Dithiazolodithiazolyl Radicals: Substituent Effects on Solid State Structures and Properties

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A general synthetic route to the pyridine-bridged dithiazolodithiazolyl framework R2BPR1, involving N-alkylation of a 4-substituted 2,6-dichloropyridine, followed by amination and double Herz cyclization with S2Cl2, has been developed. The radicals R2BPMe (R2 = Me, Ph) have been prepared and characterized by EPR spectroscopy and cyclic voltammetry. Their crystal structures have been determined by X-ray crystallography. Both structures consist of undimerized slipped radical π-stacks. Lateral interactions in MeBPMe (space group P21/c) generate chainlike arrays with radicals linked by inversion centers; there are no close interchain S–S contacts. By contrast, in PhBPMe (space group P3121) the radical π-stacks are nested about 31 axes, so as to produce an extensive 2-dimensional network of intermolecular S–S interactions. Variable-temperature magnetic susceptibility measurements reveal that MeBPMe is essentially paramagnetic, whereas PhBPMe displays strong antiferromagnetic coupling. A value of $U = -149 \text{ cm}^{-1}$ has been estimated by using a Bonner–Fisher anti-ferromagnetic chain model. Pressed pellet conductivity measurements indicate values of $\sigma_{RT} \approx 10^{-5} \text{ S cm}^{-1}$ for both R2BPMe compounds (R2 = Me, Ph), suggesting Mott insulating ground states. The structural results and transport properties are discussed in the light of extended Hückel theory band structure calculations.

Introduction

The concept of using neutral radicals as building blocks for molecular conductors provides an appealing alternative to conventional charge-transfer salts.1 The model is based on the idea that a stacked array of π-radicals, each with one unpaired electron, will be associated with a half-filled energy band, and hence possess a metallic ground state.2 There are, however, several shortcomings to this model. First, any 1-dimensional half-filled energy band is prone to Peierls instability, i.e., the radicals associate into closed shell dimers.3 Second, if dimerization can be suppressed, e.g., by steric bulk, the resulting low bandwidth $W$, coupled with the high on-site Coulomb repulsion energy $U$, proves conductivity thus requires materials with a high $W/U$ ratio, i.e., systems with a large bandwidth and a small on-site Coulomb repulsion energy $U$ associated with a half-filled band, leads to a Mott insulating state.4 Essentially the spins are trapped on the radicals and charge transport is suppressed. Improved conductivity thus requires materials with a high $W/U$ ratio, i.e., systems with a large bandwidth and a small on-site Coulomb repulsion energy $U$.


(6) $\Delta H_{\text{disp}}$ is the enthalpy change for the conversion of two gas-phase radicals R into a cation/anion pair, i.e., $2 R \rightarrow \text{R}^+ + \text{R}^-$; and accordingly is equal to the difference between the ionization potential (IP) and electron affinity (EA) values. The solution-based cell potential $E_{\text{cell}} = E_{\text{ox}} - E_{\text{red}}$ is the difference between the half-wave potentials for the oxidation and reduction processes.
computation. Alternatively, solution based cell potential $E_{\text{cell}}$ which are generally accessible by experiment, provide an effective mirror to solid-state characteristics. Using either criterion, the working prescription for good conductivity requires radicals with good ion energetics, i.e., low $\Delta H_{\text{disp}}$ and $E_{\text{cell}}$ values. The resonance-stabilized 1,2,3-dithiazolo-1,2,3-dithiazoulol (or bis-DTA) framework $R_2BPR_1$ represents an appealing system, conforming to both the energetic and structural criteria noted above. Recently, we reported the synthesis and structural characterization of the first examples ($R_1 = Me, Et, Pr; R_2 = Cl$). A recent study (R1 = Me) has also been carried out and is reported in detail in this issue.

