet}$ due to the coupling with 9,10-hydrogens (a_H = 0.54 mT, g = 2.003). After evaporation, a black solid was obtained, which was considered as cation radical salt $\mathbf{4}^{+\bullet}SbCl_6^-$ since it provided the same ESR spectrum upon dissolution in dichloromethane.

When a solution of **4** in CD_2Cl_2 was treated with a large excess of a stronger oxidant, SbF_5, at −78 °C in a vacuum-sealed tube, the color of the solution immediately changed to greenish-blue. The ^1H and ^{13}C NMR spectra of this solution (Fig. 3) clearly indicated the generation of dication $\mathbf{4}^{2+}$ as described below. In ^1H NMR, signals of both bridgehead and 9,10-protons are up-field shifted compared to **4** due to the effect of paramagnetic ring current. In ^{13}C NMR, the most deshielded peak can be assigned to that of C–9,10 from the comparison with the parent anthracene dication,[6] and the averaged chemical shift of sp^2-carbons (δ_{av} 155.1) is in good agreement with that predicted by the extended Spiesecke-Schneider correlation:[6] $\delta^{13}C_{av}(calc) = -156.8e_{av} + 289.9 = 155.5$.

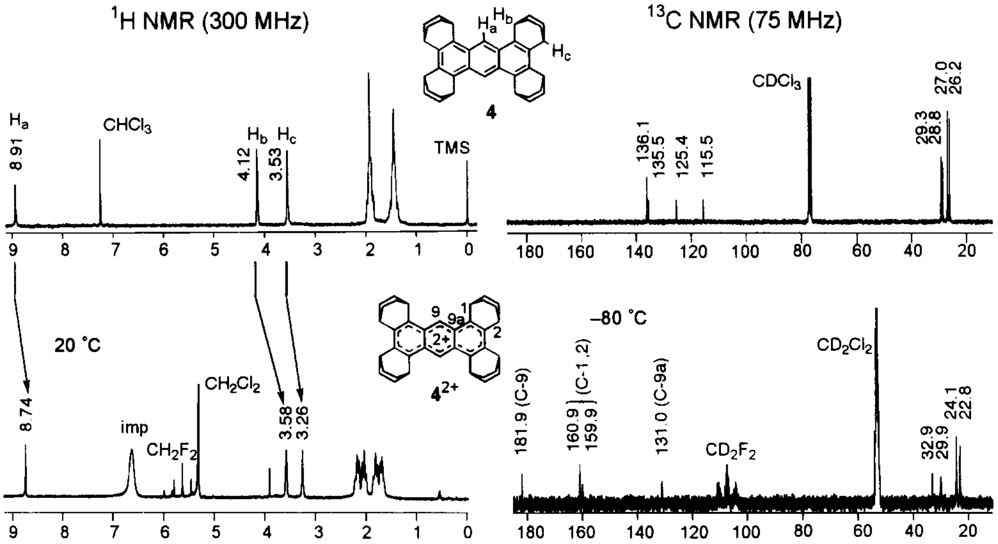
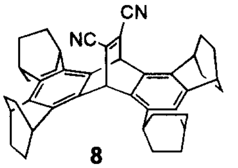


Fig. 3. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra of **4** (in $CDCl_3$) and $\mathbf{4}^{2+}$ (in CD_2Cl_2).

It is well-known that anthracene serves as a diene in Diels-Alder reaction under forcing conditions. Normally it requires heating at 100 °C for anthracene to undergo the [4+2] cycloaddtion with highly reactive dienophiles such as dicyanoacetylene.[22] In sharp contrast, compound **4** readily reacted with dicyanoacetylene in dichloromethane at room temperature to give [4+2] adduct **8** [23] a single product. Compound **4** reacted also with TCNE under the same conditions to give adduct **9** [24] in a quantitative yield. These results can be taken as another piece of evidnce for the substantial elevation of the HOMO in **4**.



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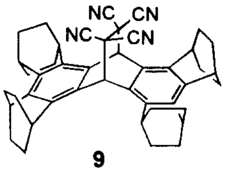

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16. **4**; yellow prisms from CS_2/hexane; mp > 400 °C ; UV–vis (CH_2Cl_2) λ_{max} 233 nm (log ε 4.19), 262 (4.43), 356 (3.28), 375 (3.56), 395 (3.75), 419 (3.69); ^1H NMR (300 MHz, $CDCl_3$) δ 8.91 (s, 2H, Ar-H), 4.12 (br s, 4H, CH), 3.53 (br s, 4H, CH), 1.89 (br m, 16H, CH_2), 1.42 (br m, 16H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 135.5, 125.4, 115.5, 29.3, 28.8, 27.0, 26.2; HRMS calcd for $C_{38}H_{42}$ 498.3286, found 498.3311.
17. X-Ray diffraction data for **4**, $C_{38}H_{42}$: triclinic, space group $P\bar{1}$(≠2), a= 9.612(2) Å, b= 11.331(2) Å, c= 6.646(1) Å, α= 95.14(2)°, β= 106.94(1)° , γ= 96.32(2)°, V= 682.6(2) $Å^3$, Z= 1, D_{calcd} = 1.213 g cm^{-3}. The intensity data were collected on a Rigaku AFC7R diffractometer by using graphite monochromated Cu-Kα radiation at 293 K. A total of 2182 reflections were measured, of which 2040 were unique. The structure was solved by direct methods (SHELXS86). Final R = 0.051, R_w = 0.069. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.
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23. **8**; pale yellow solid; UV (CH_2Cl_2) λ_{max} 235 nm (log ε 4.36), 276 sh (3.27), 322 (3.23); ^1H NMR (300 MHz, $CDCl_3$) δ 5.92 (s, 2H, CH), 3.43 (br s, 4H, CH), 3.26 (br s, 4H, CH), 1.82 (br m, 16H, CH_2), 1.50 (br m, 4H, CH_2), 1.36 (br m, 4H, CH_2), 1.18 (br m, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 135.8, 134.9, 132.2, 114.7, 46.0, 29.7, 28.6, 25.9 (overlapped signals); MS (–APCI) *m/z* 574 (M^-).
24. **9**; white solid; UV (CH_2Cl_2) λ_{max} 237 nm (log ε 4.34), 276 (4.18); ^1H NMR (300 MHz, $CDCl_3$) δ 5.70 (s, 2H, CH), 3.47 (br s, 4H, CH), 3.34 (br s, 4H, CH), 1.86 (br m, 16H, CH_2), 1.60 (br m, 4H,

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