

## A Stable Neutral Hydrocarbon Radical: Synthesis, Crystal Structure, and Physical Properties of 2,5,8-Tri-*tert*-butyl-phenalenyl

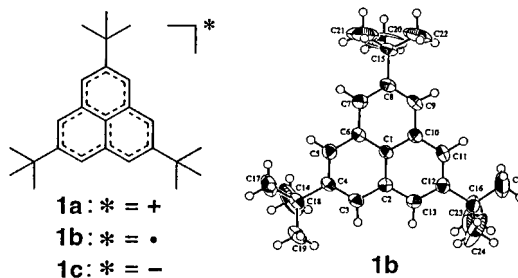
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Phenalenyl, the odd alternate hydrocarbon with high symmetry ( $D_{3h}$ ),<sup>1</sup> has the ability to form three redox species, cation,<sup>2a</sup> radical,<sup>2b</sup> and anion.<sup>2c</sup> Such characteristic features have been widely utilized for exploring new conjugated electronic systems such as extended conjugated radicals,<sup>3</sup> amphoteric redox species,<sup>4</sup> and electrically<sup>5</sup> and magnetically<sup>6</sup> intriguing materials. Among them, phenalenyl radicals link to the studies on solid-state properties of neutral radicals with heteroatoms which have attracted renewed attention to search magnetically interesting materials.<sup>7</sup> Although hydrocarbon radicals are prototypes of radicals, no phenalenyl radicals have been characterized in detail in the solid state because of easy dimerization and/or air oxidation. In this context, isolation of persistent phenalenyls in the crystalline state has been an important issue. Recently, the cyclopentadienyl radical stabilized by five isopropyl groups has been reported, as the first example of the neutral hydrocarbon radical to be characterized by X-ray crystal structure analysis.<sup>8</sup> We have introduced tertiary

butyl groups at three  $\beta$ -positions because the highly reactive phenalenyl radical requires substituents for stabilization. We now report the synthesis, crystal structure, and physical properties of the 2,5,8-tri-*tert*-butyl-phenalenyl radical **1b**, emphasizing salient features of the electronic structure of **1b** in the crystalline state.



The radical **1b** was synthesized from 2,7-di-*tert*-butyl-naphthalene **2** in 10 steps.<sup>10</sup> Bromination of **2** gave **3** exclusively in high yield, which was converted to the aldehyde **4** through a lithiated species. The ester **5**, obtained by the Reformatsky reaction of **4**, was reduced with triethylsilane to afford **6**.<sup>10</sup> Hydrolysis of **6** with LiI gave the acid **7** in high yield, although the conventional hydrolysis failed. The Friedel–Crafts cyclization at low temperature of the acid chloride derived from **7** gave the phenalanone **8** in quantitative yield. The key precursor, the phenalene **10**, was obtained as pale yellow crystals by reduction of **8** and subsequent dehydration (Scheme 1). Treatment of **10** with *p*-chloranil in degassed toluene gave a blue neutral radical solution. Similar treatment in hexane gave the crystalline products as deep blue needles.<sup>11</sup> The radical **1b** in the crystals is stable in the absence of air. A slight change was observed after exposure of **1b** to air for 2 h at room temperature, and it took more than one week for them to completely change to a mixture of yellow phenalene derivatives and unidentified products.

We have succeeded in crystal structure analysis of an odd alternant hydrocarbon radical for the first time. Single crystals of **1b** suitable for X-ray crystal structure analysis were obtained by recrystallization from degassed hexane at  $-30$  °C.<sup>12</sup> The phenalenyl ring possesses a slightly distorted  $D_{3h}$  symmetry and nearly planar geometry (Figure 1). The carbon atoms bonded to the *tert*-butyl group deviate by  $+0.064$  to  $+0.070$  Å from the least-squares plane of the ring. The carbon–carbon bond lengths in the ring range from 1.374 to 1.421 Å, comparable to those of naphthalene. The molecule forms a dimeric pair in a staggered arrangement of *tert*-butyl groups to avoid steric repulsion. In such an arrangement, effective maximum overlaps are expected between the  $\alpha$ -carbon atoms having a large coefficient in the singly occupied molecular orbital (SOMO). The nonbonded distances in the dimeric pair range from 3.201(8) to 3.323(6) Å, which are shorter than twice the van der Waals radius of carbon atom (3.4

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(11) For radical **1b**: mp 232.0 °C (in a sealed tube in vacuum); Anal. Found (Calcd for  $C_{25}H_{33}$ ) C, 89.84 (90.03); H, 9.97 (9.97)%. UV(cyclohexane)  $\lambda_{max}$  ( $\epsilon$ ) = 544 (103), 393 (308), 374 (3390), 342 (26700), 301 (3700), 238 nm (21300); KBr pellet  $\lambda_{max}$  = 612, 486, 332 nm.

