Charge-Transfer Complexes of 4-Phenyl-1,2,3,5-dithiadiazolyl and 4-Phenyl-1,2,3,5-diselenadiazolyl with Iodine. Preparation and Solid-State Characterization of [PhCN₂E₂][I₃] (E = S, Se) and [PhCN₂S₂][I₃]

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Received December 16, 1993. Revised Manuscript Received February 4, 1994

The 1:1 reaction of the heterocyclic radicals [PhCN₂E₂]⁺ (E = S, Se) and iodine affords the mixed valence salts [PhCN₂E₂][I₃], while reaction of PhCN₂S₂ with an excess of iodine affords the simple salt [PhCN₂S₂][I₃]; the solid-state structures of these complexes have been determined by X-ray crystallography. Crystals of both of the mixed valence compounds belong to the triclinic space group P̅1; for E = S, α = 10.278(4), b = 11.508(2), c = 13.333(4) Å, β = 114.97(2), γ = 92.21(3), FW = 308.15, Z = 6; for E = Se, α = 10.368(6), b = 10.818(8), c = 13.421(8) Å, α = 80.64(5), β = 81.20(5), γ = 75.18(6)°, FW = 401.95, Z = 6. Crystals of the simple salt belong to the monoclinic space group P2₁/a; α = 7.366(4), b = 11.734(1), c = 15.166(2) Å, β = 95.29(3), FW = 1303.99(7), Z = 4. In each of the mixed valence compounds the molecular (asymmetric) unit consists of a trimeric [PhCN₂E₂]⁺ cation and an associated triiodide anion. Within the cations the mean interannular E-E contacts are 3.13-3.37 Å; for E = S, the crystal structure does not exhibit stacking of the trimeric molecular building blocks, but for E = Se the trimer units form dovetailed stacks in which consecutive layers are oriented in a trans-antipodal fashion. This arrangement introduces close interannular contacts between the blocks along the stack, as well as close lateral contacts. The asymmetric unit of [PhCN₂E₂][I₃] consists of a single PhCN₂E₂⁺ cation and an associated triiodide anion; there are no unusual stacking features. The magnetic and conductivity properties of [PhCN₂E₂][I₃] are reported, and the results discussed in the light of extended Hückel band structure calculations.

Introduction

The chemical and physical properties of heterocyclic thiazyl and selenazyl radicals have been investigated by several research groups. Much of our work in this area has focused on derivatives of 1,2,3,5-dithiadiazolyl and 1,2,3,5-diselenadiazolyl (E = S, Se), our intent being to design neutral π-radicals that will serve as building blocks for molecular conductors. To this end we have prepared a wide range of mono-, di-, and trifunctional radicals (and their dimers), determined their solid-state structures and measured their transport properties.

While considerable advances have been made in the synthesis and characterization of the neutral materials, the use of the radicals as donors for the generation of

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charge transfer (CT) salts has been largely unexplored. There was an early suggestion that the phenyl derivative (R = Ph, E = S) formed a thermally unstable iodide salt, but no experimental details were provided. The layered salt [PhCN₂S₂]⁺[S₃N₃]⁻ and the mixed dimer/cation salt [CF₂CN₂S₂]a(Cl) have also been described. Recently, however, we reported the preparation and structural characterization of two highly conductive mixed valence salts, one based on the prototypical radical 1 (E = S, R = H), i.e., [1I]⁺[I]⁻ and the other on the bifunctional 1,4-phenylene derivative 2, i.e., [2][I]⁻. In both compounds the molecular building blocks form uniformly spaced stacks (at ambient temperatures), with the iodines aligned in one-dimensional arrays exhibiting disorder along the stacking direction. In the case of [2][I]⁻ the conductivity is similar to that of a neutral radical. Upon slow cooling of the dark red solution to room temperature, but below 190 K a charge density wave (CDW) driven instability sets in and the conductivity drops sharply. Analysis of the CDW wave vector indicates a degree of charge transfer corresponding to the formulation [2]⁺1/2[I]⁻1/2.

