

Supporting Information

A nm-Sized High-Spin Polyradical: Poly(4-phenoxy-1,2-phenylenevinylene) Planarily Extended in a Non-Kekulé Fashion and its Magnetic Force Microscopic Images

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2-Iodo-4-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene. 2-Bromo-4-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene⁸ (11.0 g, 24.6 mmol) was dissolved in a dry THF (213 mL) and the solution was cooled down at -78 °C. To this solution was added *n*-butyllithium (16.0 mL of a 1.6 M hexane solution, 25.8 mmol), stirred for 1 h at -78 °C, and then an iodine (12.5 g, 49.2 mmol) dissolved in a dry THF (23.2 mL) was added slowly using a syringe. The solution was allowed to warm to ambient temperature overnight. The reaction was quenched with aqueous NH₄Cl and then extracted with CHCl₃. After evaporation, the crude product was purified by column chromatography on silica gel with a hexane eluent and recrystallization from ethanol to give white crystals: yield 69 %; Mp 104 °C; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 0.4 (s, 9H, -Si(CH₃)₃), 1.4 (s, 18H, *tert*-butyl), 2.3 (s, 3H, -CH₃), 7.3 – 8.0 (m, 5H, phenyl); ¹³C-NMR (CDCl₃, ppm): δ 4.0, 22.7, 31.3, 35.3, 101.5, 124.5, 126.8, 129.7, 131.2, 137.2, 139.3, 141.2, 141.5, 153.1; IR (KBr pellet, cm⁻¹) 1256 (ν_{Si-C}), 929 (ν_{Si-O}); MS (m/z) 494 (M⁺), calcd for M = 494.53.

2-Iodo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene. 2-Iodo-4-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)toluene (6.9 g, 14.0 mmol) was dissolved in THF (48 mL), and methanol (24 mL) was added to this solution. The solution was acidified with aqueous 10N HCl (7.3 mL) under nitrogen atmosphere. After stirring for 3 h, the mixture was evaporated to remove methanol, extracted with ether, and washed with water. The ether layer was dried over anhydrous sodium sulfate and evaporated. The crude product was recrystallized from hexane to give white crystals: yield 70 %; Mp 93 °C; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 1.5 (s, 18H, *tert*-butyl), 2.4 (s, 3H, -CH₃), 5.2 (s, 1H, -OH), 7.3 – 8.0 (m, 5H, phenyl); ¹³C-NMR (CDCl₃, ppm): δ 27.6, 30.3, 34.5, 101.5, 123.9, 126.9, 129.7, 130.8, 136.3, 137.3, 139.2, 141.8, 153.7; IR (KBr pellet, cm⁻¹) 3622 (ν_{O-H}); MS (m/z) 422 (M⁺), calcd for M = 422.3.

2-Iodo-4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)toluene. A few drops of perchloric acid were added to 2-iodo-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)toluene (4.7 g, 11.1 mmol) suspended in acetic anhydride (21.2 mL). After stirring for 15 h, unreacted acetic anhydride was hydrolyzed by adding excess water. The mixture was extracted with ether, and washed with water. The ether layer was dried over anhydrous sodium sulfate and evaporated. The crude product was recrystallized from hexane to give white crystals: yield 80 %; Mp 107 °C; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 1.4 (s, 18H, *tert*-butyl), 2.3 (s, 3H, -CH₃), 2.4 (s, 3H, -O-CO-CH₃), 7.3 – 8.0 (m, 5H, phenyl); ¹³C-NMR (CDCl₃, ppm): δ 22.7, 27.7, 31.5, 35.6, 101.5, 125.3, 127.2, 129.8, 136.6, 137.6, 140.0, 141.1, 142.8, 147.7, 171.1; IR (KBr pellet, cm⁻¹) 1763 (ν_{C=O}); MS (m/z) 464 (M⁺), calcd for M = 464.4.

