Synthesis of Tetrachalcogenide-Substituted Phenalenyl Derivatives: Preparation and Solid-State Characterization of Bis(3,4,6,7-tetrathioalkyl-phenalenyl)boron Radicals

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Ⓢ *Supporting Information*

ABSTRACT: We report the synthesis and properties of a series of spiro-bis(3,4,6,7-tetrachalcogenide-substituted-phenalenyl)boron salts and two of the corresponding tetrathioalkyl-substituted spiro-bis(phenalenyl)boron radicals [tetrathiomethyl (**10**) and tetrathioethyl (**11**)] in which all of the active positions of the phenalenyl (PLY) nucleus are functionalized. In the solid state, radicals **10** and **11** exist as a weak π-dimers due to the steric congestion of the thioalkyl groups in the superimposed PLY units. As a result, the spins are localized in the isolated (nonsuperimposed) PLY rings, and the structure, magnetic susceptibility measurements, and band structure calculations confirm that these PLY units are unable to undergo strong intermolecular interaction as a result of the orientation of the thioalkyl groups.

There has been substantial progress in organic conductors based on neutral π-radicals and charge-transfer salts.[1−24] The neutral radical conductor approach involves the use of solid-state radicals possessing one unpaired electron.[25−28] Considerable effort has been invested in modifying both the functionality and geometry of the neutral radicals within the phenalenyl framework, and significant progress has been achieved with respect to molecular magnetism, bistability, switchable and spintronic materials, and conductivity.[8,10,29−35]

An important advantage of the spiro-bisphenalenyl boron radicals (Chart 1) is the quarter-filled band which reduces the on-site Coulomb correlation energy in comparison to that which is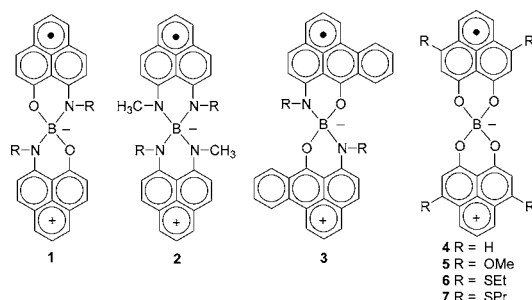 characteristic of the half-filled band associated with radicals containing a single phenalenyl unit.[36] Improved conductivity is associated with materials of large bandwidth (W) and a small on-site Coulomb correlation energy (U), that is, a higher ratio of W/U.[27] The experimentally measured solution-based cell potentials $E^{1/2}$ are often used as a measure of U;[37] although *a priori* estimation of the magnitude of the bandwidth (W) is not practical, the disproportionation potentials for a series of bisphenalenyl boron radicals provide logical trends in the on-site Coulomb correlation energy U.[12] Thus we require radical molecules that do not dimerize in the solid state yet display strong intermolecular interactions, so that sufficiently large electronic bandwidth W is generated to circumvent the on-site Coulomb barrier U. Understanding, let alone controlling, the manner in which phenalenyl radicals interact in the solid state poses a major challenge. Thus the design of new materials begins with the identification and exploration of low ΔE radical systems that can be easily modified, both structurally and electronically.

Recently we have explored the introduction of substituents into the phenalenyl ring system with the goal of reducing the ΔE values of the derived radicals.[12,38,39] The use of chalcogenide substituents is known to enhance intermolecular interactions and to electronically stabilize open-shell oxidation states, and this approach has led to the isolation of a number of organic conductors, ferromagnets, metals, and superconductors.[6,18,19,40−48]

Our previous synthetic work on the introduction of chalcogenides into the phenalenyl nucleus was primarily focused on the incorporation of the disulfide linkage and made use of oxidative conditions for the final step of the reaction, thereby leading to the initial isolation of a series of cations which could serve as precursors for the radicals shown in Chart 2.[39,49−51] Related compounds have been introduced by other research groups by use of similar methods.[52]

More recently we have explored the use of direct nucleophilic substitution on the 9-hydroxyphenalenone unit via the incorporation of the tosylate leaving group,[12,39] and it is the purpose of this Communication to report our successful synthesis of a number of spiro-bis(3,4,6,7-tetrachalcogenide-substituted-phenalenyl)boron salts (**10⁺−14⁺**, Chart 3) and the
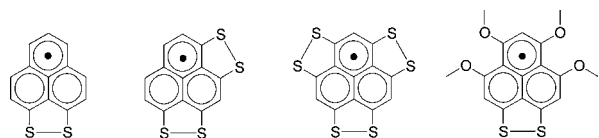
Chart 1. Spiro-bisphenalenyl Radicals