(12) X-ray crystal structure analysis of **1b** was performed at room temperature with a crystal sealed in a capillary tube under an argon atmosphere:  $C_{25}H_{33}$ ,  $M = 333.54$ , crystal dimensions  $0.20 \times 0.20 \times 0.30$  mm<sup>3</sup>, blue color, Rigaku AFC7R diffractometer, Mo K $\alpha$  radiation,  $T = 23.0$  °C, monoclinic, space group  $P2_1/n$  (No. 14),  $a = 11.195(6)$  Å,  $b = 11.017(7)$  Å,  $c = 17.778(6)$  Å,  $\beta = 104.61(3)^\circ$ ,  $V = 2121(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{calcd} = 1.044$  g cm<sup>-3</sup>, 6786 reflections collected, 1891 unique intensities reflections observed [ $I > 3.00\sigma(I)$ ],  $2\theta_{max} = 60.0^\circ$ , structure solution with direct methods (SHELX86) and refinement on  $F$  with 251 parameters,  $R(R_w) = 0.069$  (0.069),  $S(GOF) = 2.36$ .

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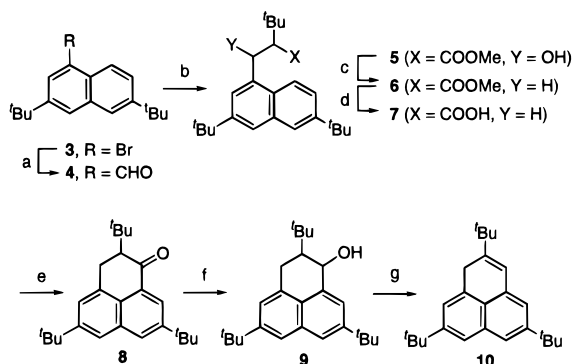
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Scheme 1<sup>a</sup>

<sup>a</sup> Reagents and conditions: (a) *n*-BuLi, then DMF, THF,  $-78\text{ }^{\circ}\text{C}$  to rt, 85%. (b) <sup>t</sup>BuCHBrCOOMe, Zn, benzene, reflux, 95%. (c) Et<sub>3</sub>SiH, TFA, CH<sub>2</sub>Cl<sub>2</sub>, rt, 82%. (d) LiI, DMF, reflux, 76%. (e) (1) (COCl)<sub>2</sub>, reflux. (2) AlCl<sub>3</sub>/I, CH<sub>2</sub>Cl<sub>2</sub>,  $-78$  to  $-30\text{ }^{\circ}\text{C}$ , 98%. (f) LAH, THF, rt 84%. (g) PTSA, benzene, reflux, 86%.

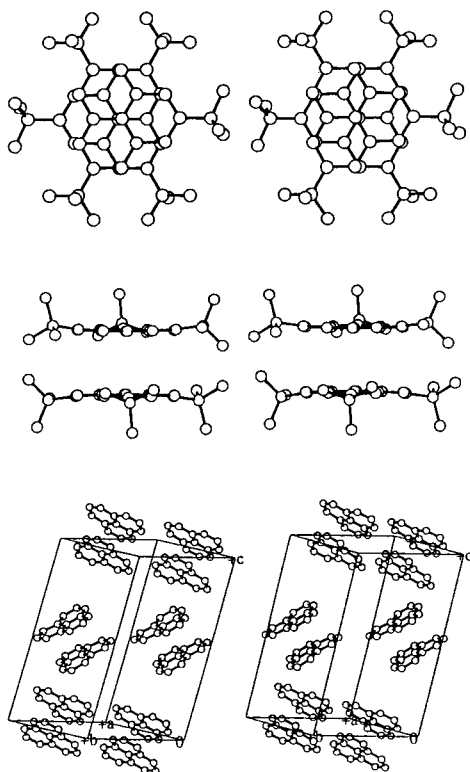


Figure 1. Stereoviews of crystal structure for **1b**

Å). Such short distances produce strong antiferromagnetic interactions and an electronic transition (see below). The dimeric pair stacks in a herringbone motif along the *c* axis.

The ESR spectrum of  $10^{-5}$  M toluene solution of **1b** showed a dominant septet hyperfine structure with an intensity ratio of 1:6:15:20:15:6:1. The hyperfine structure is due to six equivalent protons which are assigned to the phenalenyl ring protons. The observed *g* value is 2.0028, which is consistent with genuine spin-doublet hydrocarbon radicals. The observed hyperfine coupling constant is 0.620 mT, which is comparable with that of the parent phenalenyl.<sup>13</sup> Satellite signals arising from <sup>13</sup>C hyperfine interactions were observed. To characterize the bulk magnetic properties of the crystalline state, SQUID measurements of a polycrystalline sample were carried out in the range from 2 to 350 K in the

presence of 1T of static magnetic field.<sup>14</sup> The results showed that a ground-state spin-singlet formation occurred due to the dimerization of **1b** in the crystalline state. The observed large antiferromagnetic intermolecular exchange interaction ( $2J/k_B = -2000$  K) gave evidence for a strong bonding interaction between the phenalenyl radicals in the crystals.