2-Bromo-2'-vinyl-4,5'-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene. 2-Bromo-2'-methyl-4,5'-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene was prepared by coupling 2-bromo-4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)styrene⁸ with 2-iodo-4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)toluene via the Heck reaction. Palladium acetate (235 mg, 1.05 mmol), tri-*o*-tolylphosphine (636 mg, 2.09 mmol), and triethylamine (5.29 g, 52.3 mmol) were added to a DMF (26.1 mL) solution of 2-bromo-4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)styrene (2.24 g, 5.22 mmol) and 2-iodo-4-(3,5-di-*tert*-butyl-4-acetoxyphenyl)toluene (2.43 g, 5.23 mmol), and stirred for 18 h at 45 °C: yield 48 %; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 1.40 (s, 36H, *tert*-

butyl), 2.38 (s, 6H, -O-CO-CH₃), 2.48 (s, 3H, CH₃), 7.25 – 7.81 (m, 12H, Ar, -HC=CH-); ¹³C-NMR (CDCl₃, ppm); δ 19.65, 22.69, 31.45, 35.61, 124.52, 125.01, 126.52, 126.98, 128.95, 129.24, 130.83, 131.62, 134.88, 136.00, 136.41, 136.45, 138.19, 139.90, 142.37, 142.68, 143.03, 147.49, 148.06, 171.08, 171.07; IR (KBr pellet, cm⁻¹) 1763 (ν_{C=O}), 964 (δ_{transHC=CH}); FAB-MS (*m/z*) 765, 767 (found), calcd for M = 765.9.

N-Bromosuccinimide (737 mg, 4.31 mmol) and α,α'-azobisisobutyronitrile (a few mg) were suspended in the CCl₄ solution (20.0 mL) of 2-bromo-2'-methyl-4,5'-bis(3,5-di-*tert*-butyl-4-acetoxyphenyl)stilbene (2.80 g, 3.66 mmol), and refluxed until succinimide floated on the solution. The mixture was cooled to room temperature and filtered off. After the filtrate was evaporated, benzene (12.0 mL) and triphenylphosphine (1.09 g, 4.14 mmol) were added to it. The resulting solution was stirred at 50 °C for 18 h. The solution was poured into diethylether to give the phosphonium salt (2.30 g): yield 57 %.

The phosphonium salt (2.20 g, 1.99 mmol) was suspended in 25 % formaldehyde (13.0 mL), and 5N NaOH (2.9 mL) was added dropwise over 20 min at room temperature. The mixture was stirred for 1.5 h and extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, and then evaporated. The crude product was purified by silica gel column separation with a hexane/CHCl₃ (1/3) eluent to give a white powder: yield 78 %; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 1.40 (s, 36H, *tert*-butyl), 2.38 (s, 6H, -O-CO-CH₃), 5.38 (d, 1H, 11 Hz, -CH=CH₂), 5.74 (d, 1H, 17 Hz, -CH=CH₂), 7.09 (dd, 1H, 11 Hz, 17 Hz, -CH=CH₂), 7.43 – 7.79 (m, 12H, Ar, -HC=CH-); ¹³C-NMR (CDCl₃, ppm); δ 22.68, 31.58, 35.61, 116.79, 124.52, 125.20, 125.38, 125.75, 126.52, 126.95, 127.04, 127.07, 129.21, 129.91, 131.61, 134.56, 135.44, 135.64, 135.82, 136.36, 137.81, 141.30, 142.44, 142.79, 143.02, 147.70, 148.05, 171.06, 171.14; IR (KBr pellet, cm⁻¹) 1763 (ν_{C=O}), 1626 (ν_{C=C}), 964 (δ_{transHC=CH}); FAB-MS (*m/z*) 777, 779 (found), calcd for M = 778.9.

1,3,5-Tris[2'-styryl-2''-bromo-{5',4''-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)stilbene}]benzene (1c). **1b** (87.0 mg, 36.2 μmol) was dissolved in a slight amount of THF. To its suspension in DMSO (21 mL) was added 2.5N KOH (1.04 mL), the solution was stirred at 40-50 °C for 12 h, cooled to room temperature, and neutralized with 1N HCl. The organic product was extracted with CHCl₃, washed with water, and dried over anhydrous sodium sulfate. The CHCl₃ layer was evaporated and the crude product was purified by column chromatography on silica gel with a hexane/CHCl₃ (1/1) eluent to give a pale yellow powder of **1c**: yield 63%; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 1.52 (s, 108H, *tert*-butyl), 5.31 (s, 18H, -OH), 7.15 – 7.78 (m, 45H, Ar, -HC=CH-); ¹³C-NMR (CDCl₃, ppm); δ 30.30, 34.46, 123.67, 123.81, 123.86, 124.56, 125.83, 126.17, 126.76, 127.03, 127.01, 129.00, 130.37, 130.51, 131.14, 131.98, 134.24, 135.05, 135.09, 136.22, 136.38, 138.33, 138.39, 141.84, 143.12, 153.75, 154.03; IR (KBr pellet, cm⁻¹) 3632 (ν_{O-H}), 962 (δ_{transHC=CH}); FAB-MS (*m/z*) 2153.0 (found), calcd for M = 2153.5.

