ORGANIC LETTERS

2009
Vol. 11, No. 13
2816−2818

Pyrene-Dihydrophenazine Bis(Radical Cation) in a Singlet Ground State

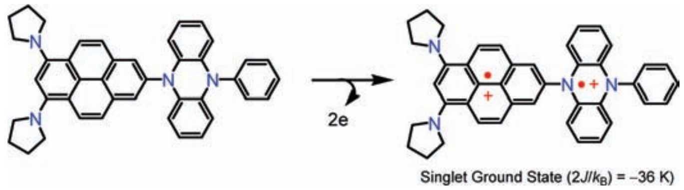
Shuichi Suzuki, Takuma Takeda, Masato Kuratsu, Masatoshi Kozaki, Kazunobu Sato, Daisuke Shiomi, Takeji Takui, and Keiji Okada*

Departments of Chemistry and Materials Science, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

okadak@sci.osaka-cu.ac.jp

Received May 6, 2009

ABSTRACT



A new pyrene-dihydrophenazine dyad was prepared. Oxidation of the neutral species produced a bis(radical cation) species, which was characterized by the absorptions of their component radical cations in the visible region. A thermally accessible triplet state was observed in the ESR measurement in frozen *n*-PrCN. The energy gap between the singlet and triplet states was determined to be $2J/k_B = -36 \pm 3$ K.

Pyrene (**1**) is a unique alternant hydrocarbon with a nodal plane σ passing through the C2 and C7 carbon atoms in the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). These carbon sites in the pyrene radical ions are occupied by negative spin densities (Figure 1). Because of this nature, 2,2′-bipyrene bis(radical anion) has been experimentally shown to have a relatively stable triplet state with a singlet ground state with a small S-T (singlet−triplet) energy gap.[1a] The cationic version of pyrene derivatives has been theoretically investigated in previous studies. Karabunarliev and Baumgarten reported that 1,2′-bipyrene and 2-(anthracen-9-yl)pyrene bis(radical cation) possess triplet ground states using AM1-ROHF calculations with extended CI (configuration interaction).[1b] The calculated S-T gap was rather small, +97 cal/mol (+49 K) for 2-(anthracen-9-yl)pyrene bis(radical cation). There have been no experimental reports on bis(radical cation) of pyrene derivatives, probably because of the high oxidation potential of pyrene and the poor availability of 2-substituted pyrene derivatives.

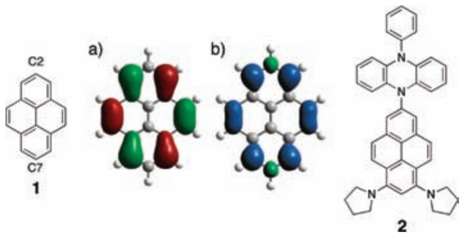


Figure 1. Structures of **1** and **2** with pictures of (a) KS (Kohn−Sham)-HOMO of **1** and (b) spin density distribution of $\mathbf{1}^{\bullet+}$ (blue and green colors denote positive and negative spin densities, respectively).

In connection with our studies on the development of ionic high-spin molecules[2] as spin-building blocks of molecular magnets,[3] we decided to investigate bis(radical cation) of pyrene derivatives. In this paper, we report the synthesis and

---

(1) (a) Kreyenschmidt, M.; Baumgarten, M.; Tyutyulkov, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1957–1959. (b) Karabunarliev, S.; Baumgarten, M. *Chem. Phys.* **2000**, *254*, 239–247.

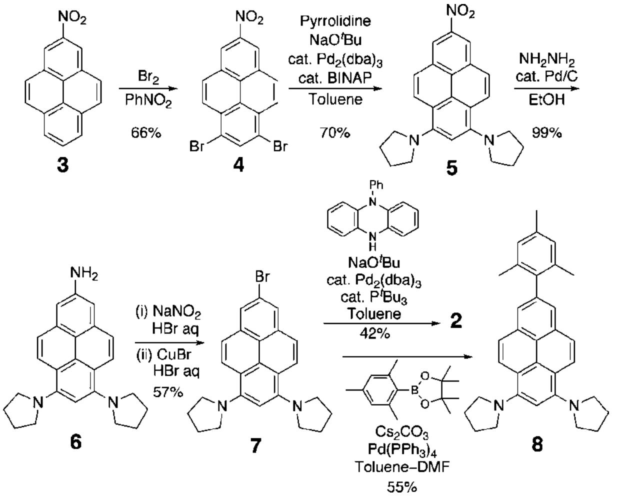
(2) (a) Masuda, Y.; Kuratsu, M.; Suzuki, S.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Hosokoshi, Y.; Lan, X.-Z.; Miyazaki, Y.; Inaba, A.; Okada, K. *J. Am. Chem. Soc.* **2009**, *131*, 4670–4673. (b) Hiraoka, S.; Okamoto, T.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Okada, K. *J. Am. Chem. Soc.* **2004**, *126*, 58–59. (c) Terada, E.; Okamoto, T.; Kozaki, M.; Masaki, M. E.; Shiomi, D.; Sato, K.; Takui, T.; Okada, K. *J. Org. Chem.* **2005**, *70*, 10073–10081.

