The First Electronically Stabilized Phenalenyl Radical: Effect of Substituents on Solution Chemistry and Solid-State Structure

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ABSTRACT: We report an investigation into the effect of oxygen and sulfur substitution on the dimerization of phenalenyl-based neutral radicals; these substituents are expected to electronically stabilize the free radical while sterically interfering with dimerization. The 1,3,4,9-tetramethoxyphenalenyl (**7a**) and 1-ethoxy-3,4,9-trimethoxyphenalenyl (**7b**) radicals are prepared by chemical reduction of the cation salts, but the crystals that are isolated from these solutions are shown to be composed of alkoxy-substituted peropyrenes by X-ray crystallography. Crystallization of 1,9-dithiophenalenyl (**8**) gives rise to a π-dimer, and this is the first example of a radical based on a single phenalenyl unit that has been stabilized against σ-dimerization in the solid state by electronic effects rather than by the presence of sterically bulky substituents.

Introduction

The development of organic conductors has depended on the generation of charge carriers by means of charge transfer between a donor and an acceptor species.[1−5] This has led to the development of a number of two-component materials, although recently both donor and acceptor were incorporated into a single molecule.[6,7] An alternative approach to the design of single component molecular conductors obviates the need for charge transfer. The synthesis of neutral radical conductors depends on the crystallization of spin-bearing molecules so that intermolecular orbital overlap provides the pathway for electronic conduction in the same way that it occurs between atoms in an elemental metal. The unpaired electrons serve as charge carriers, and the orbital overlap between the molecules usually leads to a half-filled energy band.

Odd-alternant hydrocarbons (OAHs) were the initial target of this approach;[8,9] phenalenyl (**1**) is especially attractive due to its high symmetry (D_{3h}) and an accessible triad of oxidation states: the diamagnetic cation, the paramagnetic radical, and the diamagnetic anion are all stable, planar species that have been characterized spectroscopically under anaerobic conditions.[10−15] However, despite numerous observations of phenalenyl-based radicals in solution, isolation of materials in the solid state has proven difficult, and reports of solid-state structures for phenalenyl radicals are sparse. This difficulty can be explained by the propensity of **1** to undergo dimerization by σ-association (Scheme 1), although the mode of dimerization has usually been inferred rather than unambiguously demonstrated. Additionally, phenalenyl radicals can undergo dimerization by π-association.[10,16] The σ-dimerization of **1** has been monitored by solution-phase EPR spectroscopy: cooling a sample of **1** gives the diamagnetic dimer **2**, which disassociates back to the radical on warming.[17] The dimer undergoes further reaction at room temperature to produce peropyrene **3** and another unidentified hydroaromatic compound.[13,18,19] Recently, it was shown by electron spin resonance (ESR) studies that the

Scheme 1
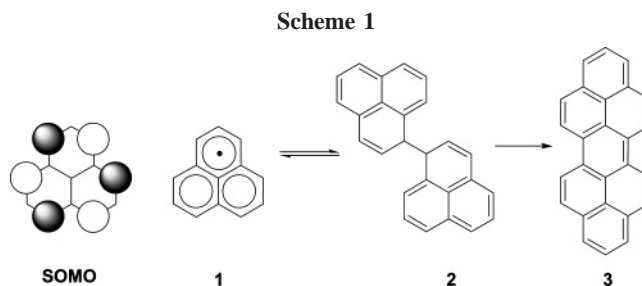
2-azaphenalenyl radical is stabilized toward dimerization in solution as a result of the replacement of one CH by a nitrogen atom, while attempts to trap the radical by complexation to copper led to the isolation and solid-state characterization of the σ-dimer chelated with the copper(II) center.[17b]

The suppression of the σ-dimerization process is an important aspect of the successful development of phenalenyl-based neutral radical conductors, and the accomplishment of this goal has been the key development in realizing conductors based on the spiro-bis(1,9-disubstituted phenalenyl)boron neutral radicals (**4a**, **4b**, and **4c**, Chart 1).[20−28] In these systems, the unpaired spin is stabilized by resonance over two phenalenyl units via spiro-conjugation at the boron center. This strategy is effective in suppressing dimerization in most cases, although association through σ- and π-dimers is known.[21,22,25−27,29]
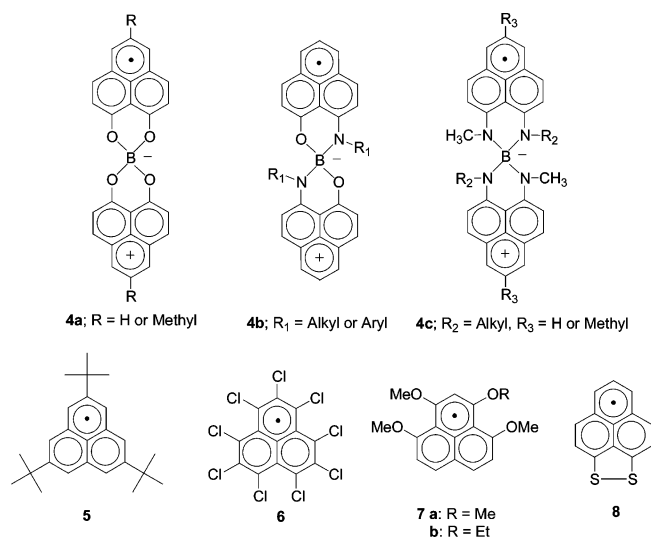
Radicals based on a single phenalenyl unit are less common, and structural characterization has been previously accomplished on only two compounds. In both of these systems, σ-dimerization has been suppressed by using steric bulk on the periphery of **1**. The crystallization of the tris(t-butyl)-substituted compound **5** was the first example of the solid-state characterization of a neutral radical based on a single phenalenyl unit.[10] The radical **5** crystallizes as centrosymmetric π-dimers, and as a result the bulk material is electrically insulating. More recently, the perchlorophenalenyl radical **6** was structurally characterized, and it was shown that the molecules stack in columns of quasi-superimposed radicals.[30] The bulky chlorine atoms on the periphery of the molecule prevent close contacts between the phenalenyl units, and accordingly orbital overlap within the stacks is small, leading to a Mott insulating state.