In the present work, we have explored these issues by using a “double Herz” condensation of bis-DTAs is unlikely to change as a function of $R_1$ and $R_2$, the electronic bandwidth $W$ will very much depend on the way in which the substituents modify solid-state packing. To explore these issues we have sought to develop synthetic routes to $R_2BPR_1$ radicals, with the focus being on the need to incorporate a wide range of substituents in the $R_2$ site. Herein we describe the preparation, EPR, and electrochemical characterization of the methyl- and phenyl-substituted compounds $MeBPM$ and $PhBPM$

**Results**

**Synthesis.** We have reported a convenient synthesis of bis-DTA derivatives by using a “double Herz” condensation of N-methyl-2,6-diaminopyridinium triflate 2 ($R_2 = H$) with sulfur monochloride (Scheme 1). The reaction is performed at reflux in acetonitrile, the product is the triflate salt of the corresponding chloro-substituted cation, i.e., $[1][OTf]_2$ ($R_2 = H, R_2 = Cl$). Using milder reaction conditions (room temperature in the presence of an auxiliary base) the prototypical derivatives $[1][Cl]_2$ ($R_1 = Me, R_2 = H$) can be obtained.

To explore the generality of this reaction, with a view to incorporating a range of $R_2$ substituents into the bis-DTA framework, we have developed a straightforward method for preparing 4-substituted 2,6-diaminopyridinium salts $[2][OTf]_2$ ($R_2 = H, Me, Ph$) starting from the corresponding 2,6-dichloropyridine. Thus, methylation of 3 ($R_2 = H, Me, Ph$) with methyl triflate provides the N-methylated salt 4 ($R_2 = H, Me, Ph$) in high yield. Treatment of 4 with ammonia then affords the desired N-methyl-diaminopyridinium triflate 2 ($R_2 = H, Me, Ph$). The double Herz condensation of 2 ($R_2 = Me, Ph$) with $S_2Cl_2$ at reflux in acetonitrile proceeds in moderate to high yields to give the appropriate bis-DTA triflate $[1][OTf]_2$ ($R_1 = Me, R_2 = Me, Ph$), although for $R_2 = Me$ reaction times must be minimized in order to prevent chlorination of the methyl group. As in our earlier work, decamethylferrocene serves as an effective one-electron reducing agent for converting the salts $[1][OTf]_2$ ($R_1 = Me, R_2 = Me, Ph$) into the radicals $1$, i.e., $MeBPM$ and $PhBPM$.

**EPR Spectra and Electrochemistry.** The X-band EPR spectra of $R_2BPM$ ($R_2 = Me, Ph$), recorded in CH$_2$Cl$_2$ at room temperature, are similar to those observed for other bis-DTA radicals, with a rich hyperfine pattern dominated by coupling to two equivalent dithiazolyl nitrogens, the value of $a_N$ being approximately one-half of that observed in monofunctional 1,2,3-DTA radicals. There is also weaker coupling to the pyridine nitrogen and to the N-methyl protons. The presence of a phenyl group in $PhBPM$ introduces additional coupling, as a result of which the spectrum collapses to a broad interaction.

### Chart 1

![Chart 1](image1)

### Scheme 1

![Scheme 1](image2)

the basal (R2) methyl group, were extracted by full
(Figure 1), and all the MeBPMe, however, a well resolved spectrum is observed
coupling constant can be extracted (Table 1). For
a unresolved quintet, from which only the largest
three waves are observed (Figure 2), corresponding to
in the
unresolved.

Figure 1. EPR spectrum of MeBPMe in CH2Cl2 (above) and
simulation (below); SW = 3.0 mT; L/G ratio = 1.00; LW = 0.01 mT.