10.1021/ol9009927 CCC: $40.75

two-electron (2e) oxidation of a novel pyrene-dihydrophenazine dyad **2**. The bis(radical cation) $\mathbf{2}^{2(\bullet+)}$ is shown to be in a singlet ground state with an S-T gap of $2J/k_B = -36$ K, $H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$.

Compound **2** was prepared from 2-nitropyrene (**3**),[4] as shown in Scheme 1. Bromination (bromine, 2.7 equiv, 90−120 °C for 2 h) of **3** in nitrobenzene gave **4** in moderate yield. The cross-coupling of **4** with pyrrolidine was achieved by using $Pd_2(dba)_3$ and BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthalene) as catalysts,[5] giving **5** in good yield. Reduction of the nitro group **5** to an amino group followed by a Sandmeyer reaction with CuBr afforded bromide **7**. Compound **7** was successfully transformed into the target compound **2** following our procedure for the synthesis of unsymmetric 5,10-diaryldihydrophenazine derivatives through a Pd(0)-mediated cross coupling.[6] The structure of **2** was confirmed by NMR and HRMS.[7] Figure 2 shows the molecular structure of **2** determined by X-ray analysis (Figure 2, Table S1, Supporting Information).[8] Although the *R*-value is considerably large because of the disorder in the pyrrolidine moieties and the incorporated CH_2Cl_2 molecules, it is quite apparent that the pyrene plane was almost perpendicular to the dihydrophenazine plane in the neutral state. A model compound, 2-mesitylpyrene (**8**) was also prepared.

Scheme 1. Syntheses of **2** and **8**



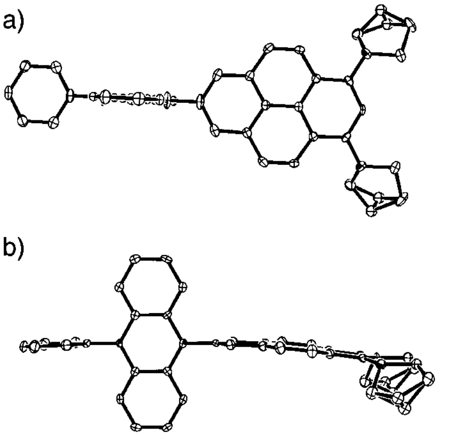


Figure 2. Crystal structure of **2**; (a) top and (b) side views. The hydrogen atoms and the incorporated solvents ($2CH_2Cl_2$) were omitted for clarity.

In the cyclic voltammogram of **2**, two reversible oxidation waves were observed at $E_{ox1} = -0.27$ and $E_{ox2} = -0.07$ V vs Fc/Fc$^+$ (Figure S2 and Table S2, Supporting Information). These values are comparable to those of reference compounds **8** ($E_{ox} = -0.22$ V vs Fc/Fc$^+$) and 5,10-diphenyl-5,10-dihydrophenazine (**9**) ($E_{ox} = -0.24$ V vs Fc/Fc$^+$), suggesting that E_{ox1} and E_{ox2} of **2** are attributed to the oxidation of the dihydrophenazine and pyrene moieties, respectively. The considerable shift of E_{ox2} in the positive direction compared to $E_{ox} = -0.22$ V of **8** is attributed to the inductive effect of the dihydrophenazine radical cation moiety in $\mathbf{2}^{\bullet+}$. Electrochemical oxidation was carried out in a stepwise manner in CH_2Cl_2 at suitable applied voltages (−0.06 and +0.14 V vs Fc/Fc$^+$, Figure S3, Supporting Information, for the spectral change). The final spectrum in the stationary state for the 2e oxidation state is denoted by a black line in Figure 3. The molar absorptivity is an approximate value assuming complete conversion. Figure 3 also shows the electrochemical oxidation of the model compounds (the red line for $\mathbf{8}^{\bullet+}$, the blue line for $\mathbf{9}^{\bullet+}$). The observed spectrum (262, 350, 437, 470, and 550−800 nm) for the 2e oxidation state of **2** is almost superimposed with the spectra of the components (348, 444, and 500−700 nm for 1e oxidation of **8** and 262, 373, 444, 472, and 600−800 nm for 1e oxidation of **9**). This observation reflects the node of pyrene in the HOMO and the perpendicular geometry that is probably maintained in the 2e oxidation state. On the other hand, an entirely new absorption may be expected if the orbitals of the two radical cations are directly overlapped yielding, for instance, a quinoid type electronic structure.

