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Design and Synthesis of a Highly Amphoteric Condensed Hydrocarbon with the Highest Reduction Potential: Pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene[1]

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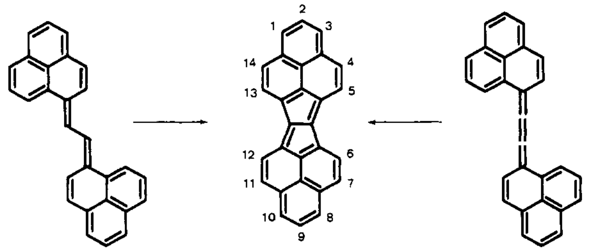
Some conjugated hydrocarbons are known to exhibit the amphoteric multi-stage redox property that a molecule is oxidized at anode and reduced at cathode by multi-stage electron transfer.[2-4] Adopting the numerical sum (E^{sum}) of oxidation potential (E^{ox}) and reduction potential (E^{red}), i.e., $E^{\mathrm{sum}} = E^{\mathrm{ox}} + (-E^{\mathrm{red}})$, as a convenient experimental measure to estimate the amphotericity of a molecule, we have recently described that 1,2-bis(phenalen-1-ylidene)ethane (BPLA, **1**)[4a] and ethene (BPLE, **2**)[4b] show appreciably small E^{sum} values as hydrocarbons, and in this sense both compounds are reputed to be highly amphoteric systems.

In principle, the ultimate molecule that exhibits the highest amphotericity, $E^{\mathrm{sum}} = 0$, is graphite, which is regarded as a limiting member of a series of polycyclic arenes.[5] The relatively small polycyclic conjugated hydrocarbon designed so as to maximize such a redox property modeled on graphite will be expected to demonstrate intriguing chemical and physical properties. We now report our approach to explore a novel hydrocarbon, pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene (PDPL, **3**) that actually displays the smallest E^{sum} and the highest E^{red} values as a hydrocarbon.



BPLA, 1 PDPL, 3 BPLE, 2

Design and Synthesis. A well-known model compound of graphite is violanthrene (**4**),[6,7] which is a dibenzo derivative of peropyrene (**5**).[8] We assume that peropyrene bears phenalenyl moieties,[4a,9] the cation, the radical and the anion, as an essential structural unit in its redox behavior. Therefore, the energy in each of the four ionic redox states of peropyrene is lowered by contribution of the three redox states of the phenalenyl system. A reasonable way to enhance the amphotericity of a certain peri-condensed polycyclic hydrocarbon is that the aromatic stabilization in the neutral closed-shell state of a molecule should be minimized while the phenalenyl stabilization in the redox states of the molecule should be maintained. Such a modification can be accomplished by replacement of the central benzene ring in peropyrene by 8π-electron antiaromatic pentalene[10] leading to PDPL. Thus, the neutral state of PDPL will be substantially destabilized by the electronic contribution of a pentalene system while the redox states will be stabilized by the formation of two terminal phenalenyl systems with destruction of the pentalene conjugation, $\mathbf{3}^{2+} \rightleftharpoons \mathbf{3}^{+\cdot} \rightleftharpoons \mathbf{3} \rightleftharpoons \mathbf{3}^{-\cdot} \rightleftharpoons \mathbf{3}^{2-}$.

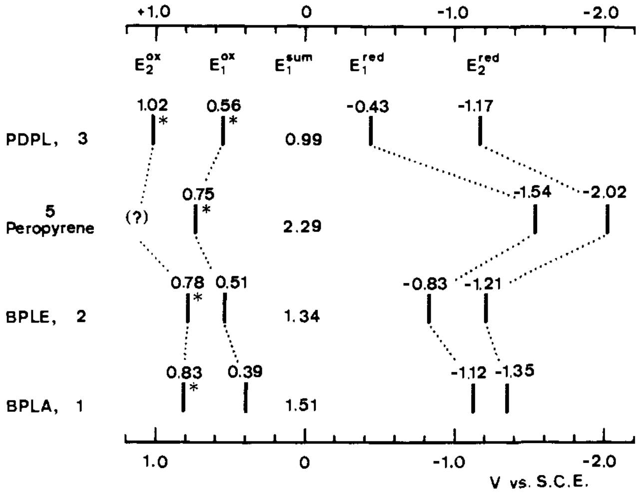
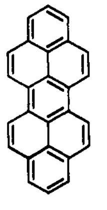