Table 2. Solution Half-Wave\(^a\) and Cell\(^b\) Potentials (V) for
R2BPMe Radicals 1 (R2 = Cl, H, Me, Ph)

<table>
<thead>
<tr>
<th></th>
<th>E(_{1/2}) ((^{-1/2}))</th>
<th>E(_{1/2}) ((^{-1/2}))</th>
<th>E(_{1/2}) ((^{-1/2}))</th>
<th>E(_{1/2}) ((^{-1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIBPMe</td>
<td>-0.835</td>
<td>0.005</td>
<td>1.415</td>
<td>0.830</td>
</tr>
<tr>
<td>HBPMe</td>
<td>-0.95()</td>
<td>-0.130</td>
<td>1.294</td>
<td>0.78()</td>
</tr>
<tr>
<td>PhBPMe</td>
<td>-0.956</td>
<td>-0.104</td>
<td>1.305</td>
<td>0.852</td>
</tr>
<tr>
<td>MeBPMe</td>
<td>-0.94()</td>
<td>-0.136</td>
<td>1.278</td>
<td>0.86()</td>
</tr>
</tbody>
</table>

\(^a\) In CH3CN, ref. SCE. \(^b\) E\(_{cell}\) = E\(_{1/2}\)((E1 - E0) - E\(_{1/2}\)((E1 - E0)).

unresolved quintet, from which only the largest \(a_N\) coupling constant can be extracted (Table 1). For MeBPMe, however, a well resolved spectrum is observed (Figure 1), and all the a values, including those from the basal (R2) methyl group, were extracted by full spectral simulation.

The results of cyclic voltammetric (CV) measurements on the [R2BPMe][OTf] salts (R2 = Me, Ph) are summarized in Table 2. As with other bis-DTA derivatives three waves are observed (Figure 2), corresponding to the \(-1/2, 1/1\), and \(-1/2, 1/1\) processes. In the case of PhBPMe all three waves are reversible, as they are in CIBPMe. For MeBPMe however, the \(-1/0\) process is irreversible (as it is for HBPMe). This feature we attribute to the more electropositive core of these latter radicals, and a greater tendency toward cleavage of one of the S–S bonds upon reduction of the radical. The effect of the more electropositive core is also manifested in the E\(_{1/2}\) values, which are shifted by 100–150 mV to

Figure 2. CV scan of [PhBPMe][OTf] in CH3CN, [n-BuH4][PF6] supporting electrolyte.

Table 3. Crystallographic Data

<table>
<thead>
<tr>
<th></th>
<th>MeBPMe</th>
<th>PhBPMe</th>
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<tr>
<td>formula</td>
<td>C7H6N3S4</td>
<td>C12H8N3S4</td>
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<td>260.39</td>
<td>322.45</td>
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<td>3.9919(7)</td>
<td>16.182(3)</td>
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<tr>
<td>b, Å</td>
<td>17.836(3)</td>
<td>16.182(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>13.888(2)</td>
<td>4.2947(12)</td>
</tr>
<tr>
<td>a, deg</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>b, deg</td>
<td>95.91(7)</td>
<td>90.0</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90.0</td>
<td>120.0</td>
</tr>
<tr>
<td>V, Å(^3)</td>
<td>983.5(3)</td>
<td>974.0(4)</td>
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<tr>
<td>(\rho) (calcd), g cm(^{-3})</td>
<td>1.758</td>
<td>1.649</td>
</tr>
<tr>
<td>space group</td>
<td>P2(_1)/c</td>
<td>P3(_2)/1</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>temp, K</td>
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<td>295(2)</td>
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<tr>
<td>(\mu), mm(^{-1})</td>
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</tr>
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<td>0.71073</td>
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<td>1500/0/101</td>
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<td>direct methods</td>
<td>direct methods</td>
</tr>
<tr>
<td>R, Rw (on F(^2))</td>
<td>0.0685, 0.1549</td>
<td>0.0363, 0.0725</td>
</tr>
</tbody>
</table>

more anodic potentials relative to those seen in CIBPMe. Nonetheless, the trends in both E\(_{1/2}\) and E\(_{cell}\) map well onto those observed for CIBPR radicals, and are broadly consistent with the computed gas phase IP, EA, and disproportionation enthalpy\(^\(\Delta H\)_{disp} = 1P - EA\) data for a model HBPH radical.\(^\(11\)\)