---

(3) (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (b) *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha, and Gordon and Breach Science Publishers: Tokyo, 2000. (c) *Magnetism: Molecules to Materials*; Miller, J. S.; Drillon, M., Eds.; Wiley-VCH: New York, 2001. (d) Hicks, R. G. *Org. Biomol. Chem.* **2007**, *5*, 1321–1338.

(4) Miller, D. W.; Herreno-Saenz, D.; Huang, K. H.; Heinze, T. M.; Fu, P. P. *J. Org. Chem.* **1992**, *57*, 3746–3748.

(5) Witulski, B.; Senft, S.; Thum, A. *Synlett* **1998**, 504–506.

(6) Okamoto, T.; Terada, E.; Kozaki, M.; Uchida, M.; Kikukawa, S.; Okada, K. *Org. Lett.* **2003**, *5*, 373–376.

(7) Selected physical data of **2**: mp 279 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, $J = 9.28$ Hz, 2H), 7.89 (s, 2H), 7.75 (d, $J = 9.28$ Hz, 2H), 7.73 (t, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.58$ Hz, 1H), 7.47 (d, $J = 7.08$ Hz, 2H), 7.09 (s, 1H), 6.28−6.19 (m, 4H), 5.55−5.52 (m, 4H), 3.58 (br, 8H), 2.03 (br, 8H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ (ppm) 147.35, 141.45, 138.56, 137.93, 137.25, 136.20, 131.79, 131.34, 128.91, 128.50, 126.70, 125.36, 124.96, 122.32, 121.60, 121.20, 118.04, 113.77, 113.11, 104,18, 53.19, 25.42 ppm; HRMS (FAB$^+$) *m/z* Calcd. for $C_{42}H_{36}N_4$: 596.2940. Found: 596.2950.

(8) Crystallographic data for $\mathbf{2}\cdot(CH_2Cl_2)_2$: monoclinic; space group $P2_1/m$ (#11); $a = 12.2153(17)$ Å, $b = 12.1148(14)$ Å, $c = 12.4071(17)$ Å, $\beta = 101.044(7)°$; $V = 1802.1(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.413$ g cm^{-3}; $T = 93$ K; $R = 0.0900$, $R_w = 0.1079$, GOF = 1.467. The crystallographic data is given in the Supporting Information and has been deposited with the Cambridge Crystallographic Data Centre (CCDC 730413).

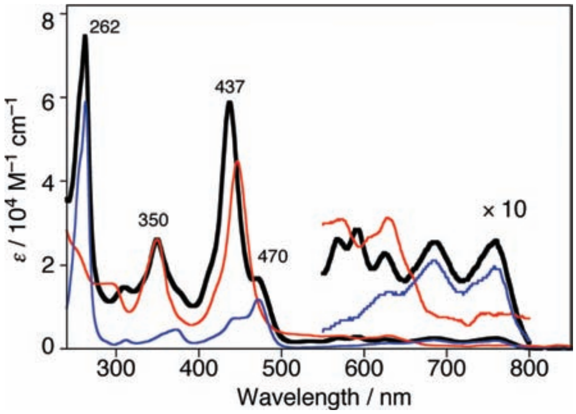


Figure 3. UV−vis spectra of the electrochemically generated $\mathbf{2}^{2(\cdot+)}$ (black line), $\mathbf{8}^{\cdot+}$ (red line), and $\mathbf{9}^{\cdot+}\cdot ClO_4^-$ (blue line) in CH_2Cl_2.

Thus, the spectrum observed for 2e oxidation of **2** is assigned to an open shell structure for $\mathbf{2}^{2(\cdot+)}$.