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Chart 1

4a; R = H or Methyl   **4b**; R₁ = Alkyl or Aryl   **4c**; R₂ = Alkyl, R₃ = H or Methyl

5   **6**   **7 a**: R = Me **b**: R = Et   **8**

Systems **5** and **6** illustrate the balance that must be achieved when employing substituents to prevent dimerization in phenalenyl radicals; the substituents must act to prevent dimerization without disrupting the communication between the radicals in the solid-state that is necessary for conductivity. Achieving this balance is a difficult challenge, and it was not met in **5** and **6** as both systems are electrical insulators. In this report, we have taken an alternative approach to the design of neutral radical conductors in which oxygen and sulfur substitution is employed to examine the role of functionalization in stabilizing the phenalenyl system against dimerization. Heteroatoms are known to be effective in the delocalization of spin density and concomitant stabilization of radicals,[31–38] so the use of these substituents at the active carbon positions of **1** should act to electronically stabilize the radical while also sterically interfering with dimerization.

While the target molecules **7a** and **8** have been observed in solution,[39,40] neither the radicals or their corresponding cations have been subjected to solid-state characterization. In this manuscript, we report the synthesis and solid-state characterization of the cationic species **7a**⁺OTf⁻ and **8**⁺PS₂(OMe)₂⁻. While the electrochemistry of the cations is apparently well behaved, it is only the solutions of **8** that give rise to a radical product in the solid state. Reduction of both **7a**⁺OTf⁻ and **7b**⁺OTf⁻ leads to solutions of the radicals; however, on crystallization the radicals dimerize and rearrange to form derivatives of peropyrene (Scheme 1). The product resulting from rearrangement of **7b** has been investigated by X-ray crystallography and constitutes the only structurally characterized peropyrene molecule.

Crystallization of **8** does not yield a peropyrene derivative, and the radicals remain discreet, although a strong π-association is observed in the solid state. This is the first example of a neutral radical based on a single phenalenyl unit that has been stabilized against σ-dimerization in the solid state by delocalization of the electron onto the substituents,[39] rather than by relying on steric hindrance.

Experimental Section

Materials. All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk and vacuum-line techniques. 3-Hydroxy-4,9-dimethoxyphenalenone[40] and 9-hydroxyphenalenone[50] were synthesized according to literature procedures. Methyl trifluoromethanesulfonate (Aldrich), ethyl trifluoromethanesulfonate (Aldrich), methyl *p*-toluenesulfonate (Aldrich), iodopentane (Aldrich), silver(I) oxide (Aldrich), phosphorus pentasulfide (Aldrich), and bis-

(pentamethylcyclopentadienyl)manganese(II) (Aldrich) were used as received. Tetrakis(dimethylamino)ethylene (TDAE, Aldrich) was distilled under argon prior to use. *N,N*-Dimethylformamide (VWR) and diethyl ether (EMD) were anhydrous grade and used as received. 1,2-Dichloroethane, chloroform, methanol, and isopropanol were ACS grade and used as received. Toluene and dichloromethane were ACS grade and distilled over sodium or calcium hydride, respectively, prior to use. The acetonitrile and toluene used for reduction chemistry were anhydrous grade (99.9%, Aldrich) and used as received. NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts downfield from the reference standard were assigned positive values. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer (at 2 cm⁻¹ resolution). Elemental analyses were performed by the Microanalysis Laboratory, University of Illinois, Urbana, IL.

3,4,9-Trimethoxyphenalenone 10. The reaction was carried out by a modification of the literature method.[40] Anhydrous potassium carbonate (2.0 g, 14.5 mmol) was added to a stirred solution of 3-hydroxy-4,9-dimethoxyphenalenone (1.0 g, 3.9 mmol) in 15 mL of anhydrous *N,N*-dimethylformamide. After 10 min, methyl *p*-toluenesulfonate (1.5 mL, 10 mmol) was slowly added, and the reaction mixture was taken to 100 °C. After 16 h, the reaction was filtered, and the solvent was distilled from the filtrate under reduced pressure to yield a viscous pale yellow oil. Purification by flash chromatography (silica gel, methanol:methylenechoride (5:95 v/v) eluant) afforded analytically pure material, yield: 0.72 g (2.7 mmol, 69%). Analytical data were identical to that reported previously.[40]

1,3,4,9-Tetramethoxyphenalenylium Trifluoromethanesulfonate 7a⁺OTf⁻. Methyl trifluoromethanesulfonate (0.65 mL, 5.5 mmol) was added to a stirred solution of **10** (1.35 g, 5.0 mmol) in 50 mL of dry dichloromethane. A yellow precipitate formed almost immediately. The reaction mixture was stirred at room temperature for 14 h, and the yellow solid was collected by filtration. Recrystallization from hot methanol afforded yellow needles of analytical purity, yield: 1.5 g (3.5 mmol, 70%). mp >300 °C. IR: 1623 (s), 1601 (m), 1565 (s), 1503 (w), 1490 (w), 1463 (vs), 1394 (m), 1379 (m), 1361 (w), 1280 (vs), 1261 (s), 1224 (m), 1189 (w), 1160 (s), 1110 (w), 1025 (vs), 954 (w), 905 (w), 856 (w), 828 (m), 753 (w), 723 (w), 681 (w), 667 (w), 660 (w), 635 (w) cm⁻¹. ¹H NMR (δ, CD₃CN): 8.57 (d, 2H), 7.58 (d, 2H), 6.93 (s, 1H), 4.31 (s, 6H), 4.26 (s, 6H). Anal. Calcd for C₁₈H₁₇O₇SF₃: C, 49.76; H, 3.95. Found: C, 49.58; H, 4.00.