4 R = H
5 R = OMe
6 R = SEt
7 R = SPr
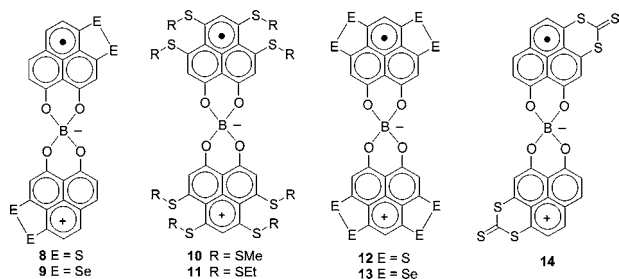
Chart 2. Dithio-Bridged Monophenalenyl Radicals

crystallization and solid-state characterization of two of the corresponding radicals, **10** and **11**.

Chart 3. Chalcogenide-Substituted Spiro-bisphenalenyl Radicals

8 E = S
9 E = Se
10 R = SMe
11 R = SEt
12 E = S
13 E = Se
14

The key intermediates in the present work are the tetratosylate (**V**) and the tetramesylate (**VI**), and we have found that the use of the mesylate considerably simplifies the workup of the reactions. The reaction of 9-hydroxyphenalenone-3,4,6,7-tetramesylate derivatives with potassium thio/selenoacetate gave the tetrachalcogenide-bridged 9-hydroxyphenalenone derivatives, whereas the thiocarbonato-bridged variant was obtained by the reaction of a mixture of carbon disulfide and potassium sulfide with 9-hydroxyphenalenone-3,4-ditosylate (Scheme 1). The spiro-bisphenalenyl boron salts were prepared by the reaction of the ligand and boron trichloride, with subsequent replacement of the counteranion by a metathesis reaction.

Cyclic voltammetry (CV) measurements were carried out for the spiro-bisphenalenyl boron salts 10^+-12^+, and the results are summarized in Table 1. The first two reductions of **10** and **11** are very close in acetonitrile, and the peaks merge in the CV
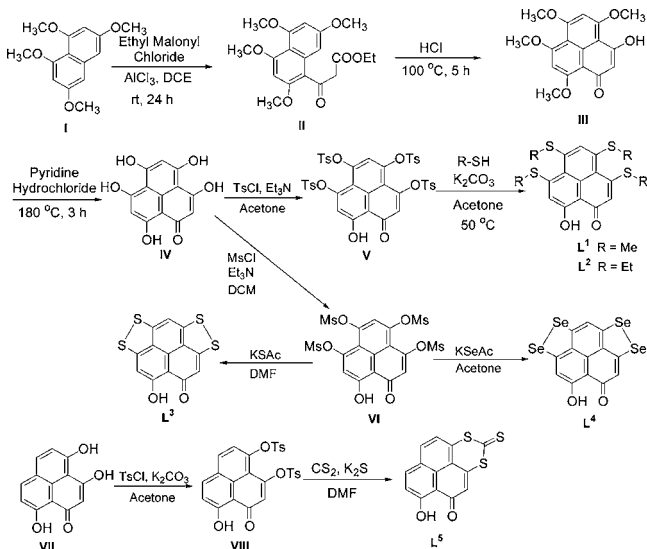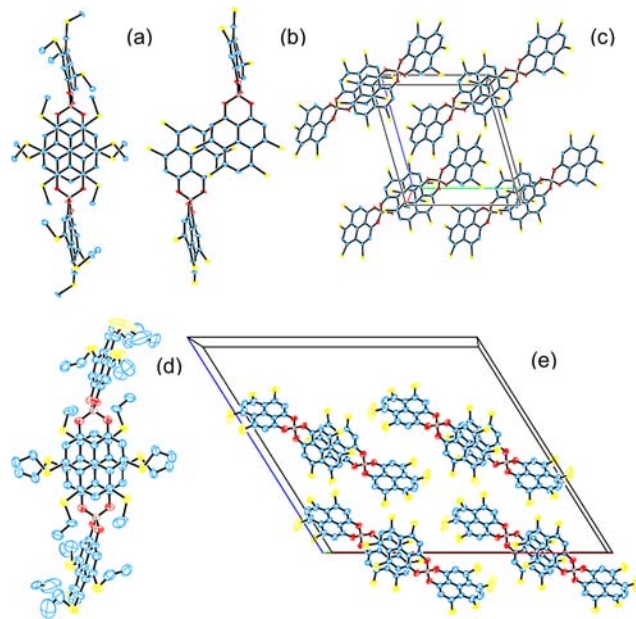
Scheme 1. Syntheses of Ligands