As a further exploration of the structural consequences of partial oxidation of both dithia- and diselenodiazolyls, we have investigated the reaction of 1 (R = Ph; E = S, Se) with iodine. Two classes of iodide salts have been prepared and structurally characterized: (i) the mixed valence salts of nominal composition [1I][I]⁻ and (ii) a simple triiodide salt of the dithiadiazolium cation, i.e., [1I][I]⁻. In contrast to the neutral radicals, which associate in the solid state as dimers, e.g., 3, and to the previously reported mixed valence dithiadiazolyl/iodine complexes noted above, we have found that the 1:1 CT salts of the phenyl derivatives are based on the novel triple-decker cation [PhCN₂S₂]⁺, 4 (E = S, Se), associated with a triiodide anion. Herein we describe the synthesis, crystal structures, and transport properties of these materials, and discuss the results in light of extended Hückel band structure calculations.

Results and Discussion

Synthesis. The reaction of 1 (R = Ph, E = S) with iodine can be performed either in solution or in the gas phase. When carried out in solution, equivalent quantities of iodine can be performed either in solution or in the gas phase. We describe the synthesis, crystal structures, and transport properties of these materials, and discuss the results in light of extended Hückel band structure calculations.

Figure 1. ORTEP drawings (30% ellipsoids) of [PhCN₂E₂]⁺[I]⁻, E = S (above) and Se (below). The interannular E-E bonds are omitted for clarity.

PhCN₂S₂I are produced. The compound can also be prepared, as suggested by Banister, by a metathesis reaction between [PhCN₂S₂][Cl] and KI. Larger needles, with the same composition and infrared spectrum, can be grown by very slow sublimation of the two reagents in a sealed, evacuated tube (see Experimental Section). While materials suitable for bulk analysis was obtained in several days, crystals suitable for X-ray work required a long (5-6 week) sublimation period. The reaction involving (1 (R = Ph, E = S) and iodine is best performed by the gas-phase route, although it too can be made in microcrystalline form by metathesis of [PhCN₂E₂][PF₆] with n-Bu₄NI in acetonitrile. Crystals of the selenium-containing product obtained by cosublimation with iodine are nominally larger than those of the corresponding sulfur compound, but prolonged sublimation times are again critical in order to obtain crystals suitable for X-ray work. As confirmed below, the structural unit in both these 1:1 compounds (E = S and Se) is [PhCN₂E₂][I]⁻.

In addition to the 1:1 compounds described above, we have been able to isolate a salt of composition [PhCN₂E₂][I]⁻ by cosublimation of iodine and radical in a molar ratio of greater than 3:1. Structural analysis on this material (below) shows it to be a simple triiodide salt [PhCN₂E₂][I]⁻.

Crystal Structures. Crystals of both [PhCN₂E₂][I]⁻ (E = S, Se) obtained as described above, belong to the triclinic space group P1. ORTEP drawings of the asymmetric units are provided in Figure 1, and atomic (non-hydrogen) coordinates are listed in Tables 1 and 2. A summary of pertinent bond lengths and angles within the asymmetric units is shown in Table 3, and interannular E-E bonds are omitted for clarity.


the crystal structures show few unusual features. The structure of the [PhCNzSe1+] cation, in its PF6– salt, has been characterized by X-ray crystallography; pairing to a halide is not uncommon. It is observed in the CT salt [2][I] (although the iodines are disordered) and 3.543 Å for E

\[ \text{for } E = \text{Se} \]

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\[ \text{for } E = \text{S}, \text{Se}^{\text{0}} \]

\[ \text{for } E = \text{S} \]
lengthening is not expected to be as great as in the simple dimers. Figure 2 illustrates a qualitative MO diagram for the interaction of the SOMOs of three CN$_2$E$_2$ rings. Given the formal positive charge on 4, the occupation level and phase pattern is reminiscent of those seen in the π-manifold of the allyl cation; only the lowest orbital, which is bonding with respect to the interannular interactions, is occupied. Interannular binding within the trimer units is therefore weak; the entire trimer unit is essentially held together by just two electrons. The mean E- -E contacts (3.181/3.377 Å for E = S/Se) are thus predictably longer than the interdimer E- -E contacts seen in 4 (R = Ph, 3.109/3.254 Å for E = S/Se).