1-Ethoxy-3,4,9-trimethoxyphenalenylium Trifluoromethanesulfonate 7b⁺OTf⁻. Ethyl trifluoromethanesulfonate (0.3 mL, 2.2 mmol) was added to a stirring solution of **10** (0.54 g, 2.0 mmol) in 50 mL of dry dichloromethane. A yellow precipitate formed almost immediately. The reaction mixture was stirred at room temperature for 14 h, and the yellow solid was collected by filtration. Recrystallization from hot methanol afforded yellow needles of analytical purity, yield: 0.47 g (1.05 mmol, 52%). mp 281 °C. IR: 1622 (s), 1598 (m), 1565 (s), 1500 (w), 1487 (w), 1463 (vs), 1428 (w), 1406 (w), 1395 (w), 1377 (m), 1359 (w), 1293 (s), 1275 (vs), 1261 (s), 1248 (m), 1221 (m), 1184 (m), 1170 (w), 1153 (s), 1138 (m), 1114 (w), 1029 (vs), 998 (w), 953 (w), 924 (w), 867 (w), 855 (m), 825 (m), 789 (w), 750 (w), 724 (w), 683 (w), 655 (m), 636 (s) cm⁻¹. ¹H NMR (δ, CD₃CN): 8.55 (d, 1H), 8.54 (d, 1H), 7.58 (br s, 1H), 7.55 (br s, 1H) 6.84 (d, 1H), 4.55 (dq, 2H), 4.27 (s, 3H), 4.25 (s, 6H), 1.62 (t, 3H). Anal. Calcd for C₁₉H₁₉O₇SF₃: C, 50.88; H, 4.28. Found: C, 50.89; H, 4.27.

Octamethoxyperopyrene 9a. A solution of TDAE (50 mg, 0.25 mmol) dissolved in 2 mL of dry acetonitrile was slowly added to an unstirred solution of **7a⁺OTf⁻** (87 mg, 0.2 mmol) in 5 mL of dry acetonitrile. The yellow solution turned brown immediately. The container was sealed inside of the glovebox for 4 days to afford dark orange microcrystals of **9a**, which were washed repeatedly with dry acetonitrile and dried to yield 20 mg (35%) of analytically pure material; mp >230 °C dec IR: 1612 (m), 1464 (vs), 1418 (w), 1377 (s), 1362 (m), 1348 (w), 1265 (m), 1201 (m), 1188 (m), 1132 (w), 1114 (w), 1093 (w), 1042 (w), 1017 (w), 959 (w), 831 (w), 806 (w), 720 (w), 681 (w), 666 (w), 618 (w) cm⁻¹. ¹H NMR (δ, CD₂Cl₂): 8.05 (s, 4H), 7.35 (s, 2H), 4.30 (s, 12H), 4.20 (s, 12H). Anal. Calcd for C₃₄H₃₀O₈: C, 72.06; H, 5.35. Found: C, 72.33; H, 5.18.

Diethoxy-hexamethoxyperopyrene 9b. A solution of TDAE (40 mg, 0.20 mmol) dissolved in 2 mL of dry acetonitrile was slowly added to an unstirred solution of **7b⁺OTf⁻** (66 mg, 0.15 mmol) in 6 mL of dry acetonitrile. The yellow solution turned brown immediately. The container was sealed inside of the glovebox for 4 days to afford red

crystals of **9b**, which were washed repeatedly with dry acetonitrile and dried to yield 18 mg (40%) of analytically pure material; mp >250 °C dec IR: 1613 (m), 1461 (vs), 1398 (w), 1376 (s), 1352 (m), 1267 (m), 1207 (m), 1193 (m), 1138 (w), 1115 (w), 1096 (w), 1047 (w), 833 (w), 812 (w), 797 (w), 722 (w), 680 (w), 667 (w), 634 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, The ^{1}H NMR spectrum of **9b** in CD$_2$Cl$_2$ was quite broad. The broadening is most likely a result of the presence of a mixture of cis- and trans-isomers, as evidenced by X-ray crystallography: δ 8.04 (br.s), 7.30 (br.s), 4.36 (br.), 4.26 (br.s), 4.15 (br.s), 1.62 (br.t). Anal. Calcd for C$_{36}$H$_{34}$O$_8$: C, 72.70; H, 5.77. Found: C, 73.23; H, 5.64. Because of the unstable nature of this compound, we were unable after numerous attempts on crystalline samples to obtain elemental analysis less than 0.5%.

9-Pentyloxyphenalenone 11. Iodopentane (2.2 mL, 0.017 mol) was added to a stirred slurry of 9-hydroxyphenalenone (10.0 g, 0.051 mol) and silver oxide (11.81 g, 0.051 mol) in 400 mL of 1,2-dichloroethane. The reaction was taken to reflux, and an additional 2.2 mL of iodopentane was added after 2, 4, and 6 h. After 16 h at reflux the reaction was cooled, and the brown precipitate of AgI was collected by filtration and washed with chloroform until the washes were colorless. The solvent was removed from the filtrate using a rotary evaporator to yield a yellow oil, which solidified on standing; yield: 9.60 g (0.036 mol, 71%). The material was of sufficient purity to be used in subsequent reactions; however, purification by column chromatography (Al$_2$O$_3$, diethyl ether eluant) afforded analytically pure material; mp 76−78 °C. IR: 3031 (vw), 1637 (vs), 1615 (s), 1578 (s), 1556 (vs), 1500 (m), 1400 (w), 1279 (s), 1251 (m), 1235 (s), 1186 (m), 1160 (m), 1124 (m), 1106 (vw), 1081 (vw), 1055 (vw), 1028 (s), 957 (w), 925 (w), 887 (vw), 841 (vs), 807 (w), 785 (vw), 761 (vw), 737 (w), 704 (w), 684 (w), 642 (m), 494 (m) cm^{-1}. ^{1}H NMR (δ, CDCl$_3$): 8.17 (d, 1H), 7.96 (d, 1H), 7.78 (d, 1H), 7.69 (d, 1H), 7.50 (t, 1H), 7.48 (d, 1H), 6.76 (d, 1H), 4.35 (t, 2H), 2.02 (p, 2H), 1.61 (m, 2H), 1.44 (m, 2H), 0.96 (t, 3H). Anal. Calcd. for C$_{18}$H$_{18}$O$_2$: C, 81.17; H, 6.81%. Found: C, 29.91; H, 0.51%.