Crystal Structures. Crystal data for R2BPMe 1 (R1 = Me; R2 = Me, Ph) are summarized in Table 3, and a summary of pertinent intra- and intermolecular distance and angle information is given in Table 4. From a molecular perspective the bond lengths in each compound are slightly shorter than those seen in, for example, the oxidized ring of \([\text{PhBPMe}]\)\([\text{OTf}]\) in CH3CN, \([\text{n-BuH4}][\text{PF6}]\) Supporting electrolyte.


ring, and comparable to those seen between closed-shell benzo-bis(dithiazoles) and their radical cations.20

Crystals of MeBPMe belong to the monoclinic space group \(P2_1/c\), and consist of \(\pi\)-stacked arrays of undimerized radicals running along the \(x\) direction. The molecules are planar to within 0.037 Å. Figure 3 shows the unit cell, as viewed down the stacking axis, and illustrates the chainlike arrangement of radicals running parallel to \(y\). Linking these chains is a single intermolecular \(S1\)–\(S1'\) interaction (\(d1 = 3.368(2)\) Å) which is inside the van der Waals contact for two sulfurs (3.6 Å).21 There are no \(S\)–\(S\) contacts between the chains; the methyl groups on either side of the molecules serve as buffers to keep neighboring chains apart. Figure 4A shows a cartoon representation of this packing along with an analogous drawing of the arrangement of the radicals in \(R2\)BPMe \(1\) (\(R1 = Me\); \(R2\) = \(Me\)), and \(B\) (\(R2 = H, Cl\)).

Like MeBPMe, the crystal structure of PhBPMe consists of slipped \(\pi\)-stacks running along the \(z\) direction. In contrast to MeBPMe, there is a slight ruffling of the molecules, as a result of which the \(S1\) and \(N1\) atoms are tipped out of the mean plane (by 0.197 and 0.120 Å, respectively). A view of the unit cell down the stacking axis is shown in Figure 5. As can be seen the radicals form intersecting chains running parallel to both \(x\) and \(y\). The chains adopt a zigzag orientation as found in the \(R2\)BPMe (\(R2 = H, Cl\)) structures. However, as a result of the large size of the phenyl groups and the pseudo triangular shape of the molecule, the trigonal space group \(P3_121\) is adopted, and, given this crystal symmetry, the arrangement of radicals in the \(xy\) plane resembles a set of close-packed “wheels” (Figure 6), with the methyl and phenyl groups being corralled within these wheels. At the connector points for the wheels, the radicals are related by \(31\) screw axes, to produce a strong network of lateral \(S\)–\(S\) interactions. Figure 7 illustrates one of these 3-fold spiral arrays, as viewed from the side, and defines the close contacts between the inner \(S1\) and outer \(S2\) atoms along the spiral. Of these, the \(S1\)–\(S1'\) contact \(d1 = 3.287(1)\) Å along the spiral backbone is, to our knowledge, the shortest ever observed in a formally undimerized thiazyl radical. In addition, each \(S1\) atom is linked by slightly longer...
interactions d2 (3.507(1) Å) and d3 (3.467(1) Å) to neighboring S2′ atoms.

In both MeBPMe and PhBPMe the radicals form slipped π-stacks which pack into corrugated or herringbone arrays, as illustrated in Figure 8. The slipped stacks themselves can be characterized in terms of the slippage angle \( \theta \) and the perpendicular separation \( \delta \) between the mean planes (Figure 9). A comparison of the observed values for \( \theta \) and \( \delta \) in the known R2BPMe 1 radicals (Table 5) reveals a fairly tight distribution over a range of \( \theta \) values known\(^{12}\) to be associated with somewhat weak intermolecular overlap along the stacks. These issues, and their effect on conduction bandwidths, are explored below.