Figures 3–5 provide comparative views of the packing patterns for the two structures. When viewed from a direction approximately perpendicular to the plane of the heterocyclic rings (Figure 3) the crystal structures appear remarkably similar. In both cases the molecular units form ribbons which run to-and-fro in antiparallel arrays; within each ribbon a triiodide iodine follows onto the tail of the next phenyl ring. The associated dovetailing of heterocyclic rings gives rise to a series of lateral E- -E contacts (see also Figure 4 and Table 4). Given the van der Waals radii of S (radius 1.80 Å) and Se (radius 1.90 Å), and in comparison to similar contacts seen in the structures of neutral dimers, these contacts are relatively long. In contrast to the perspective shown in Figure 3, the arrangements of the ribbons of trimers as viewed from the side are quite different (Figure 5). For the sulfur compounds consecutive layers of molecular ribbons run in the same direction. Moreover, the layers are offset, so that each heterocyclic trimmer is sandwiched between a triiodide and set of phenyl rings, i.e., there is no opportunity for extended interactions perpendicular to the layered ribbons. By contrast, in the selenium compound, consecutive layers run antiparallel, with a dovetailed overlap between each trimmer unit and those above and below. While the intertrimer Se- -Se contacts (4.233 and 4.497 Å) occasioned by this dovetailed overlap are relatively remote, the Se- -N interactions (Table 4) are close to the van der Waals separation for Se (radius 1.90 Å) and N (radius 1.55 Å).

Table 4. Summary of Intermolecular E- -E and E- -N Contacts (angstroms) in 4 (E = S, Se).* ESDs in Parentheses

<table>
<thead>
<tr>
<th>E</th>
<th>Contacts</th>
<th>ESDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>S1-S21 (at -x, 1 - y, 2 - z)</td>
<td>3.961(5)</td>
</tr>
<tr>
<td></td>
<td>S1-S11 (at -x, 1 - y, 2 - z)</td>
<td>4.084(5)</td>
</tr>
<tr>
<td></td>
<td>S11-S11 (at -x, 1 - y, 2 - z)</td>
<td>3.947(7)</td>
</tr>
<tr>
<td></td>
<td>S2-S22 (at 1 - x, 1 - y, 2 - z)</td>
<td>4.103(5)</td>
</tr>
<tr>
<td></td>
<td>S2-S12 (at 1 - x, 1 - y, 2 - z)</td>
<td>4.114(5)</td>
</tr>
<tr>
<td></td>
<td>S12-S12 (at 1 - x, 1 - y, 2 - z)</td>
<td>3.860(6)</td>
</tr>
<tr>
<td>S</td>
<td>Se1-Se1 (at 1 - x, 2 - y, 1 - z)</td>
<td>4.008(12)</td>
</tr>
<tr>
<td></td>
<td>Se1-Se11 (at 1 - x, 2 - y, 1 - z)</td>
<td>4.094(13)</td>
</tr>
<tr>
<td></td>
<td>Se11-Se11 (at 1 - x, 2 - y, 1 - z)</td>
<td>3.956(17)</td>
</tr>
<tr>
<td></td>
<td>Se2-Se22 (at 1 - x, 1 - y, 1 - z)</td>
<td>3.973(13)</td>
</tr>
<tr>
<td></td>
<td>Se2-Se12 (at 1 - x, 1 - y, 1 - z)</td>
<td>4.092(15)</td>
</tr>
<tr>
<td></td>
<td>Se12-Se12 (at 1 - x, 1 - y, 1 - z)</td>
<td>3.998(20)</td>
</tr>
<tr>
<td></td>
<td>Se1-Se22 (at 1 + x, y, z)</td>
<td>4.006(15)</td>
</tr>
<tr>
<td></td>
<td>Se1-N2 (at 2 - x, 1 - y, 1 - z)</td>
<td>3.64(5)</td>
</tr>
<tr>
<td></td>
<td>Se2-N1 (at 2 - x, 1 - y, 1 - z)</td>
<td>3.65(5)</td>
</tr>
<tr>
<td></td>
<td>Se22-N22 (at -x, 2 - y, 1 - z)</td>
<td>3.67(5)</td>
</tr>
<tr>
<td></td>
<td>Se22-N21 (at -x, 2 - y, 1 - z)</td>
<td>3.58(5)</td>
</tr>
</tbody>
</table>

* The coordinates refer to the symmetry position of the second atom.

Figure 2. Qualitative energy level diagram for the frontier orbitals of the trimeric (PhCN$_2$E$_2$)$_3$ cation (E = S, Se), and the resulting solid-state band structure.

Figure 3. Packing patterns of [PhCN$_2$E$_2$]$_3$[I$_2$], E = S (above) and Se (below), showing lateral E- -E contacts (dashed lines).


Figure 4. End-on view of sets of [E₂][I₃] units, showing lateral E--E contacts (dashed lines).