¹H-¹H COSY Correlation of **1b** (Figure 1S) clearly resolved the complex ¹H-NMR signals in the aromatic region. This spectrum supported both the stilbene structure (4 kinds of doublet chemical shift attributed to the stilbene's protons; 7.12 and 7.18 ppm to the inner stilbene's, 7.47 and 7.52 ppm to the outer stilbene's) and the 1,3,5-substituted benzene core structure (singlet 7.59 ppm). The HMQC measurement (Figure 2S) gave only thirteen peaks at high field ascribed to the aromatic region and only twelve peaks to the 4° carbon at low field. These results were also supported by the APT and DEPT measurement of **1b**.

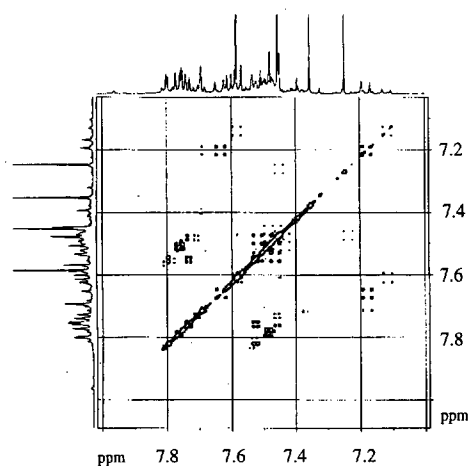


Figure 1S ^1H - ^1H COSY correlation in the aromatic region of **1b**.

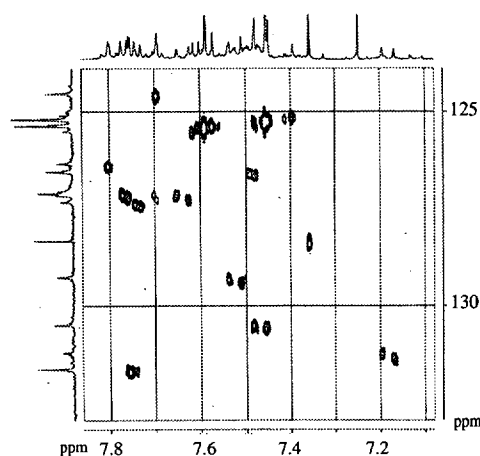


Figure 2S NMQC spectra in the aromatic region of **1b**.

4-(3,5-Di-*tert*-butyl-4-trimethylsiloxyphenyl)-*m*-xylene. (4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (62.8 g, 0.176 mol) and a dry THF (75.4 mL) were added to a dry magnesium (4.28 g, 0.176 mol) under nitrogen atmosphere. The mixture was stirred and refluxed until the magnesium completely reacted. The Grignard reagent was cooled to room temperature and diluted with a dry THF (160 mL). It was added in portions, with stirring, to a dry THF (105 mL) solution of 4-bromo-*m*-xylene (25.0 g, 0.135 mol) with dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (0.171 g, 0.314 mmol) annealed in an ice bath for 0.5 h. The mixture was refluxed for 6 h, then treated with aqueous 2N HCl (176 mL), extracted with ether, and washed with aqueous sodium bicarbonate and water. The ether layer was dried over anhydrous sodium sulfate. After evaporation, the crude product was recrystallized from ethanol to give white crystals: yield 76 %; Mp 107 °C; ^1H -NMR (CDCl_3 , 500 MHz, ppm): δ 0.41 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 1.46 (s, 18H, *tert*-butyl), 2.37 (s, 3H, $-\text{CH}_3$), 2.45 (s, 3H, $-\text{CH}_3$), 7.04 – 7.25 (m, 5H, phenyl); ^{13}C -NMR (CDCl_3 , ppm): δ 3.93, 20.64, 21.01, 31.26, 35.19, 125.72, 126.40, 126.76, 129.84, 131.22, 133.42, 135.28, 136.23, 140.06, 151.91; IR (KBr pellet, cm^{-1}) 1256 ($\nu_{\text{Si-C}}$), 922 ($\nu_{\text{Si-O}}$); MS (m/z) 382 (M^+), calcd for $\text{M} = 382.7$.