1,9-Dithiophenalenylium Dithiophosphate Acid *O,O′*-Dimethyl Ester 8$^+$PS$_2$(OMe)$_2$$^-$. 9-Pentyloxyphenalenone **11** (4.0 g, 15.0 mmol) was added to a stirred slurry of phosphorus pentasulfide (8.0 g, 18.0 mmol) in 300 mL of toluene under inert atmosphere. The mixture turned brown immediately. After the reaction mixture was stirred for 16 h at room temperature, the toluene was removed by cryogenic distillation, and the resulting brown solid was dried in vacuo. Methanol (350 mL) was added, and the reaction was heated at reflux under inert atmosphere for 2 h, after which hot filtration through a medium glass frit afforded a brown solution. The solution was held at −20 °C for 2 h to afford a red microcrystalline precipitate of the product. This was collected by filtration, washed with methanol, and dried in air; yield: 1.20 g (3.0 mmol, 21%). Recrystallization from methanol afforded dark red needles of X-ray quality, mp 135−137 °C. IR: 3050 (vw), 1612 (m), 1579 (m), 1547 (m), 1408 (m), 1314 (w), 1302 (vw), 1244 (m), 1198 (w), 1172 (w), 1160 (vw), 1128 (w), 1088 (vw), 1062 (w), 1043 (w), 1017 (s), 902 (m), 855 (m), 800 (m), 779 (m), 768 (m), 749 (m), 668 (vs), 576 (vw), 525 (w), 486 (vw), 457 (w), 419 (s) cm^{-1}. ^{1}H NMR (δ, CD$_3$CN): 9.11 (d, 2H), 9.03 (d, 2H), 8.81 (d, 2H), 8.50 (t, 1H). MS (IE), m/z = 227. Anal. Calcd. for C$_{15}$H$_{13}$O$_2$PS$_4$: C, 46.86; H, 3.41%. Found: C, 47.29; H, 3.19%.

1,9-Dithiophenalenylium Trifluoromethanesulfonate 8$^+$OTf$^-$. Methyl trifluoromethanesulfonate (0.9 mL, 8.20 mmol) was added to a stirred slurry of **8$^+$PS$_2$(OMe)$_2$$^-$** (2.57 g, 6.68 mmol) in 100 mL of 1,2-dichloroethane under inert atmosphere, and the reaction was allowed to proceed overnight at room temperature. The resulting yellow solid was collected by filtration and dried in air; yield: 2.19 g (5.82 mmol, 87%). Recrystallization from isopropanol afforded yellow crystals, mp 296 − 298 °C. IR: 3057 (vw), 1615 (m), 1584 (m), 1551 (m), 1414 (m), 1315 (vw), 1250 (vs, br), 1222 (s), 1166 (s), 1130 (m), 1088 (w), 1065 (w), 1028 (s), 903 (m), 887 (w), 854 (m), 799 (m), 782 (w), 756 (w), 722 (w), 677 (m), 636 (vs), 573 (m), 517 (m), 482 (w) cm^{-1}. Anal. Calcd. for C$_{14}$H$_7$F$_3$O$_3$S$_3$: C, 44.67; H, 1.87%. Found: C, 44.98; H, 1.73%.

1,9-Dithiophenalenyl 8. **8$^+$OTf$^-$** (0.500 g, 1.33 mmol) and bis-(pentamethylcyclopentadienyl)manganese(II) (0.442 g, 1.35 mmol) were loaded into a Schlenk tube with 10 mL of anhydrous acetonitrile in a drybox. The reaction was sealed, removed from the dry box, and stirred at room temperature for 1 h to afford a black microcrystalline precipitate of **8**. This was collected by filtration on a fine glass frit, washed with dry acetonitrile, and dried in vacuo; yield: 0.242 g (1.06 mmol, 80%).

Scheme 2
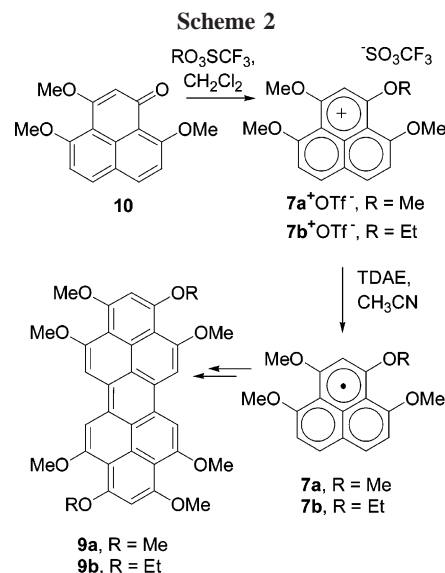
Recrystallization from carefully degassed anhydrous toluene (five freeze−pump−thaw cycles) afforded black crystals of X-ray quality, mp >120 °C (decomp). IR: 3042 (vw), 1525 (w), 1319 (w), 1266 (w), 1180 (w), 1145 (w), 1101 (w), 1056 (w), 929 (w), 882 (w), 860 (w), 841 (w), 828 (m), 798 (w), 777 (m), 743 (m), 672 (m), 660 (m), 559 (m), 531 (w), 517 (w), 466 (w) cm^{-1}. Anal. Calcd. for C$_{13}$H$_7$S$_2$: C, 68.68; H, 3.10%. Found: C, 67.10; H, 2.55%. Because of the unstable nature of this compound, we were unable after numerous attempts on crystalline samples to obtain elemental analysis less than 0.5%.
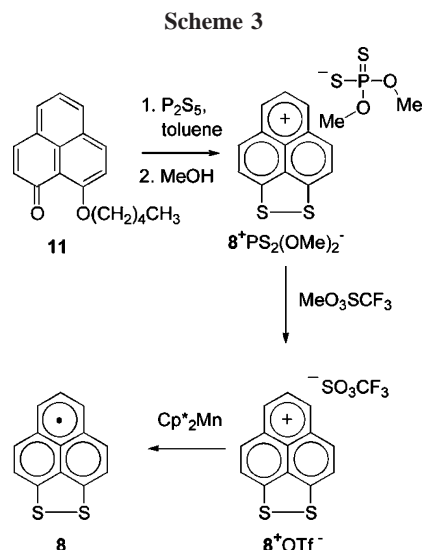
Cyclic Voltammetry. Cyclic voltammetry experiments were performed with a PINE Bipotentiostat, model AFCC1BP1, with scan rates of 50−100 mV s^{-1} on solutions (<10^{-3}M) of **7a$^+$OTf$^-$**, **7b$^+$OTf$^-$**, and **8$^+$OTf$^-$** in oxygen-free acetonitrile (dried by distillation from CaH$_2$) containing 0.1 M tetra-*n*-butyl-ammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc$^+$ couple of ferrocene at 0.38 V vs SCE. The $E_{pa} − E_{pc}$ separation of the reversible couple was within 10% of that of the Fc/Fc$^+$ couple.