**Magnetic and Conductivity Measurements.** Magnetic susceptibility (\( \chi \)) measurements on MeBPMe reveal a temperature dependence (Figure 10A) which is consistent with normal Curie–Weiss\(^{22}\) behavior for a S = \( \frac{1}{2} \) system. Values of \( \chi_0 \), C, and \( \Theta \) are provided in Table 6. A plot of \( \chi T \) against T (Figure 10C) is relatively constant over the range 50–300 K, although the value of \( \chi T \) is a little less than that expected (0.375) for a S = \( \frac{1}{2} \) system. Below 50 K a slight antiferromagnetic tail is observed. These properties mirror those found in HBPMe and CIBPMe, although in the latter two cases weak ferromagnetic coupling was observed at lower temperatures. In contrast to all of these systems, a plot of \( \chi \) vs T for PhBPMe (Figure 10B) shows a marked deviation from Curie–Weiss behavior, with the value of \( \chi \) rising to a maximum and then falling away with decrease in T. The values of \( \chi_0 \), C, and \( \Theta \) extracted from a Curie–Weiss fit to the data above 230 K (Table 6) indicate a strongly antiferromagnetically coupled system. The rapid decrease in a plot of \( \chi T \) vs T (Figure 10C) below 300 K also heralds strong antiferromagnetic coupling. By applying a Bonner–Fisher anti-ferromag-

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**Table 5. π-Stack Slippage and Interplanar Separation Parameters in R2BPMe Radicals**

<table>
<thead>
<tr>
<th></th>
<th>HBPMe(^b)</th>
<th>CIBPMe(^c)</th>
<th>MeBPMe</th>
<th>PhBPMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta ) (deg)</td>
<td>62.04(7)</td>
<td>54.81(13)</td>
<td>61.34(2)</td>
<td>55.92(16)</td>
</tr>
<tr>
<td>( \delta ) (Å)</td>
<td>3.598(8)</td>
<td>3.470(5)</td>
<td>3.53(5)</td>
<td>3.557(6)</td>
</tr>
</tbody>
</table>

\(^a\) See Figure 9 for definitions of \( \tau \) and \( \delta \). \(^b\) Reference 13. \(^c\) Reference 12.
Setting $k$ seen in other radical (or 213 K). This value is large in comparison to those

Table 6. Magnetic Data for R2BPMe Radicals

<table>
<thead>
<tr>
<th>compound</th>
<th>$\chi_0$ (emu mol$^{-1}$)</th>
<th>C</th>
<th>$\Theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeBPMe$^a$</td>
<td>$-126$ H $10^{-6}$</td>
<td>0.326</td>
<td>-12</td>
</tr>
<tr>
<td>PhBPMe$^b$</td>
<td>$-172$ H $10^{-6}$</td>
<td>0.475</td>
<td>-177</td>
</tr>
</tbody>
</table>

$^a$ From a fit to the data above 5 K. $^b$ From a fit to the data above 230 K.

Plots of $\chi$ (A and B) and $\chi T$ (C) as a function of $T$ for R2BPMe 1 (R2 = Me, Ph).

Figure 10. Magnetic data for R2BPMe 1 (R2 = Me, Ph).

PhBPMe (Z = 3) would constitute the half-filled conduction band if the materials were metallic. The magnetic and conductivity data, however, indicate Mott insulating states, in which each orbital within the bands is half-filled.

Conclusions and Summary

The development of a simple, flexible 3-step procedure for producing the R2BPR1 framework starting from a 4-substituted 2,6-dichloropyridine opens the way for the design of new radical conductors. We have demonstrated the use of this technology in the preparation of two seminal examples, one with an alkyl and one with an aryl group in the R2-position. The crystallographic results reveal how the relative sizes and shapes of the R1 and R2 substituents can dramatically affect the packing of radical $\pi$-stacks and hence the dimensionality of lattice-wide electronic interactions. When the two substituents (R1 and R2) are of similar size, the radical $\pi$-stacks pack into chain-like arrays. However, when one

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(26) MeBPMe is monoclinic, and PhBPMe is trigonal. In neither case is there an exact equivalence of all the directions of the unit cell vectors in real and reciprocal space.
of the groups is more bulky, as in PhBPMe, clustering of the substituents, and therefore the radical π-stacks, can occur, to produce 2-dimensional networks of intermolecular S–S interactions. In the case of PhBPMe these tight (3.287(1) Å) S–S contacts are related by the 3-fold screw axes, and produce a unique close-packed array of molecular wheels.

