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New Stable Neutral Radical with Intramolecular Hydrogen Bonding: Synthesis and Characterization of 2,5,8-Tri-*tert*-butyl-7-hydroxy-6-oxophenalenoxyl

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Supporting Information

General. ¹H NMR spectra were recorded at 270 MHz with CDCl₃ as solvent and Me₄Si as an internal standard. Infrared spectra were recorded using KBr plates or CCl₂CCl₂ solution. The liquid-phase ESR, ¹H ENDOR, and ¹H TRIPLE spectra of the radical were recorded in toluene solution (1 x 10⁻⁴ M) on a Bruker ESR/ENDOR 300/350 X-band spectrometer at temperature range of T = 200–298 K. The solution of the radical was degassed by freeze-pump-thaw method before measurements. EI-MS was recorded at 70 eV. Melting points were measured with a hot-stage apparatus and are uncorrected. Elemental analyses were performed at the Graduate School of Science and Osaka University. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F₂₅₄ plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% ethanol and then heated until the spots became clearly visible. Silica gel 60 (100–200 mesh) was used for column chromatography. Toluene, HMPA, and CH₂Cl₂ were dried and distilled over CaH₂ under argon atmosphere prior to use. Active PbO₂ was prepared according to the reference procedure.⁷ All reactions requiring anhydrous conditions were conducted under argon atmosphere.

2,5,8-Tri-*tert*-butyl-4,9-dimethoxyphenalenone. Dimethoxyphenalanone derivative **4**⁴ (5.58 g, 13.6 mmol) was placed in a 500-mL three-necked round-bottomed flask and dissolved with toluene (200 mL). To this solution was added DDQ (6.10 g, 26.9 mmol) and the mixture was stirred at 110 °C for 8.5 h. After being cooled to room temperature, the reaction mixture was directly subjected to the short silica gel column chromatography with benzene as eluant, to give an analytically pure dehydrogenated compound (5.55 g, 100%) as a yellow solid. mp 223–225 °C; TLC R_f 0.59 (5:1

hexane/ethyl acetate); ^1H NMR (270 MHz, CDCl_3) δ 1.50 (s, 9), 1.51 (s, 18), 4.02 (s, 3), 4.04 (s, 3), 7.80 (s, 1), 7.94 (s, 1), 7.98 (s, 1); IR (KBr) 2955, 1628, 1578, 1558 cm^{-1} ; EI-MS, m/z 408 (M^+ , 39%), 393 ($\text{M}^+ - \text{CH}_3$, 100%); Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{O}_3$: C, 79.37; H, 8.88; N, 0.00. Found: C, 78.84; H, 8.83; N, 0.00.

2,5,8-Tri-*tert*-butyl-4,9-dihydroxyphenalenone (3). Dimethoxyphenalenone derivative (3.96 g, 9.70 mmol) obtained by the above method was placed in a 2-L three-necked round-bottomed flask and dissolved with HMPA (370 mL). To this solution LiI (16.9 g, 126 mmol) was added and the mixture was stirred at 170 $^\circ\text{C}$ at 1.5 h. After being cooled to room temperature, 2 M HCl aq (300 mL) was added to the reaction mixture. The resulting powder was collected by the filtration, and subjected to the short silica gel column chromatography with benzene as eluant. The resulting crude product was recrystallized from benzene, to give **3** (3.50 g, 95%) as a strong reddish yellow powder. mp 245–247 $^\circ\text{C}$; TLC R_f 0.71 (5:1 hexane/ethyl acetate); ^1H NMR (270 MHz, CDCl_3) δ 1.54 (s, 9), 1.56 (s, 9), 1.57 (s, 9), 6.18 (s, 1), 7.88 (br s, 1), 7.91 (br s, 1), 8.28 (br s, 1); IR (KBr) 3619, 2959, 1629, 1589 cm^{-1} ; IR (CCl_2CCl_2) 3629, 2960, 1629, 1589 cm^{-1} ; EI-MS, m/z 380 (M^+ , 42%), 365 ($\text{M}^+ - \text{CH}_3$, 100%); Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_3$: C, 78.91; H, 8.48; N, 0.00. Found: C, 78.86; H, 8.43; N, 0.00.

2,5,8-Tri-*tert*-butyl-7-hydroxy-6-oxophenalenoxyl (2). Dihydroxyphenalenone derivative **3** (156.1 mg, 0.410 mmol) was placed in a 50-mL round-bottomed flask and dissolved with CH_2Cl_2 (20 mL). To this mixture was added active PbO_2 (340.2 mg, 1.420 mmol) and stirred at room temperature for 30 min. The solid was filtered through the celite column and rinsed with CH_2Cl_2 (20 mL). The filtrates were concentrated under reduced pressure at room temperature for 20 h, to give oxophenalenoxyl radical **2** (147.3 mg, 92%) as a dark grayish green powder. mp 66–68 $^\circ\text{C}$ (dec); TLC R_f 0.68 (5:1 hexane/ethyl acetate); IR (KBr) 2962, 1564, 1539 cm^{-1} ; IR (CCl_2CCl_2) 2962, 1565, 1538 cm^{-1} ; Anal. Calcd for $\text{C}_{25}\text{H}_{31}\text{O}_3(\text{CH}_2\text{Cl}_2)_{0.15}$: C, 77.01; H, 8.04; N 0.00. Found: C, 77.19; H, 8.10; N, 0.00.