X-ray Crystallography. Data were collected on an X8-APEX Bruker Kappa four circles X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å) for **7a$^+$OTf$^-$**, **7b$^+$OTf$^-$**, and **9b**. The X-ray data for **8$^+$PS$_2$(OMe)$_2$$^-$** and **8** were collected on a Bruker APEX2 (version 1.0−22) platform-CCD X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å). The crystals were mounted onto a glass fiber with epoxy resin. The crystallographic parameters and unit cell dimensions are summarized in Table 2. Absorption corrections were applied to the raw intensity data using the SADABS program.[51] Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. Full details, including bond lengths and bond angles, are given in Supporting Information.

Results and Discussion

Synthesis. Preparative routes to the cations **7a$^+$** and **8$^+$** have been described in the literature,[39,40] although in low yields. A new synthesis for **7a$^+$** and **7b$^+$** has been devised (Scheme 2), which involves the reaction of 3,4,9-trimethoxyphenalenone **10** with methyl or ethyl trifluoromethanesulfonate to afford the corresponding tetraalkoxyphenalenylium cations as triflate salts. Reduction of these salts in acetonitrile by use of tetrakis-(dimethylamino)ethylene (TDAE) produces solutions of the radical species **7a** and **7b**, as evidenced by EPR spectroscopy and cyclic voltammetry. However, on crystallization from solution σ-dimerization and ultimately rearomatization occurs, leading to the formation of the peropyrene derivatives **9a** and **9b**.

Scheme 3

A synthetic route to **8**$^+$Cl$^-$ was reported in 1978, which involved the reaction of 9-ethoxyphenalenone with excess phosphorus pentasulfide followed by treatment with hydrochloric acid.[39] We have used 9-pentyloxyphenalenone **11** as starting material since it is a tractable solid; reaction of this material with excess phosphorus pentasulfide in toluene affords a brown solid upon removal of the solvent (Scheme 3). Refluxing the solid in methanol generates the dithiophosphate *O,O'*-dimethyl ester anion and ultimately affords a dark red crystalline precipitate of **8**$^+$ PS$_2$(OMe)$_2$$^-$. Anion methathesis was accomplished by reaction of **8**$^+$PS$_2$(OMe)$_2$$^-$ with methyl trifluoromethanesulfonate to afford **8**$^+$OTf$^-$, which could be reduced to the corresponding radical by reaction with Cp*$_2$Mn. The resulting black microcrystalline precipitate of **8** was recrystallized from hot, carefully degassed toluene to afford black blocks
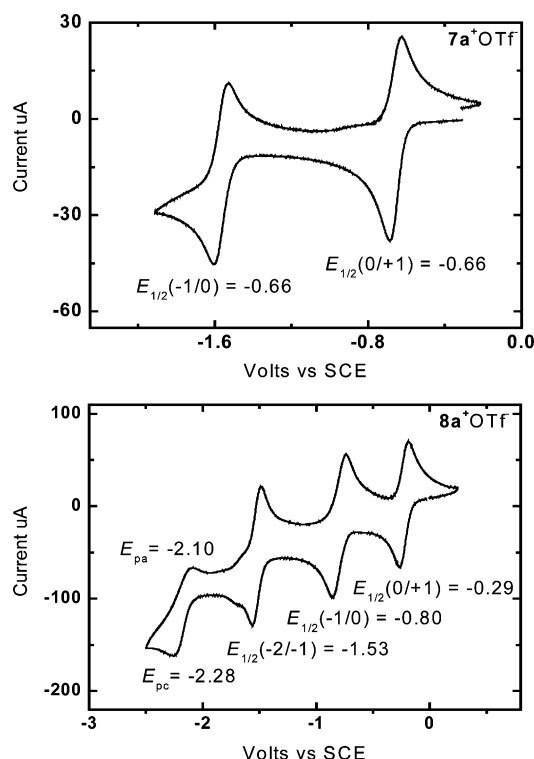
Figure 1. Cyclic voltammograms for **7a**$^+$OTf$^-$ (above) and **8**$^+$OTf$^-$ (below) in CH3CN, *n*-Bu4N$^+$PF6$^-$ supporting electrolyte. The cyclic voltammogram for **7b**+OTf- was almost identical to that for **7a**+OTf-.