Table 1. Half-Wave Potentials and Disproportionation Potentials (Volts vs SCE) of Spiro-bisphenalenyl Boron Salts

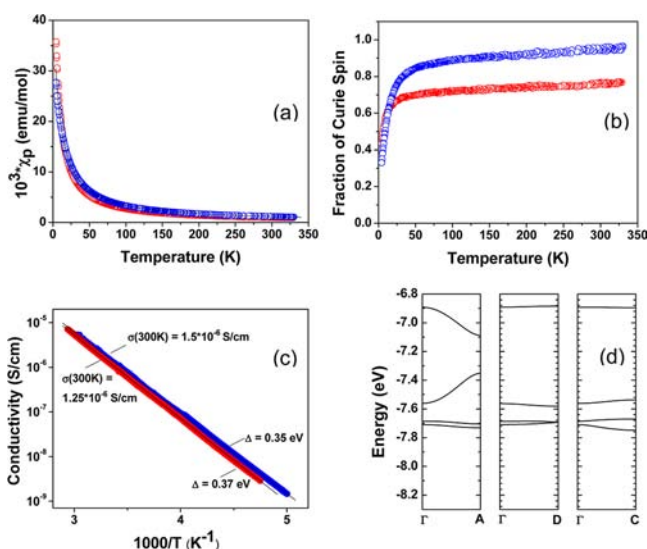| compound	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	$\Delta E_{2-1} = E_2^{1/2} - E_1^{1/2}$ (V)
[(PLY(NHx,O)]₂B (**1**)	−0.74	−1.11	−0.37[a]
[(PLY(NMe,NMe)]₂B (**2**)	−1.02	−1.37	−0.35[a]
[(PLY(O,O)]₂B (**4**)	−0.36	−0.65	−0.29[a]
[3,7-(OMe)₂-PLY(O,O)]₂B (**5**)	−0.78	−0.99	−0.21[a]
[3,7-(SR)₂-PLY(O,O)]₂B (**6, 7**)	−0.55	−0.75	−0.20[a]
[3,4,6,7-(SR)₄-PLY(O,O)]₂B (**10, 11**)	−0.73	−0.80	−0.07[a]
[3,4,6,7-(SR)₄-PLY(O,O)]₂B (**10, 11**)	−0.57	−0.72	−0.15[b]
[3,4-S,S-PLY(O,O)]₂B (**8**)	−0.49	−0.56	−0.07[c]
[3,4-Se,Se-PLY(O,O)]₂B (**9**)	−0.47	−0.55	−0.08[c]
[3,4,6,7-S,S,S,S-PLY(O,O)]₂B (**12**)	−0.72	−0.79	−0.07[c]

[a]MeCN. [b]1,2-Dichloroethane. [c]1,2-Dichlorobenzene.

experiments (Figure S1), while the two reduction processes are distinguishable in 1,2-dichloroethane, with potentials of −0.57 and −0.72 V, respectively (Figures S2 and S3). Differential pulse voltammetry (DPV) experiments show two reduction processes for **10** and **11**, with $\Delta E_{2-1} = -0.07$ V in acetonitrile (Figure S1). The CV and DPV for the tetrasulfide-bridged compound **12** in 1,2-dichlorobenzene ($\Delta E_{2-1} = -0.07$ V) are quite similar to those of compound **8**[12] (Figures S4 and S5), and we were not successful in obtaining well-resolved CVs for **13** or **14** in any of the solvents that we tested. Radicals **10** and **11** were crystallized, and they have the lowest disproportionation potentials (Table 1) among the phenalenyl-based and heterocyclic radicals that have been characterized in the solid state.[7,31,53]

Figure 1. (a) Radical π-dimers of **10**. (b) Interdimer interaction of the superimposed PLY rings, showing S⋯C (3.59 Å) and C⋯C (3.68 Å) interactions along the *a* axis. (c) Packing of **10**. Alkyl groups are omitted for clarity. (d) Radical π-dimers of **11** [solvent (MeCN) and disordered alkyl groups omitted]. (e) Packing of **11**. Alkyl groups are omitted for clarity.

Single crystals of radicals **10** and **11** suitable for X-ray diffraction were obtained by reducing the respective cationic salts with tetrakis(dimethylamino)ethylene (TDAE) from an acetonitrile–dichloromethane solvent mixture inside a glovebox (Figure S6, Table S1). Both radicals exist as dimers (Figure 1a–d) with full superposition of six spin-bearing carbon atoms, although the intradimer C⋯C interactions are well over 3.4 Å due to the steric congestion between the alkyl groups in the superimposed PLY rings. The alkyl groups attached to the nonsuperimposed PLY rings are nearly perpendicular to the PLY plane, whereas the alkyl groups attached to the superimposed PLY ring are in-plane for both radicals **10** and **11**.

