Synthesis, Structure, and Properties of a Cyclopent[*fg*]acenaphthylene-1,2-bis(*p*-quinone methide)s Derivative. An Extended Pyracyloquinone

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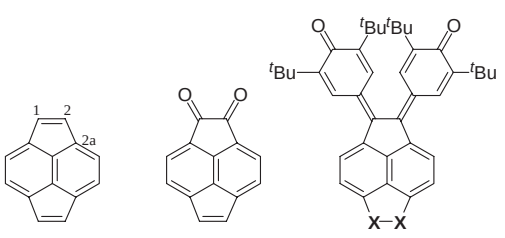
The extended-quinone derivative of cyclopent[*fg*]acenaphthylene-1,2-dione (pyracyloquinone) is first synthesized and characterized. An X-ray analysis exhibits the non-planar structure involving bent of two 3,5-di-*tert*-butyl-4-oxo-cyclohexadienylidene units, and bond alternation along the molecular periphery. The facile formation of trianion radical on cyclic voltammetry reflects high-electron affinity enhanced by antiaromatic character of the formed pyracylene moiety on the dianion state.

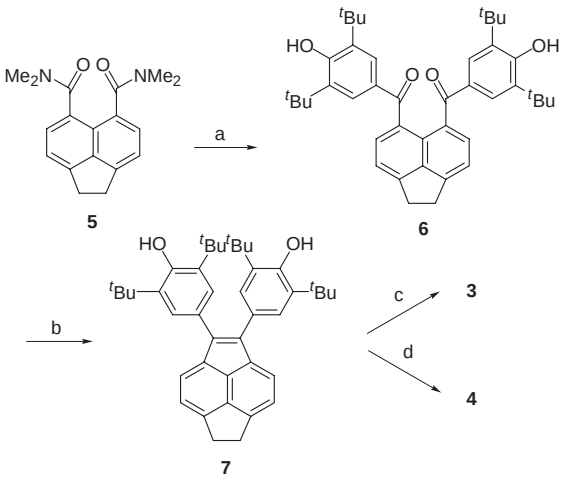
Pyracylene (cyclopent[*fg*]acenaphthylene, **1**) has been attractive from organic and physical chemistry as a "perturbed [12] annulene."[1] Despite of its formal 12π electron perimeter, **1** is a relatively stable hydrocarbon, and has been characterized by various spectroscopic methods and X-ray crystallography as well as theoretical caluculation.[2] Furthermore, many derivatives of **1** have been prapared from viewpoints of ladder-type π-conjugated polymers, and substructures of fullerenes.[3] On the other hand, pyracyloquinone (cyclopent[*fg*]acenaphthylene-1,2-dione, **2**), a quinone derivative of **1**, was synthesized at almost the same time with **1**, and has been studied its redox properties, radical anion,[4] and unique photochemical behavior.[5] Although **2** has been often used as a synthetic intermediate for extended π-conjugated molecules having pyracylene skeleton,[6] extended quinonoid derivatives of **2** have not been reported. We thus have designed a new bis-quinone methides **3** as an extended quinone of **2**. Because of intramolecular steric repulsion caused by the two quinone methide units, compound **3** cannot take a planar structure. Therefore, its molecular deformation and physicochemical properties attract our interest connecting with our current research of non-planar extended quinones.[7–9] Here, we report the synthesis and properties of **3** as the first extended pyracyloquinone (Chart 1).

Synthesis of **3** was outlined in Scheme 1. A key intermediate was 5,6-diketo-acenaphthylene derivative **6**. Among some accesible synthetic routes for **6**, we chose *N*,*N*,*N*′,*N*′-tetramethyl-5,6-acenaphthylenedicarbamide **5**[1] as the starting material. At first, three equivalents of 4-lithio-2,6-di-*tert*-butylphenoxide, generated by treatment of 4-bromo-2,6-di-*tert*-butylphenol with three equivalents of *tert*-BuLi,[10] reacted with **5** to afford the desired **6** in only 2.5% yield. Reactivity of **5** toward nucleophiles would be poor probably owing to steric hindrance. To enhance the nucleophilicity of 4-lithio-2,6-di-*tert*-butylphenoxide, addition of TMEDA (2 equiv.) was effective; the yield of **6** was improved up to 12%. Bisphenol **7** was obtained from **6** in 87% yield by intramolecular McMurry coupling. Oxidation of **7** with DDQ in refluxing benzene afforded **3** as air-stable brown crystals in 61% yield.[11] On the other hand, oxidation of **7** with alkaline $K_3Fe(CN)_6$ afforded **4** as deep purple crystals in 89% yield.[11] From ^{1}H NMR spectra of **3** and **4**, the rotation of the exomethylene bonds (pinch bonds) is not observed around room temperature.