Table 1. Half-Wave Redox and Cell Potentials (Volts vs SCE, in CH$_3$CN)

compound	1	7a	7b	8
$E^1_{1/2}$(0/+1)	0.7[a]	−0.66	−0.65	−0.23
$E^2_{1/2}$(−1/0)	−0.9[a]	−1.57	−1.55	−0.80
ΔE^{2-1}	−1.6[a]	−0.90	−0.90	−0.57
$E^3_{1/2}$(−2/−1)				−1.53

[a] Previously reported.[39]

Table 2. EPR Hyperfine Coupling Constants *a* (mT) and *g*-Values

Positions	**1**[a]	**7a**	**8**
a(a, i)	0.630	0.618	---
a(b, h)	0.182	0.152	0.151 (0.149)[b]
a(c, g)	0.630	0.045 (6H, methyl)	0.507 (0.506)[b]
a(d, f)	0.630	0.059 (6H, methyl)	0.540 (0.545)[b]
a(e)	0.182	0.206	0.156 (0.149)[b]
g	2.0027	2.0036	2.0051 (2.0042)[b]

[a] Literature values.[17]   [b] Literature values.[39]

of the radical. These recrystallization experiments were carried out quickly (over 1−2 h) as **8** decomposes readily in solution, even in the absence of oxygen. Crystals of **8** are stable in air for up to 24 h.

Electrochemistry. The ratio of the bandwidth *W* to the on-site Coulomb repulsion energy *U* is particularly important in molecular conductors and for a metal *U/W* < 1 is required.[41,42] Although *U* is a solid-state property that cannot be measured directly, it is usually approximated by the solution disproportionation potential (ΔE^{2-1}). The cyclic voltammetry of the triflate salts of **7a**$^+$, **7b**$^+$, and **8**$^+$ show two reversible waves (Figure 1) corresponding to the expected triad of oxidation states: a reversible (0/+1) wave and a reversible (−1/0) wave, together with additional reductions in the case of **8**;[39] the reduction potentials and the disproportionation potentials (ΔE^{2-1} = $E^2_{1/2}$ − $E^1_{1/2}$) are given in Table 1; E_{Pa}, E_{Pc}, and ΔE_P are provided in Supporting Information (Table S2).

The results of EPR experiments for **1**, **7**, and **8** are summarized in Table 2. The X-band EPR spectrum of **7a** (Figure 2), generated in situ by reduction of **7a**$^+$OTf$^-$ with cobaltocene in dichloromethane, exhibits a three line pattern as a result of a large coupling (0.618 mT) to the two equivalent hydrogen atoms that sit on the only two open active carbon positions of the molecule. There is a rich hyperfine pattern as a result of a much smaller coupling to the remaining hydrogen atoms on the
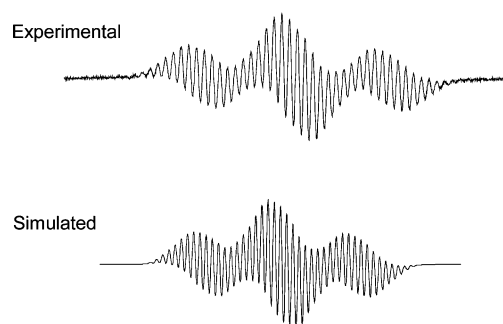
Figure 2. EPR spectrum of **7a** in CH2Cl2 at 293 K.
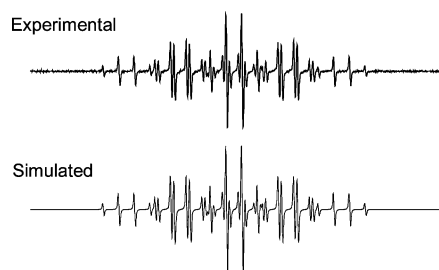
Figure 3. EPR spectrum of **8** in CH_2Cl_2 at 293 K.

periphery of the radical, and an even smaller coupling to the 12 methyl protons (two sets of six equivalent protons). An EPR spectrum was obtained for **7b**; however, the additional coupling produced by the ethoxy substituent caused the spectrum to collapse to a broad, unresolved triplet (Figure S1 in Supporting Information).

The X-band EPR spectrum of **8** (Figure 3) was generated from a crystalline sample of the radical dissolved in CH_2Cl_2 and consists of a five line pattern resulting from coupling to the hydrogen atoms at the four open active positions of the radical. It should be noted that the coupling constants at these positions, 0.507 and 0.540 mT, are significantly smaller than the values that were obtained for the open positions of **7a** (0.618 mT).

There is a marginal decrease in coupling at the active carbon positions on phenalenyl as a result of the methoxy substituents, from 0.630 mT for the parent radical **1** to 0.618 mT in **7a**. However, the use of a disulfide bridge in **8** produces a much more dramatic decrease to 0.507 and 0.540 mT as compared to **1**. This provides an explanation for the different modes of crystallization for these two materials. Radical **7a** undergoes the same type of σ-dimerization and rearrangement as the parent radical **1**, whereas **8** crystallizes as discreet dimers (vide infra).

Crystal Structures. X-ray crystal structures were obtained for **7a**⁺OTf⁻, **8**⁺PS₂(OMe)₂⁻, **9b**, and **8**, and the crystal data are summarized in Table 3. The X-ray structure for **7b**⁺OTf⁻ is provided in Supporting Information (Figure S2).

Packing diagrams of **7a**⁺OTf⁻ and **8**⁺PS₂(OMe)₂⁻ are given in Figure 4; both salts form a layered structure of cations and anions, wherein the cations are stacked in a head-to-tail fashion along the *x*-axis. The asymmetric unit of both structures is comprised of a single cation/anion pair, and the cations align into evenly spaced π-stacks.