Conductivity and magnetic measurements indicate that these materials are Mott insulators. Although substantial for a molecular species, the electronic bandwidth arising from the interacting radicals is still insufficient to overcome the onsite Coulomb repulsion U; i.e., all levels of the conduction band are half-filled (Figure 12). However, the extremely close S–S interactions found in PhBPMe, and the concomitant observation of strong antiferromagnetic coupling, suggests the incipient formation of a chemical bond. Materials exhibiting larger bandwidths, a necessary condition for metallic ground state, cannot be far away.

Experimental Section

General Procedures and Starting Materials. The reagents ethyl cyanocarbonate, ethyl benzoyl acetate, ethyl acetoacetate, phosphorus oxychloride, methyl trifluoromethanesulfonate (methyl triflate), ammonia gas, sulfur monochloride, and decamethylferrocene were obtained commercially and used as received. All solvents were of at least reagent grade; acetonitrile and dichloroethane were dried by distillation from CaH2 and K2CO3, and concentrated to dryness. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ).

Preparation of 2,6-Dichloro-4-phenylpyridine 3 (R2 = Ph). A mixture of 2,6-dichloro-4-phenylpyridine (8.37 g, 44.7 mmol) and 40 mL of POCl3 was heated in a Parr pressure reactor to 145 °C for 16 h. The reactor was cooled to room temperature, and the contents were carefully added to 500 mL of crushed ice. The brown mixture was extracted with 150 mL of dichloromethane, and the combined extracts were dried over K2CO3 and concentrated to dryness. The product 3 (R2 = Ph) was recrystallized from pentane; yield 8.89 g (21.8 mmol, 48%), mp 50–51 °C. IR: 1600 (w), 1580 (s), 1530 (s), 1496 (m), 1463 (m), 1417 (w), 1366 (s), 1316 (w), 1291 (w), 1234 (m), 1175 (s), 1120 (s), 1066 (w), 1000 (m), 985 (s), 869 (s), 810 (s), 767 (s), 695 (s), 628 (s) cm⁻¹. 1H NMR (δ, CDCl3): 7.47 (s, 2H), 7.58–7.61 and 7.49–7.51 (m, 5H, 3H).

Preparation of N-Methyl-2,6-dichloro-4-methyl-pyridinium Triflate 4 (R2 = Me). Methyl triflate (4.80 g, 29.2 mmol) was added to a stirred solution of 2,6-dichloro-4-methylpyridine 3 (R2 = Me) (4.4 g, 27.1 mmol) in 30 mL of dichloroethane. After 30 min a heavy white precipitate began to form. The mixture was then cooled to −20 °C for 1 h, and the white precipitate was collected by filtration and washed with cold dichloroethane. The product 4 (R2 = Me) was dried in vacuo and recrystallized from hot dichloroethane; yield 6.27 g (19.2 mmol, 71%), mp 137–138 °C. IR: 3075 (w), 3054 (w), 1616 (s), 1561 (w), 1549 (m), 1267 (s), 1227 (s), 1125 (s), 1180 (w), 1159 (s), 1144 (s), 1116 (m), 1082 (w), 1032 (s), 879 (w), 826 (w), 638 (s), 573 (w), 547 (w), 518 (w) cm⁻¹. 1H NMR (δ, CDCl3): 7.92 (s, 2H), 4.27 (s, 3H), 2.55 (s, 3H). Anal. Calcd for C18H12Cl2F3NO3S·ClO4: C, 29.46; H, 2.50; N, 3.45%. Found: C, 29.46; H, 2.29; N, 3.35%.