1 **2** **3** (X-X : CH=CH) **4** (X-X : CH_2CH_2)

Chart 1.



Scheme 1. Synthesis of **3** and **4**: a) lithium 4-lithio-2,6-di-*tert*-butylphenoxide, TMEDA, ether, 0 °C then rt, overnight, 12%, b) $TiCl_4$, Zn, CuI, DME, reflux, overnight, 87%, c) DDQ, benzene, reflux, 3 h, 61%, d) $K_3Fe(CN)_6$, benzene, 0.1 M KOHaq, rt, 3 d, 89%.

Recrystallization of **3** from benzene–*n*-hexane afforded single crystals suitable for X-ray diffraction analysis.[12] ORTEP drawings of **3** are shown in Figure 1. As expected, the pyracylene moiety is nearly planar, but the central five-membered ring is slightly twisted; the torsion angle (C14–C13–C24–C23) is 13.5°. The pinch bonds are distorted from the plane with the dihedral angle of 38.4° (C4–C13–C24–C10), and are twisted with the avarage torsion angle of 17.6°. The avarage length of the pinch bonds (1.379 Å) is similar to that of the dibenzo-*ortho*-terphenoquinone derivative **10** (1.378 Å), while the bond length of C13–C24 (1.509 Å) is slightly longer than the corresponding bond in **10** (1.490 Å). The bond alternation along the molecular periphery is observed. For example, C14–C15 is 1.388 Å, whereas C15–C16 is 1.425 Å. The bond lengths in the

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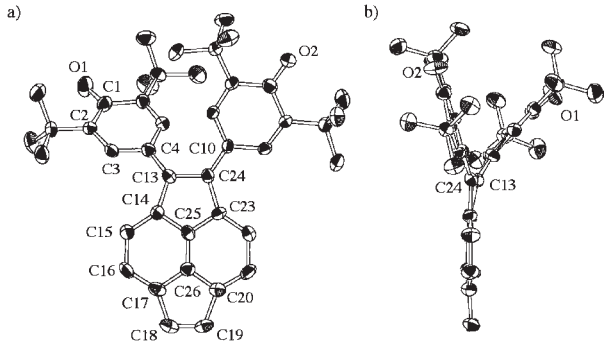

Figure 1. ORTEP drawings (50% thermal ellipsoids) of **3**; a) front view, b) side view. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–C1 1.232(4), C1–C2 1.484(5), C2–C3 1.354(5), C3–C4 1.442(5), C4–C13 1.378(5), C13–C14 1.487(5), C13–C24 1.509(5), C14–C15 1.388(5), C15–C16 1.425(5), C16–C17 1.385(5), C17–C18 1.483(6), C18–C19 1.355(6), C25–C26 1.361(5), C4–C13–C14 124.6(4), C4–C13–C24 126.7(4), C14–C13–C24 107.2(4), C13–C14–C25 104.4(4), C16–C17–C18 139.5(5), and C17–C18–C19 108.6(4).

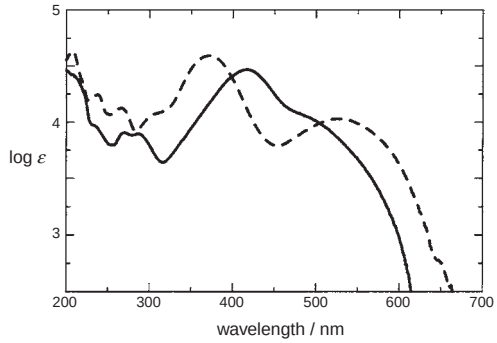

Figure 2. UV–vis spectra of **3** (solid line) and **4** (dashed line) in cyclohexane.

fused cyclopentene moiety of **3** (C18–C19, 1.355; C17–C18, 1.483 Å) is similar to that in pyracylene **1** (C1–C2, 1.346; C2–C2a, 1.492 Å).[2] Additionally, the central double bond of **3** (C25–C26; 1.361 Å) is as short as that of **1** (1.360 Å). In crystal, one *n*-hexane molecule contains for one molecule of **3**, which is positioned between two pyracylene moieties. No significant intermolecular interaction between **3** and *n*-hexane is observed.

The UV–vis spectra of **3** together with **4** are shown in Figure 2. Semiempirical molecular orbital method (ZINDO) indicates that HOMO of **3** is lower than that of **4** whereas NHOMO of **3** is higher than that of **4**. This is the reason of the hypochromic shift of the first absorption band as well as the bathochromic shift of the second absorption band in **3**. Compound **4** have a broad absorption in whole visible region. Its concentrated solution is thus nearly black.