Reduction of **7a**⁺OTf⁻ and **7b**⁺OTf⁻ using either TDAE or cobaltocene yielded peropyrene derivatives (Scheme 1); while
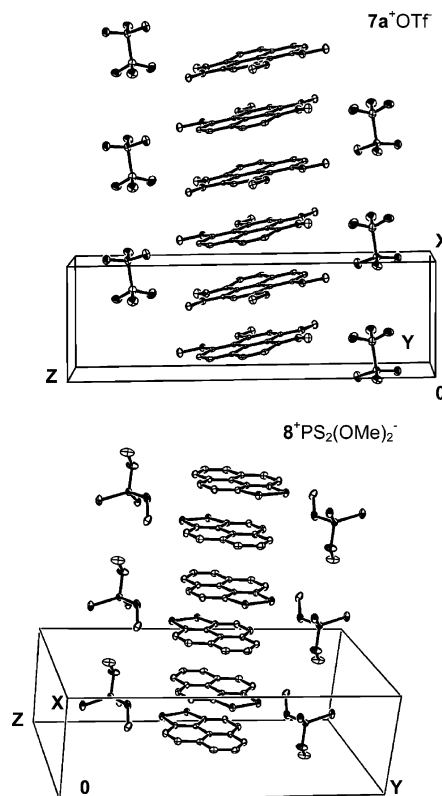
Figure 4. Crystal structures of **7a**⁺OTf⁻ (above) and **8**⁺PS₂(OMe)₂⁻ (below) illustrating the segregated stacks of cations and anions. The cations arrange into evenly spaced π-stacks in a head-to-tail fashion.

peropyrenes have been isolated previously, there are no reports of the solid-state characterization of a compound with this framework. It was not possible to obtain crystals of **9a** that were suitable for X-ray analysis, but in the case of **9b** suitable crystals were grown from acetonitrile. These large aromatic molecules (Figure 5) stack in a herringbone motif (Figure 6); note that the solid is a disordered 1:1 mixture of *cis*- and *trans*-ethoxy-isomers.
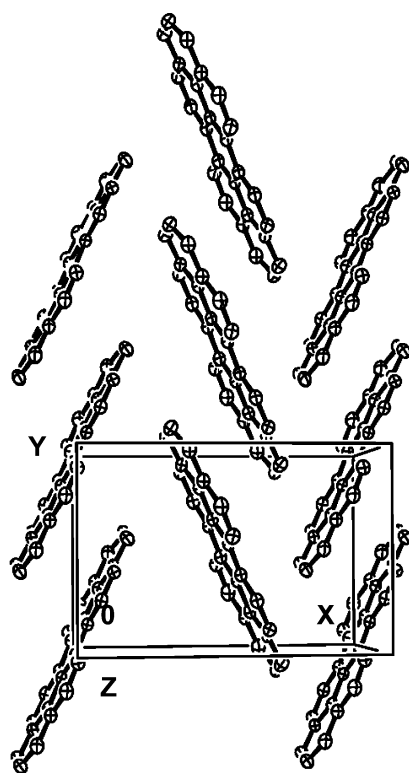
The reduction of **8**⁺OTf⁻ with Cp*₂Mn to give **8**, followed by recrystallization from toluene, affords black blocklike crystals suitable for X-ray analysis. A packing diagram for **8** is given in Figure 7. The molecule has C_{2v} symmetry and a planar geometry, with carbon−carbon bond lengths ranging from 1.383 to 1.429 Å, comparable to those in **5**.[10] The radicals stack in a sandwich herringbone motif of face-to-face π-dimers in which

Table 3. Crystallographic Data

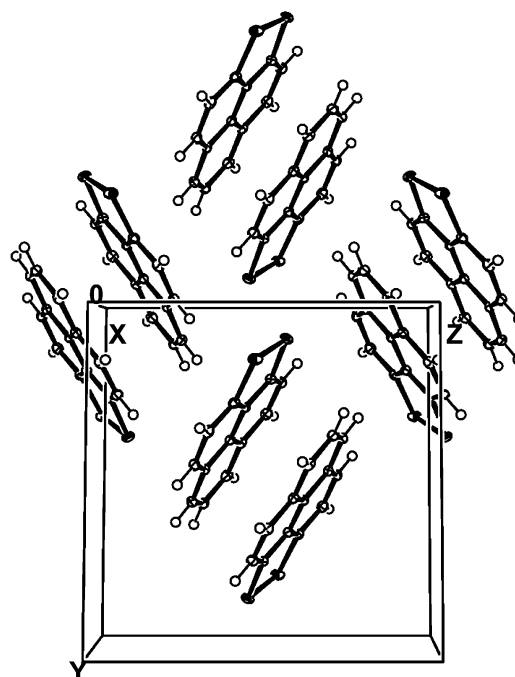| compound	**7a**⁺OTf⁻	**9b**	**8**⁺PS₂(OMe)₂⁻	**8**
formula	$C_{18}H_{17}F_3O_7S$	$C_{36}H_{34}O_8$	$C_{15}H_{13}O_2PS_4$	$C_{13}H_7S_2$
fw	434.38	594.7	384.46	227.31
temp, K	90(2)	90(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	6.8912(11)	11.9301(16)	6.8553(3)	8.0527(2)
b, Å	12.0507(18)	7.9101(11)	20.9286(8)	10.8005(3)
c, Å	21.879(3)	14.804(2)	11.2302(4)	11.1201(3)
β, (deg)	90.762(2)	97.731(3)	90.2280(10)	103.0760(10)
V, Å³	1816.8(5)	1384.3(3)	1611.20(11)	942.07(4)
Z	4	4	4	4
goodness-of-fit, F^2	1.036	1.035	1.054	1.021
data/restraints/ parameters	4253/0/266	1984/0/213	4902/0/214	2878/0/143
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0456, wR2 = 0.1159	R1 = 0.0699, wR2 = 0.1915	R1 = 0.0369, wR2 = 0.0901	R1 = 0.0268, wR2 = 0.0812
R indices (all data)	R1 = 0.0590, wR2 = 0.1245	R1 = 0.0895, wR2 = 0.2129	R1 = 0.0513, wR2 = 0.0952	R1 = 0.0309, wR2 = 0.0836
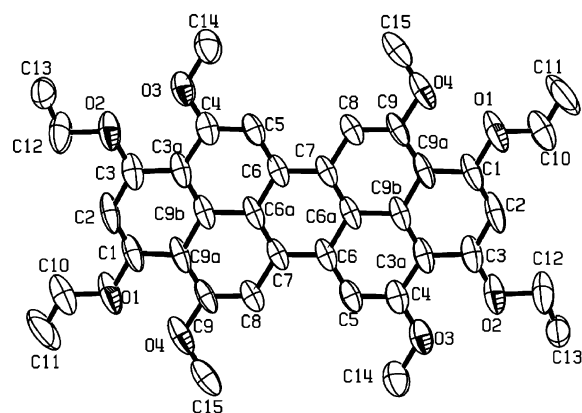
Figure 5. Molecular structure of **9b**. The asymmetric unit contains half of the molecule and the site occupancy ratio of the C11 and C13 atoms is 0.5 indicating that both the *cis-* and *trans*-isomers of **9b** are present as a 1:1 mixture.
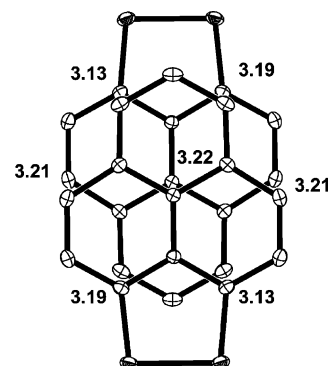