The 2e oxidation state $\mathbf{2}^{2(\cdot+)}$ was also accessible by chemical oxidation with tris(*p*-bromophenyl)ammonium perchlorate. The radical ion salt $\mathbf{2}^{2(\cdot+)}\cdot 2ClO_4^-$ was obtained as a green powder. The powder showed an absorption spectrum similar to that with the electrochemical oxidation. Figure 4a shows the ESR spectrum of the powder sample $\mathbf{2}^{2(\cdot+)}$ in a butyronitrile matrix at 123 K. Fine-structured triplet-state ESR signals ($\Delta M_s = \pm 1$) with an axial symmetry were distinctly observed in addition to five intense central lines due to monoradical impurities with a dihydrophenazine radical cation structure. The strong signals from the impurities may be a reflection of sharper lines of the monoradicals and thermally accessible triplet state (*vide infra*). The spectral simulation yields spin-Hamiltonian parameters as $S = 1$, $g_x = 2.0043$, $g_y = 2.0023$, $g_z = 2.0023$, $|D|/hc = 0.00342\ \mathrm{cm}^{-1}$, and $|E|/hc \approx 0\ \mathrm{cm}^{-1}$. The distance between two spin systems was calculated to be ca. 7.2 Å from the *D* value using the point dipole approximation. The calculated distance was slightly longer than the distance between the centers of the dihydrophenazine moiety and the pyrene moiety (6.4 Å). The longer distance is probably due to the presence of pyrrolidine substitutents. Figure 4b shows the temperature dependence of the signal intensity of the forbidden transition signals ($\Delta M_s = \pm 2$). The temperature dependence curve was convex. Simulation of the temperature-dependent signal intensities with the S-T model indicates a singlet ground state with $2J/k_B = -36 \pm 3$ K.

This study elucidates the exchange interaction of the highly twisted pyrene-dihydrophenazine bis(radical cation), which is in the singlet ground state with $2J/k_B = -36 \pm 3$ K. The electronic absorption spectrum is characterized as a spectral summation of the component radical cations, consistent with an open shell structure. The conceivable quinoid-type closed shell species would have a much higher energy. Studies on pyrene-donor systems in which the π-systems have small torsion angles are being carried out. These studies will reveal the general aspects of this subject.

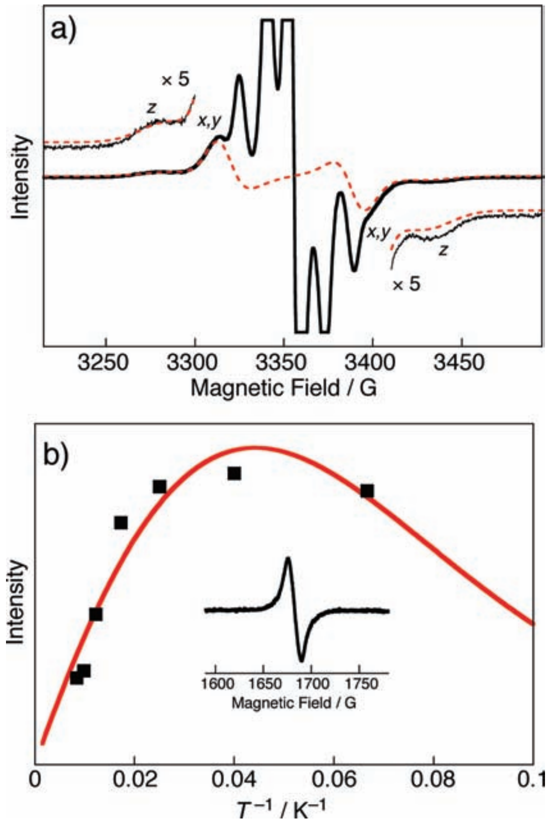


Figure 4. (a) Observed ESR spectrum (solid line) of chemically generated $\mathbf{2}^{2(\cdot+)}$ in PrCN at 123 K and its simulated spectrum (red dashed line). (b) Temperature dependence of the intesties of the forbidden transition of $\mathbf{2}^{2(\cdot+)}$ (■). (Inset) ESR spectrum of the forbidden trasition at 40 K. Red solid line: calculated value using the S-T model with $2J/k_B = -36 \pm 3$ K.

Acknowledgment. S.S. acknowledges the financial support provided by Izumi Science and Technology Foundation, and The Circle for the Promotion of Science and Engineering.

Supporting Information Available: Detailed synthetic procedures with compound data, X-ray crystallographic data (Table 1), maps showing the HOMO and the spin density for 1,3-di(pyrrolidine-1-yl)pyrene (Figure S1), a chart of cyclic voltammogram of **2** (Figure S2) and redox data of **2**, **8**, and **9** (Table S2), and UV−vis spectral change during the electrochemical oxidation of **2** and the model compounds (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

OL9009927