A) and may well provide a mechanism for electronic communication along the dovetailed stacks of trimers.

Crystals of [PhCN₂S₂][I₃] belong to the monoclinic space group P2₁/a. An ORTEP drawing of a single cation/anion pair is provided in Figure 6; atomic (non-hydrogen) coordinates are shown in Table 5 and a summary of intramolecular distances is provided in Table 6. The molecular structure is comprised of a single heterocyclic cation and an associated triiodide anion. The internal structure features of the CN₂S₂ ring are similar to those found in other simple salts and are consistent with a full positive charge on the heterocycle (vide supra). The triiodide weakly coordinates to the ring through two long (3.562 and 3.352 Å) S--I contacts to a single terminal iodine atom (II).

Figure 7 illustrates the packing pattern for [PhCN₂S₂][I₃]. In contrast to both the neutral materials and the mixed valence compounds described here, and consistent with other PhCN₂S₂⁺ salts, the heterocyclic units are well separated (there is no stacking). The packing of the planar cations and anions results in two-dimensional "sheets" in the yz plane. Within the plane there are rows of PhCN₂S₂⁺ cations alternating with rows of triiodide anions.

Band Structure Calculations. To probe the electronic consequences of the structural differences noted above we have performed a series of extended Hückel band structure calculations on the mixed valence compounds. Here, as elsewhere,[18,19] we have elected to focus the calculation by replacing the phenyl groups by hydrogen atoms; the triiodides have also been omitted. These simplifications have no effect on the valence and conduction bands, which are exclusively based on the heterocycle. The results, expressed as density of states (DOS) diagrams (Figure 8), can be understood with reference to the simplified band scheme developed above; the three flagged bands thus correspond to those developed from the three molecular orbital combinations illustrated in Figure 2. In the sulfur compound, in which stacking of trimers is absent, only lateral interactions serve to broaden the three bands, and the calculated bandgap is 0.8 eV. In the selenium compound, in which dovetailed stacking is

Figure 5. Layers of [PhCN₂E₂][I₃] ribbons, E = S (above) and Se (below), showing intertrimer Se--N contacts (dashed lines).

Figure 6. ORTEP drawing (30% ellipsoids) of [PhCN₂S₂][I₃].

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Figure 7. Projection of a single layer of [PhCN₂Sz][I₂], showing S...I contacts (dashed lines).

Table 5. Non-Hydrogen Atomic Parameters \(x, y, z\), and \(B_{eq}\) for [PhCN₂Sz][I]. ESDs Refer to the Last Digit Printed

<table>
<thead>
<tr>
<th></th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(B_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>0.82205(7)</td>
<td>0.34687(4)</td>
<td>0.49395(3)</td>
<td>3.423(24)</td>
</tr>
<tr>
<td>I2</td>
<td>0.69203(6)</td>
<td>0.51099(4)</td>
<td>0.61666(3)</td>
<td>3.055(21)</td>
</tr>
<tr>
<td>I3</td>
<td>0.56677(8)</td>
<td>0.66725(4)</td>
<td>0.74570(4)</td>
<td>4.13(3)</td>
</tr>
<tr>
<td>S1</td>
<td>0.7697(3)</td>
<td>0.60347(15)</td>
<td>0.36838(12)</td>
<td>3.22(8)</td>
</tr>
<tr>
<td>S2</td>
<td>0.8402(3)</td>
<td>0.46897(15)</td>
<td>0.29525(13)</td>
<td>3.43(8)</td>
</tr>
<tr>
<td>N1</td>
<td>0.7711(9)</td>
<td>0.6941(6)</td>
<td>0.2900(4)</td>
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<tr>
<td>N2</td>
<td>0.8548(8)</td>
<td>0.5407(5)</td>
<td>0.2070(4)</td>
<td>3.13(23)</td>
</tr>
<tr>
<td>C1</td>
<td>0.8199(9)</td>
<td>0.6501(5)</td>
<td>0.2121(5)</td>
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</tr>
<tr>
<td>C2</td>
<td>0.8284(10)</td>
<td>0.7275(6)</td>
<td>0.1353(5)</td>
<td>3.1(3)</td>
</tr>
<tr>
<td>C3</td>
<td>0.8130(11)</td>
<td>0.8421(6)</td>
<td>0.1441(6)</td>
<td>3.7(3)</td>
</tr>
<tr>
<td>C4</td>
<td>0.8235(14)</td>
<td>0.9109(7)</td>
<td>0.0698(6)</td>
<td>4.8(4)</td>
</tr>
<tr>
<td>C5</td>
<td>0.8488(13)</td>
<td>0.8777(9)</td>
<td>-0.0050(7)</td>
<td>5.1(5)</td>
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<tr>
<td>C6</td>
<td>0.8687(12)</td>
<td>0.7477(8)</td>
<td>-0.0189(5)</td>
<td>4.2(4)</td>
</tr>
<tr>
<td>C7</td>
<td>0.8611(12)</td>
<td>0.6919(6)</td>
<td>0.0559(9)</td>
<td>3.9(4)</td>
</tr>
</tbody>
</table>