Figure 7. Packing diagram of **8** illustrating the herringbone stacking motif of head-to-tail π-dimers.

Figure 6. Packing diagram for **9b** illustrating the herringbone stacking motif. The substituents have been removed for clarity.

Figure 8. The closer view of a dimeric pair of radical **8** viewed normal to the molecular plane: the selective, symmetrical, π-overlap between all six pairs of spin bearing carbon atoms of the adjacent phenalenyl units reveals that the intermolecular distances (at 100 K) are well below the sum of the van der Waals atomic separation for carbon.

one molecule of the dimer is rotated 180° with respect to the other. A perpendicular view of the dimer pair is illustrated in Figure 8, which shows almost complete superposition of all six active carbon atoms of the phenalenyl nucleus with all intermolecular distances between the spin bearing carbon centers well below the sum of the van der Waals atomic separations for carbon, with closest C···C distance of 3.13 Å and a mean plane separation within the dimer of 3.161 Å at 100 K. This configuration minimizes the steric interference and maximizes the overlap between the singly occupied molecular orbitals (SOMOs) of the adjacent phenalenyl units. This can therefore be viewed as a fairly strong π-interaction between two radicals, as these distances are shorter than those reported in the sterically protected π-dimer **5** (3.201−3.323 Å)[10] and significantly shorter that those reported in **6** (3.5−3.6 Å).[30]

There are a number of other short contacts within the lattice, perhaps the most significant of which is the distance between neighboring sulfur atoms of 3.555 Å (Figure 9); this number falls just short of the van der Waals distance for pairs of sulfur atoms (3.6 Å).[43] The different pairs of π-dimers interact by repeating this short S···S contact throughout the crystal lattice (Figure 9). It has been observed previously in heterocyclic materials that the tendency of sulfur to form intermolecular contacts in the solid state is a major driving force in the mode of crystallization of these molecules.[44−47] In this case, it appears that there are two competing modes of association: the tendency for the phenalenyl units to associate in the solid state and the propensity for sulfur to form intermolecular contacts in the crystal lattice. Despite these relatively short S···S contacts, the dimers remain isolated with the electrons trapped within the dimer pairs, and pressed pellet conductivity measurements on **8** reveal that the material is insulating, with $\sigma_{RT} < 10^{-6}$ S cm^{-1}.

The absence of σ-dimerization observed in the solid-state structure of **8** is the most important feature; for the first time,
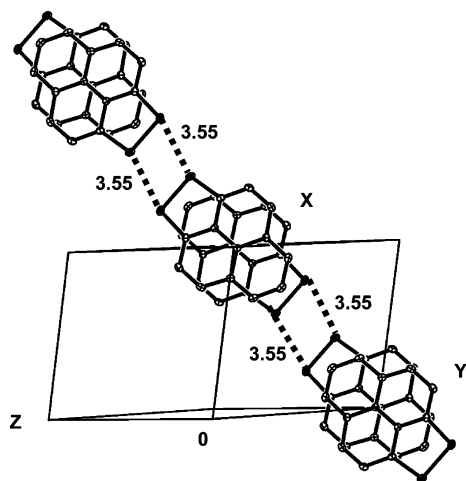
Figure 9. Illustration of the short intermolecular S···S contacts (3.55 Å at 100 K) between different dimeric pairs of radical **8**.

a neutral radical based on a single phenalenyl unit has been stabilized without the use of sterically bulky substituents to inhibit intermolecular C–C σ-bond formation. In this case, only two of the six active positions of the phenalenyl radical are occupied, yet the radicals remain discrete in the solid state. Carbon-based free radicals usually require steric hindrance to suppress σ-dimerization,[10,30,48,49] and we are not aware of any other systems that have been crystallized and characterized in the solid state purely as a result of the electronic effect of the attached substituents.

Summary and Conclusion

We have isolated and fully characterized the first phenalenyl-based neutral radical that is stabilized by electronic effects. The use of a disulfide bridge across two of the active positions of the phenalenyl unit in **8** is extremely effective in stabilizing the spin density on the radical. This was accomplished despite the fact that only two of the active positions of phenalenyl are sterically blocked. This behavior may be contrasted with the situation encountered in the presence of alkoxy substituents where we find that the presence of four of these functionalities was unable to inhibit the competing σ-dimerization with subsequent rearrangement and rearomatization to form peropyrenes **9a** and **9b**.

The stabilization of **8** without the use of steric bulk opens the door to a number of synthetic opportunities that vary the nature and number of heteroatom substituents on the phenalenyl radical periphery. Although the conductivity of **8** is low (σ_{RT} < 10^{-6} S/cm), we are optimistic that this novel approach will eventually lead to neutral radical materials with improved conductivity.

Supporting Information Available: An EPR spectrum for **7b**, as well as additional structural packing diagrams, tables of crystallographic and structural refinement data, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters are available free of charge via the Internet at http://pubs.acs.org.

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