Figure 1. Schematic representation of the redox potentials of PDPL (**3**), peropyrene (**5**), BPLE (**2**), and BPLA (**1**). Potentials of **3** and **5** are determined, in this work, by cyclic voltammetry at −50 °C under argon atmosphere. Solvent, DMF (dried over P_2O_5 and then KOH, distilled (bp 41 °C (8 torr)) under nitrogen, redistilled with picric acid, and then passed through neutral alumina); supporting electrolyte, 0.1 M Et_4NClO_4; working electrode; Pt electrode; reference electrode, SCE (saturated aqueous KCl); bridge solution for SCE, DMF/0.1 M Et_4NClO_4; scan rate, 30 mV/s. The data for **1** and **2** are taken from ref 4a and 4b, respectively. The values by an astrerisk correspond with irreversible wave.



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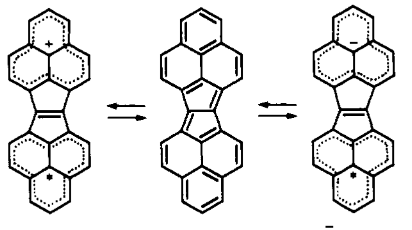

$3^{+\cdot}$, • = ·
3^{2+}, • = +

PDPL, 3

$3^{-\cdot}$, • = ·
3^{2-}, • = −

Previously synthesized BPLA and/or BPLE, containing two phenalenyl segments connected with two sp^2 and/or sp carbon atoms, are topologically appealing candidates for the synthesis of PDPL. In view of the precedent that bis(anthronylidene)ethane easily cyclized to the quinone having a pentalene skeleton by $AlCl_3$,[11] this synthetic pathway has a realizable possibility. In fact, this is the case when we used molten salt comprising aluminum chloride and sodium chloride as a condensing agent.[12] Thus, treatment of either BPLA or BPLE with the molten salt at 230 or 130 °C, respectively, afforded PDPL in 10–15% yield.[13]

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[12] Although the mechanism for the conversion, **1** and/or **2** → **3**, is not clear, ready formation of the cation radical or the dication of **1** or **2** is responsible for the cyclization.

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Physical Properties. PDPL showed the following characteristics:[14] air-sensitive greenish black fine scales with a metallic luster; mp 155 °C dec; MS, *m/e* 350 (M^+, 38%); ^1H NMR (360 MHz, CS_2 and C_6D_{12})[13a] δ 4.42 (d, 4 H, J = 8.5 Hz, H-5, -6, -12, -13), 5.23 (d, 4 H, J = 8.5 Hz, H-4, -7, -11, -14), 5.54 (4 H, B part of an AB_2 system, J = 8 Hz, H-1, -3, -8, -10), 5.57 (2 H, A part of an AB_2 system, J = 8 Hz, H-2, -9); UV/vis λ_{max} (in THF)[13a] 666 (log ϵ 5.13), 636 (4.41), 610 (4.24), 544 sh (3.69), 4.68 (3.52), 442 (3.74), 400 (4.04), 346 (4.70), 324 (4.61), 309 (4.49), 282 (4.48), 230 nm sh (4.40). The striking feature is that the chemical shifts of all protons are at markedly upfield regions for a condensed conjugated hydrocarbon and are even at higher field by over 1 ppm than those of pyracylene (δ 6.01 and 6.52), which is regarded as a perturbed 12π-electron system.[15] Interestingly, the shifts can be compared to those of the outer protons of [24]annulene (δ 4.73),[16] and 3,11,16,24-tetra-*tert*-butyl-1,12,14-trisdehydro-[24]annulene (δ 4.70, 4.71, 5.00, and 5.14).[17,18] A reasonable explanation for the NMR finding resides in the presence of an induced paramagnetic ring current in PDPL, the highly antiaromatic molecule, which implies net energy destabilization with electron delocalization in this system.