* \(B_{eq}\) is the mean of the principal axes of the thermal ellipsoid.

Table 6. Mean Intramolecular Distances (angstroms) and Angles (deg) in [PhCN₂Sz][I]. ESDs in Parentheses

|     | \(|S-S|\) | \(|N-S|\) | \(|N-C|\) | \(|S-S-N|\) | \(|11-12-13|\) |
|-----|----------|----------|----------|------------|-------------|
| S-S | 2.027(3) | 1.595(5) | 1.342(10)| 95.2(2)    | 112-12-13   |
| N-S | 1.342(10)| 1.342(10)| 95.2(2)  | 112-12-13  |             |
| N-C | 95.2(2)  | 95.2(2)  | 112-12-13| 177.34(2)  |             |
| S-N | 115.1(5) | 115.1(5) | 112-12-13| 177.34(2)  |             |

observed, the three bands are noticeably broadened, and the bandgap consequently reduced to 0.4 eV.

The dispersion curves for the highest occupied (in- and out-of-phase) and lowest unoccupied (in- and out-of-phase) crystal orbitals, as plotted along the principal axes of reciprocal space (Figure 9), afford a more detailed insight into the extent and dimensionality of interannular interactions. In the sulfur compound dispersion is minimal in all three directions, as expected. Indeed dispersion of any degree is only apparent along \(X\), this direction being approximately equivalent (in real space) to lateral inter-

actions in the \(x\) direction (real space). In the selenium compound, the correspondence between real and reciprocal unit cell vectors is closer, since all the unit cell angles are near 90°. Dispersion along \(Z\) is again negligible, as expected given the absence of interannular contacts in the \(z\) direction (real space). The strong dispersion along \(X\), coupled with the smaller but still significant dispersion along \(Y\), reflects the rather two-dimensional nature of the electronic structure.
Conductivity and Magnetic Measurements. Preliminary pressed pellet conductivity measurements on [PhCN2E2][I] \((E = S, Se)\) confirmed, as expected, a relatively weak room-temperature conductivity (near $10^{-6}$ S cm$^{-1}$) for the sulfur compound. The selenium derivative showed more promise, and its transport properties were therefore investigated more fully. Single crystals of [PhCN2Se2][I] were wired for four-point conductivity measurements along the needle axis; wires were attached with gold paint. The single-crystal conductivity of the material, as measured over the temperature range 150-300 K is shown in Figure 10. The conductivity is activated, rising to a value of $10^{-4}$ S cm$^{-1}$ at room temperature. Analysis of the high-temperature data affords an activation energy of 0.29 eV. The magnetic susceptibility of [PhCN2Se2][I] was measured between 2 K and room temperature using a Quantum Design SQUID magnetometer at 1 T. The signal was diamagnetic throughout the measurement, and the diamagnetism was found to be $140 \times 10^{-6}$ emu mol$^{-1}$, in good agreement with Pascal’s constants. The susceptibility showed a small Curie tail, arising from a residual spin concentration of <1% on a per molecule basis.

Summary and Conclusions

In previous papers we have described the solid state structural and transport properties of neutral dimers of the type [I]. These materials (for \(E = Se\)) are semiconductors, with a suggested conduction mechanism which involves thermal activation of electrons across a bandgap. The size of this bandgap can be closely correlated with the dispersive effect of the intermolecular interactions, such that more densely packed structures, with more widely dispersed valence and conduction bands, have efficient crystal packing (tighter intermolecular \(2e-3c\) binding, the dispersive effect of the intermolecular interaction leads to a solid-state structure for which the predicted (EHMO) and measured bandgap is remarkably small.