The reduction potentials of **3** as well as **4** were measured by cyclic voltammetry.[13] Upon electronic reduction, three reversible reduction waves were observed for **3** ($^1E_{1/2} = -0.70$ V, $^2E_{1/2} = -1.03$ V, and $^3E_{1/2} = -1.81$ V), whereas two waves for **4** ($^1E_{1/2} = -0.69$ V and $^2E_{1/2} = -1.03$ V). The first and second potentials of them show the formation of the anion radicals and dianions. Unlike compound **10**,[8] this good reversibility reflects their rigid structures. The relatively high third reduction potential of **3**, which corresponds to the formation of trianion radical, indicates that the electron affinity of dianion $\mathbf{3}^{2-}$ is enhanced by antiaromatic character of the formed pyracylene moiety. Further studies on **3** toward the development of photoresponsive molecular switch, like **10**, are in progress (Chart 2).

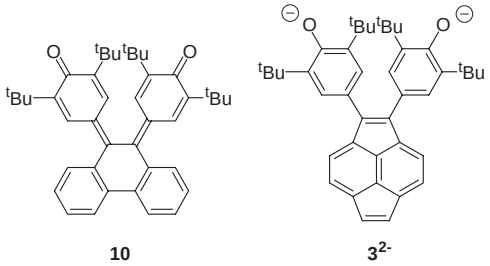

Chart 2.

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11 Selected physical and spectroscopic data **3** and **4**: **3**: brown crystals; mp >300 °C; MS (EI) *m/z* 586 ($[M+4]^+$, 89%), 584 ($[M+2]^+$, 100), 582 (M^+, 77), 293 ($[M+4]^{2+}$, 17); ^{1}H NMR (270 MHz, CD_2Cl_2) δ 8.10 (d, $J = 2.5$ Hz, 2H), 7.84 (d, $J = 7.3$ Hz, 2H), 7.69 (d, $J = 7.3$ Hz, 2H), 7.26 (d, $J = 2.5$ Hz, 2H), 7.03 (s, 2H), 1.44 (s, 18H), 1.20 (s, 18H); ^{13}C NMR (67.8 MHz, CD_2Cl_2) δ 186.73, 149.91, 149.81, 147.61, 139.85, 137.86, 135.35, 133.54, 131.76, 131.54, 128.86, 127.48, 127.17, 124.17, 36.30, 35.78, 29.90, 29.59; IR (KBr) ν 1597 cm^{-1} (CO); UV–vis (cyclohexane) λ_{max} 503sh ($\log \varepsilon = 4.00$), 418 (4.47), 289 (3.89), 270 (3.91), 233 (3.97) nm. **4**: deep purple crystals; 276.0–277.0 °C; MS (EI) *m/z* 586 ($[M+2]^+$, 100%), 584 (M^+, 29), 293 ($[M+2]^{2+}$, 17); ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.20 (d, $J = 2.5$ Hz, 2H), 8.00 (d, $J = 7.3$ Hz, 2H), 7.49 (d, $J = 7.3$ Hz, 2H), 7.15 (d, $J = 2.5$ Hz, 2H), 3.55 (s, 4H), 1.47 (s, 18H), 1.24 (s, 18H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 186.22, 149.73, 149.32, 147.92, 147.01, 137.27, 135.45, 135.23, 132.77, 132.32, 128.48, 124.83, 121.90, 36.13, 35.57, 32.27, 29.95, 29.58; IR (KBr) ν 1597 cm^{-1} (CO); UV–vis (cyclohexane) λ_{max} 558 ($\log \varepsilon = 4.03$), 388 (4.59), 272 (4.12), 241 (4.24), 209 (4.63) nm.
12 Crystal data for $\mathbf{3}\cdot C_6H_{14}$ ($C_{48}H_{60}O_2$): M_r 669.00, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.53(2)$ Å, $b = 17.21(3)$ Å, $c = 18.89(4)$ Å, $\beta = 101.31(1)°$, $V = 3672(12)$ Å^3, $Z = 4$, $D_{calcd} = 1.210$ g cm^{-1}, Mo Kα ($\lambda = 0.71070$ Å), $2\lambda_{max} = 55.0°$; 40135 reflections measured, 8373 unique, $R_{int} = 0.080$, $R1 = 0.045$ (2041 data, $I > 2\sigma(I)$), $R_w = 0.102$, GOF = 0.79, CCDC 285859.
13 V vs Ag/Ag$^+$ in 0.1 M *n*-Bu_4NClO_4/DMF at 25 °C, scan rate 100 mV s^{-1}, ferrocene/ferrocenium ion = +0.18 V.

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