Preparation of N-Methyl-2,6-dichloro-4-phenyl-pyridinium Triflate 4 (R2 = Ph). Methyl triflate (4.2 g, 25.7 mmol) was added to a stirred mixture of 2,6-dichloro-4-phenylpyridine 3 (R2 = Ph) (4.89 g, 21.8 mmol) in 30 mL of dichloroethane. The reaction mixture was stirred for 16 h, and the white precipitate was collected by filtration, washed with cold dichloroethane, and dried in vacuo. The product 4 (R2 = Ph) was recrystallized from hot dichloroethane; yield 5.91 g (21.8 mmol, 70%), mp 194–195 °C. IR: 3086 (w), 1613 (s), 1594 (m), 1549 (m), 1400 (m), 1250 (s), 1227 (s), 1125 (s), 1076 (w), 1035 (s), 890 (m), 833 (m), 777 (s), 690 (m), 641 (s), 573 (m), 516 (m) cm⁻¹. Anal. Calcd for C18H12Cl2F3NO3S·ClO4: C, 40.22; H, 2.60; N, 3.45%. Found: C, 40.39; H, 2.50; N, 3.45%. 1H NMR (δ, CDCl3): 8.38 (s, 2H), 7.94–7.96 and 7.64–7.70 (m, 5H), 4.35 (s, 3H).

Preparation of N-Methyl-2,6-diamino-4-methyl-pyridinium Triflate 2 (R2 = Me). A solution of 4 (R2 = Me) (16.5 g, 50.8 mmol) was cooled to 0 °C and saturated with ammonia gas. A white precipitate formed immediately and the solution became orange. The saturated solution was filtered and passed through a glass bead pressure reactor and heated, with stirring, to 75 °C. After 16 h the vessel was cooled to room temperature and vented. The mixture was heated to reflux for an additional 2 h to release excess ammonia, cooled to room temperature, and the white precipitate was filtered off. The filtrate was concentrated to dryness and the product 2 (R2 = Me) recrystallized from acetonitrile/dichloroethane (1:30) mixture; yield 4.93 g (15.2 mmol, 70%), mp 194–195 °C. IR: 3086 (w), 1613 (s), 1594 (m), 1549 (m), 1400 (m), 1250 (s), 1227 (s), 1125 (s), 1076 (w), 1035 (s), 890 (m), 833 (m), 777 (s), 690 (m), 641 (s), 573 (m), 516 (m) cm⁻¹. Anal. Calcd for C18H12Cl2F3NO3S·ClO4: C, 40.22; H, 2.60; N, 3.45%. Found: C, 40.39; H, 2.50; N, 3.45%. 1H NMR (δ, CDCl3): 8.38 (s, 2H), 7.94–7.96 and 7.64–7.70 (m, 5H), 4.35 (s, 3H).

Preparation of N-Methyl-2,6-diamino-4-phenyl-pyridinium Triflate 2 (R2 = Ph). A solution of 4 (R2 = Ph) (4.29 g, 11.0 mmol) was cooled to 0 °C and saturated with ammonia gas. The white precipitate formed immediately and the solution became orange. The saturated solution was filtered and passed through a glass bead pressure reactor and heated, with stirring, to 75 °C. After 16 h the vessel was cooled to room temperature and vented. The mixture was heated to reflux for an additional 2 h to release excess ammonia, cooled to room temperature, and the white precipitate was filtered off. The filtrate was concentrated to dryness and the product 2 (R2 = Ph) recrystallized from acetonitrile/dichloroethane (1:30) mixture; yield 13.2 g (45.9 mmol, 89%), mp 108–111 °C. IR: 3414 (m), 3349 (m), 3233 (m), 1672 (m), 1644 (m), 1499 (w), 1461 (s), 1275 (m), 1168 (m), 1025 (s), 818 (w), 639 (m), 516 (w) cm⁻¹. Anal. Calcd for C30H28F6N4O12S·ClO4·2H2O: C, 33.45; H, 4.21; N, 14.63%. Found: C, 33.56; H, 4.14; N, 14.60%. 1H NMR (δ, CD3CN): 6.05 (s, 2H), 3.39 (s, 3H), 2.16 (s, 3H).
gas. A white precipitate formed immediately and the solution became yellow. The saturated solution was sealed in a glass pressure reactor and heated, with stirring, to 75 °C. After 16 h the vessel was cooled to room temperature and the white precipitate was filtered off. The filtrate was concentrated to dryness and the product (R2 = Ph) recrystallized from acetonitrile yields 2.05 g (8.64 mmol; 78%).