Magnetic susceptibility measurements are shown in Figure 2a; the paramagnetic components of the magnetic susceptibility

Figure 2. (a) Magnetic susceptibilities of **10** (red) and **11** (blue). Black line shows a Curie–Weiss fit of the magnetic data for **11**. (b) Fraction of Curie spins of **10** (red) and **11** (blue). (c) Single-crystal conductivities for **10** (red) and **11** (blue). (d) EHT band structure calculated from the experimental structure of **10** at 100 K. Dispersions along reciprocal cell axes where $A = [\,^1/_2\,0\,0]$, $D = [0\,^1/_2\,0]$, and $C = [0\,0\,^1/_2]$.

χ_p for both radicals **10** and **11** follow Curie–Weiss behavior, $\chi_\text{p} = C/(T - \theta)$, with Curie constants C corresponding to 0.291 and 0.366 emu/mol, respectively. Antiferromagnetic interactions associated with the dimeric nature of the radicals are apparent in the negative Weiss constants θ of −4.0 and −8.0 K and the reduced spin counts which are seen at low temperatures (Figure 2b). At room temperature the fraction of Curie spins per molecule is about 1 for radical **11** and 0.8 for **10** (Figure 2b); radical **10** is quite air sensitive, and this is reflected in the reduced spin count (see Supporting Information for further details). The conductivities of several crystals of **10** and **11** were measured, and variable-temperature single-crystal conductivity measurements show semiconducting behavior, with maximum room-temperature conductivities of $\sigma_\text{RT} = 1.25 \times 10^{-6}$ and 1.50×10^{-6} S cm^{-1} for **10** and **11**, respectively (Figure 2c, see Supporting Information for additional conductivity data). Extended Hückel theory (EHT) band structure calculations for **10** are presented in the form of dispersion curves for the crystal orbitals arising from the PLY SOMOs in Figure 2d. The largest band dispersion in **10** is

along a^* and reflects the interdimer S⋯C and C⋯C interactions along the a axis, associated with contacts between the superimposed PLY rings (Figure 1b); bond length–bond order regression analyses of the experimental structures for the radicals **10** and **11** (Tables S3–S7, Figures S12–S14)[54,55] show that the spin density is localized in the nonsuperimposed PLY unit, and this explains the low conductivities of the radicals, as the well-developed interactions are associated with unoccupied PLY units, which in turn may be related to the long contacts between the superimposed PLY rings as a result of the steric congestion arising from the alkyl groups.

While the strategy of lowering ΔE_{2-1} values with the introduction of electron-donating substituents at the active positions of the PLY nucleus has been shown to be effective in the thioalkyl derivatives discussed above, we believe that our recent synthetic successes which allow the introduction of tetrasulfide, tetraselenide, and dithiocarbonato functionalities (Chart 3) offer more promise for the development of highly conductive phenalenyl radicals. The introduction of these functionalities into the 9-hydroxyphenalenone system represents an important direction for our work, and we expect it will allow the removal of the steric congestion associated with the alkyl groups in radicals **10** and **11**.

The synthetic protocol reported herein provides a route to the full range of tetrasulfide-, tetraselenide-, and thiocarbonato-bridged derivatives of the 9-hydroxyphenalenone nucleus (Scheme 1), and we have been successful in preparing the tetrachalcogenide-spiro-bis(phenalenyl)boron salts [3,4,6,7-E,E,E,E-PLY(O,O)]$_2$B$^+$TFPB$^-$ [E = S (**12**$^+$TFPB$^-$), Se (**13**$^+$TFPB$^-$); TFPB$^-$ = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate], and the 3,4-dithiocarbonato-spiro-bis-(phenalenyl)boron salt (**14**$^+$TFPB$^-$) (Schemes S1 and S2); the X-ray crystal structure of the selenium derivative, **13**$^+$TFPB$^-$, is shown in Figure S16.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Experimental details; CV and DPV; crystallographic data (CIF) for **10** (at 100 and 293 K), **11**, and **13**$^+$; coordinates of atoms for band structure calculation for **10**; theoretical calculations; plots of bond order versus bond length; variable-temperature magnetic susceptibility and conductivity plots for **10** and **11**; pictures of wired crystals; crystal face indexing; and crystalline radicals of **10** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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