Direct insight into the amphotericity of PDPL was obtained by electrochemical studies, and the results are summarized schematically in Figure 1. The CV measurement[13a] was carried out at −50 °C since no reversible cyclic voltammogram was obtained at room temperature due to its instability. For comparison, the corresponding data for some related compounds are included. Apparently, PDPL exhibits the smallest E_1^{sum} (0.99 V) and the highest E_1^{red} (−0.43 V) among the hydrocarbons reported so far.[4,19] The E^{red} values, which are comparable to that of well-known π-electron acceptors 1,4-benzoquinone (E_1^{red} = −0.38 V, E_2^{red} = −1.17 V)[20a,b] and 1,2-naphthoquinone (E_1^{red} = −0.46 V, E_2^{red} = −0.77 V),[20a] can be correlated to the feature that the LUMO of PDPL is a nonbonding MO (NBMO) that retains the characteristic of the NBMO of the phenalenyl in the Hückel level arguments.[21]

From the viewpoint of the electrochemical phenomena, PDPL is the potential hydrocarbon from which two types of solid complexes are isolated in which it behaves as a donor with a molecule and as an acceptor with another.[22] To test this possibility we attempted to prepare such complexes. Although PDPL forms 1:1 complexes with 2,4,7-trinitrofluorenone (greenish black solid, mp >360 °C) and tetracyanoquinodimethane (greenish black solid, mp 295 °C dec), our attempts to use donors to form complexes with PDPL have led to failure to date.[23] Further examinations are currently being pursued.

Acknowledgment. We thank Hideo Naoki (Suntory Institute for Bioorganic Research) for 360-MHz NMR measurement.

Registry No. 1, 86272-03-9; **2**, 83548-18-9; **3**, 86260-85-7; bis(phenalenyl) dication, 86260-88-0; PDPL·2,4,7-trinitrofluorenone, 86260-86-8; PDPL·tetracyanoquinodimethane, 86260-87-9.

Supplementary Material Available: Cyclic voltammograms and UV/vis spectra of BPLA (**1**), BPLE (**2**), and PDPL (**3**), ^1H NMR (360 MHz) of PDPL, and detailed experimental procedure for the preparation of PDPL (4 pages). Ordering information is given on any current masthead page.

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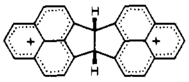
(14) In concentrated sulfuric acid, PDPL was reversibly diprotonated at the two central carbon atoms of the pentalene skeleton to form the bis(phenalenyl) dication (i) characterized by ^1H NMR spectrum: δ 7.32 (s, 2 H),



i

8.95 (t, 2 H, J = 7.7 Hz), 9.37 (d, 4 H, J = 8.1 Hz), 9.75 (d, 4 H, J = 7.7 Hz), 9.91 (d, 4 H, J = 8.1 Hz).

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(21) PDPL can be classified as a typical pentalenoid molecule in which the HOMO lies close to the vacant nonbonding level in energy. See, for example, ref 15 and: Boyd, G. V. *Tetrahedron*, **1966**, *22*, 3409. The low-energy difference of the HOMO–LUMO separation is responsible for the extremely small E_1^{sum} value observed for PDPL.

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(23) We examined here tetrathiafulvalene, tetrathiotetracene, 5,10-dimethyldihydrophenazine, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, 3,3-bis(dimethylamino)biphenyl, and 2,7-bis(dimethytlamino)pyrene as donors, all to no avail. We are grateful to Professor Soichi Misumi, Osaka University, for a generous gift of 2,7-bis(dimethylamino)pyrene(Natsume, B.; Nishikawa, N.; Kaneda, T.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1981**, 601).

An Unprecedented Ligand Set and Coordination Geometry for Copper(I)

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Activation of thermally stable polyhydrido phosphine complexes has been one of our major research objectives.[1,2] With this in mind, the oxidation of MoH_4L_4 (L = PMe_2Ph (≡P) and $PMePh_2$ (≡P′)) by Ag(I) in MeCN was investigated[3] and shown to produce $MoH_2P_4(MeCN)_2^{2+}$ and $MoH_2P'_3(CH_3CN)_3^{2+}$ along with H_2 and Ag^0. Among the many mechanisms proposed for this reaction, the intermediacy of an inner-sphere electron-transfer precursor complex $[MoL_4H_4Ag]^+$ seemed most attractive. We now report the isolation of analogues of such an intermediate from the reaction of the milder oxidant Cu(I) with the isoelectronic (d^2) hydride ReH_5L_3 as well as the unusual outcome of electrophilic attack upon $Re_2H_8L_4$.

Addition of $Cu(MeCN)_4PF_6$ to a cooled (−70 °C) THF solution of $ReH_5P'_3$ followed by warming to room temperature results in precipitation of a colorless solid. NMR spectral assay of this reaction[4] indicates an unexpected 2:1 Re/Cu stoichiometry. Lack

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(4) 220-MHz ^1H NMR (CD_3CN) (16 °C) δ −5.54 (quartet, J_{PH} = 17 Hz, 5 H)