Recrystallization from hot, degassed (5 freeze–thaw cycles) toluene afforded metallic red needles. IR: 1529 (w), 1427 (s), 1340 (w), 1284 (w), 1205 (s), 1171 (s), 1075 (m), 980 (m), 750 (w), 647 (s), 587 (w) cm⁻¹. Anal. Calc.: C, 33.11; H, 1.71; N, 8.91%. Found: C, 33.11; H, 1.71; N, 8.70%. H NMR (δ, CDCl₃): 7.73–7.55 (m, 5H), 6.35 (s, 3H).

Preparation of 5-Methyl-4-methyl-4H-bis[1,2,3]dithiazol-5,4-bis[1,2,3]dithiazolyl Radicals: Substituent Effects. Chem. Mater., Vol. 16, No. 8, 2004

EPR Spectra. X-band EPR spectra were recorded at ambient temperature using a Bruker EMX-200 spectrometer; samples of the radicals were dissolved in degassed dichloromethane. Hyperfine coupling constants were obtained by spectral simulation using Simfonia33 and WinSim.

Cyclic Voltammetry. Cyclic voltammetry was performed using a PINE Bipotentiostat, model AFC1CBP1, with scan rates of 50–100 mV s⁻¹ on solutions (~10⁻³ M) of [1][OTf] (R1 = Me, R2 = Me, Ph) in CH₂CN (dried by distillation from P₂O₅ and CaH₂) containing 0.1 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. 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 Epa – Epc separation of the reversible couples was within 10% of that of the Fc/Fc⁺ couple.

X-ray Measurements. Crystals of MeBPMe₂ (R1 = R2 = Me) suitable for X-ray work were obtained by recrystallization from degassed dichloromethane. Crystals of PhBPMe₂ (R1 = Me, R2 = Ph) were grown by slow diffusion of a solution of CP₃Fe in degassed acetonitrile into a solution of [1][OTf] (R1 = Me, R2 = Ph) in degassed acetonitrile. Samples for analysis were glued to a glass fiber with epoxy, centered on a Bruker P4/CCD diffractometer, and irradiated using 11.25 kW X-rays from a Bruker Mo rotating anode generator. Data sets on several crystals of MeBPMe₂ (R1 = R2 = Me) were collected using omega scans with a Bruker SMART6000 CCD detector on a D8 3-circle goniometer and parallel-focused Cu Kα radiation from a Rigaku RU-200 four-circle focusing rotating anode generator at 5 kW. The data were scanned using Bruker’s SMART program and integrated using Bruker’s SAINT software. For MeBPMe₂ (R1 = R2 = Me) the refinement reached a reasonable R-factor of 6.85%. High resolution data were limited by the fact that the data crystal was only a 5-μm-thick needle and it was twinned. There was no significant refraction above 120°. The twinning was a result of a 180° rotation about the 2D Me–Me interface (the ab plane of the crystal). The twinning has no effect on the S–S intermolecular contacts or their direction.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured over the temperature range 5–380 K on a George Associates Faraday balance operating at 0.5 T.

Band Calculations. Band electronic structure calculations were performed with the EHMACC suite of programs33 using the Coulomb parameters of Baasch, Viste, and Gray34 and a quasi-split valence basis set adapted from Clementi and Roetti;35 numerical values are tabulated elsewhere.36 The off-diagonal elements of the Hamiltonian matrix were calculated with the standard weighting formula.37 Atomic positions were taken from the crystallographic data.
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Supporting Information Available: Details of X-ray crystallographic data collection and structure refinement, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.