4-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-*m*-xylene. 4-(3,5-Di-*tert*-butyl-4-trimethylsiloxyphenyl)-*m*-xylene (37.0 g, 96.7 mmol) was dissolved in THF (340 mL), and methanol (155 mL) was added to this solution. The solution was acidified with aqueous 10N HCl (52.6 mL) under nitrogen atmosphere. After stirring for 3 h, the mixture was evaporated to remove methanol, extracted with ether, and washed with water. The ether layer was dried over anhydrous sodium sulfate and evaporated. The crude product was recrystallized from hexane to give white crystals: yield 64 %; Mp 71 °C; ^1H -NMR (CDCl_3 , 500 MHz, ppm): δ 1.46 (s, 18H, *tert*-butyl), 2.27 (s, 3H, $-\text{CH}_3$), 2.35 (s, 3H, $-\text{CH}_3$), 5.16 (s, 1H, $-\text{OH}$), 7.04 – 7.25 (m, 5H, phenyl); ^{13}C -NMR (CDCl_3 , ppm): δ 20.64, 21.00, 30.43, 34.41, 125.97, 126.42, 126.94, 129.94, 131.11, 132.80, 135.30, 135.31, 136.26, 139.90, 152.57; IR (KBr pellet, cm^{-1}) 3611 ($\nu_{\text{O-H}}$); MS (m/z) 310 (M^+), calcd for $\text{M} = 310.5$.

4-(3,5-Di-*tert*-butyl-4-acetoxyphenyl)-*m*-xylene. A few drops of perchloric acid were added to 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*m*-xylene (17.0 g, 54.7 mmol) suspended in acetic anhydride (75 mL). After stirring for 15 h, unreacted acetic anhydride was hydrolyzed by adding excess water. The mixture was extracted with ether, and washed with water. The ether layer was dried over anhydrous sodium sulfate and evaporated. The crude product was purified by column chromatography on silica gel separation with a hexane eluent to give colorless liquid: yield 98 %; ^1H -NMR

(CDCl₃, 500 MHz, ppm): δ 1.36 (s, 18H, *tert*-butyl), 2.28 (s, 3H, -CH₃), 2.36 (s, 3H, -CH₃), 7.05 – 7.25 (m, 5H, phenyl); ¹³C-NMR (CDCl₃, ppm): δ 20.57, 21.02, 22.65, 31.57, 35.49, 126.47, 127.43, 129.09, 131.16, 135.27, 136.77, 138.47, 139.25, 141.77, 146.68, 171.08; IR (KBr pellet, cm⁻¹) 1765 ($\nu_{C=O}$); MS (*m/z*) 352 (M⁺), calcd for M = 352.5.

4-(3,5-Di-*tert*-butylhydroxyphenyl)-*m*-bis(2'-methyl-5'-(3'',5''-di-*tert*-butylhydroxyphenyl))benzene (4c). **4b** was dissolved in a slight amount of THF. To its suspension in DMSO was added 2.5 N KOH under nitrogen atmosphere. The solution was stirred at 40 – 50 °C for 15 h, cooled to room temperature, and neutralized with 1N HCl. The organic product was extracted with CHCl₃, and the organic layer was evaporated and the crude product was purified by silica gel column separation with a hexane/CHCl₃ (3/1) eluent to give a pale yellow powder of **4c**: yield 73 %; ¹H-NMR (CDCl₃, 500 MHz, ppm): δ 1.52 (s, 54H, *tert*-butyl), 2.43 (s, 6H, -CH₃), 5.19 (s, 3H, -O-H), 7.10 – 7.82 (m, 19H, Ar, -HC=CH-); ¹³C-NMR (CDCl₃, ppm): δ 19.64, 30.33, 34.51, 123.96, 124.04, 124.32, 124.39, 125.13, 125.27, 125.51, 126.26, 126.46, 126.63, 126.87, 127.67, 128.67, 130.07, 130.50, 130.59, 130.74, 131.48, 132.71, 133.08, 133.80, 134.04, 135.47, 135.92, 136.07, 136.22, 136.41, 136.72, 136.91, 140.51, 141.52, 153.13, 153.27, 153.41; IR (KBr pellet, cm⁻¹) 3638 (ν_{O-H}), 966 ($\delta_{transHC=CH}$); FAB-MS: (*m/z*) 923 (found), calcd for M = 923.4.