The intermolecular interaction in the dimeric pair may be responsible for the strong and broad absorption band at  $\lambda_{\text{max}} = 510\text{--}700$  nm in the solid-state electronic spectrum measured in a dispersed KBr pellet, which is not observed in solution. The polarized reflection spectrum measured on the crystal plane (011) showed that the dispersion at  $15 \times 10^3\text{ cm}^{-1}$  is strongly polarized in the direction of  $\perp a$ . The line connecting the centers of the phenalenyl rings in the dimeric pair is almost perpendicular ( $80.1^{\circ}$ ) to the *a* axis, while is almost parallel ( $9.9^{\circ}$ ) to the  $\perp a$  direction on (011). Therefore, the band may be a charge-transfer band between two SOMOs in the dimeric pair, since the transition moment is polarized along the direction connecting the center of the phenalenyl rings. The energy of the SOMO was determined by the gas-phase He(I) photoelectron spectrum measured at  $153\text{ }^{\circ}\text{C}$ .<sup>15</sup> The lowest vertical ionization energy of 5.99 eV observed can be assigned to the ionization from the SOMO of the phenalenyl molecule.

Some selected properties of the ionic species were also investigated. The phenalenyl cation salt **1a**-BF<sub>4</sub> was obtained from **10** as red crystals by treatment with triphenylmethyl tetrafluoroborate in CH<sub>2</sub>Cl<sub>2</sub>.<sup>16</sup> The cyclic voltammogram of the cation gave two reduction waves at 0.27 and  $-1.26$  V.<sup>17</sup> In contrast to the parent phenalenyl cation giving irreversible waves, the corresponding waves of **1a** were found to be fully reversible. This result corresponds with the stability and isolability of the radical and also suggests the stability of the anion under experimental conditions. The  $\text{p}K_{\text{R}}^+$  value for the hexachloroantimonate of **1a** was determined to be 1.5–1.6.<sup>1a</sup> Attempted isolation of the anion **1c** failed even in an argon atmosphere, probably because of trace amounts of oxygen.<sup>18</sup> In conclusion, we have synthesized and characterized the stable neutral radical **1b** and the related ionic species **1a** and **1c** and have performed a crystal structure analysis for **1b**. To obtain a ferromagnetic overlap, the design of another overlap pattern of phenalenyl radicals by, for example, different substitution symmetry, in which the carbon atoms with positive and negative spin densities overlap each other, would an interesting future work.<sup>19</sup>

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**Supporting Information Available:** Experimental procedures, spectral data for all new compounds, and crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) For phenalenium hexachloroantimonate (red prisms): mp  $244.0\text{--}245\text{ }^{\circ}\text{C}$  dec. <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>SO<sub>4</sub>)  $\delta$  9.24 (s, 6H) H-1, 1.62 (s, 27H). <sup>13</sup>C NMR (150.85 MHz, D<sub>2</sub>SO<sub>4</sub>)  $\delta$  157.32 (C-2), 150.52 (C-1), 132.28 (C-3a), 118.36 (C-9b), 35.79 (C(CH<sub>3</sub>)<sub>3</sub>), 30.51 (C(CH<sub>3</sub>)<sub>3</sub>). UV/vis (concentrated H<sub>2</sub>SO<sub>4</sub>)  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 518 (sh, 1060), 500 (sh, 1170), 483 (sh, 1280), 466 (sh, 1280), 420 (57800), 259 (26900), 239 nm (35800).

(17) The cyclic voltammetry measurements were carried out in acetonitrile at room temperature with tetrabutylammonium perchlorate as the supporting electrolyte.

(18) (a) For anion **1c** (deep red solution): <sup>1</sup>H NMR (600 MHz, THF-*d*<sub>6</sub>)  $\delta$  5.33 (s, 6H) H-1, 1.07 (s, 27H). <sup>13</sup>C NMR (150.85 MHz, THF-*d*<sub>6</sub>)  $\delta$  150.35 (C-2), 143.86 (C-3a), 133.46 (C-9b), 100.92 (C-1), 34.35 (C(CH<sub>3</sub>)<sub>3</sub>), 31.78 (C(CH<sub>3</sub>)<sub>3</sub>). UV/vis (THF)  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 519 (2080), 439 (19700), 324 (2500), 265 (20700), 244 (13500), 217 nm (101000). (b) The anion **1c** (sodium and lithium salts) were recrystallized from hexane in a vacuum to give red prisms.

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