As with the neutral dimers, chemical modification of the exocyclic \(R\) group in 4 may afford materials with more efficient crystal packing (tighter intermolecular \(E-E\) contacts) and even better conductivity characteristics. We are therefore investigating the structures and transport properties of other \(CT\) salts of simple monofunctional radicals. In contrast to early observations,\(^5\) these materials exhibit good thermal stability, and a rich chemistry in terms of stoichiometric ratio (radical:iodine) is anticipated.

Experimental Section

Starting Materials and General Procedures. Iodine, KI, and \(n\)-Bu$_4$NI were obtained commercially (Fisher) and used as received. Acetonitrile (Fisher HPLC grade) was purified by distillation from P$_2$O$_5$. The 4-phenyl-1,2,3,5-dithiadiazolyl radicals and the PF$_6$ salts of the corresponding cations were prepared according to literature methods.\(^6\) All reactions (in solution) were performed under vacuum or under an atmosphere of nitrogen. The gas-phase reactions were performed in ATS series 3210 three-zone tube furnace, linked to a Series 1400 temperature control system. Infrared spectra were recorded on a Nicolet 20SX/FTIR spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Melting-point determinations were made on samples in tubes sealed under argon.

Preparation of [CsH$_2$CN$_2$E$_2$][I] \((E = S, Se)\) in the Gas Phase. In a typical experiment, iodine (0.252 g, 1.0 mmol) and 1 mol equiv of [PhCN$_2$E$_2$] were sealed in an evacuated (10$^{-3}$ Torr) Pyrex tube (25 mm $\times$ 250 mm). That half of the tube containing both reagents was slowly warmed over a period of several days from 50 to 80 °C (for sulfur) and 70 to 120 °C (for selenium). Throughout this period other half of the tube was maintained at 55 °C (for sulfur) and 60 °C (for selenium). Over the course of 5 weeks (for sulfur) and 2 weeks (for selenium), deep blue needles grew in the cooler portion of the tube. These mildly air-sensitive crystals were harvested in a drybox and stored under nitrogen or argon atmosphere. Yields were as high as 80%, although values of 40–50% were more typical. \(E = S\): IR (2000–200 cm$^{-1}$) for the sulfur compound. The infrared spectrum of this material was identical to that of the predicted (EHMO) and measured bandgap is remarkably small.

Preparation of [CsH$_2$CN$_2$Se$_2$][I] in Acetonitrile. (a) From [CsH$_2$CN$_2$S$_2$] and iodine. A solution of iodine (200 mg, 1.58 mmol) in 15 mL of acetonitrile was added to a solution of [CsH$_2$CN$_2$S$_2$] (285 mg, 1.57 mmol) in 36 mL of acetonitrile. A greenish-brown solid immediately precipitated. The solid dissolved on heating, giving a deep wine-red solution. Slow cooling of the solution produced very fine blue-metallic needles. The needles were filtered, rinsed with 2 × 10 mL of cold acetonitrile, and dried in vacuo (yield 370 mg, 76%). The infrared spectrum of this material was identical to that of the product of the gas-phase reaction described above.

(b) From CsH$_2$CN$_2$Se$_2$Cl and KI. Acetonitrile (50 mL was syringed into a sidearm flask containing 4-phenyl-1,2,3,5-dithiadiazolium chloride (410 mg, 1.5 mmol) and finely ground potassium iodide (330 mg, 2.0 mmol). The slurry was quickly filtered, and a greenish-brown precipitate formed. The mixture was refluxed for 30 min and hot filter to remove the KCl precipitate. The wine-red filtrate was slowly cooled to give metallic blue needles, which were then filtered, rinsed with 2 × 10 mL of cold acetonitrile, and dried in vacuo (yield 380 mg, 61%). The infrared spectrum of this material was identical to...
that of \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\) prepared by the other two routes as described above.

Preparation of \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\) in Acetonitrile. A solution of tetra-n-butylammonium iodide (240 mg, 0.65 mmol) in 10 mL of CH₃CN was added dropwise to a solution of \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\)·PF₆⁻ (275 mg, 0.65 mmol) in 20 mL of CH₃CN. A black solid was produced immediately. The mixture was stirred for 30 min at room temperature and filtered. The black solid was rinsed with 3 x 10 mL of CH₃CN and pumped to dryness to give crude \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\) (yield 210 mg, 50%). The crude material was sublimed in a high vacuum (ca. 10⁻³ Torr) in a sealed tube to give thin blue needles, yield 175 mg (78%). The infrared spectrum of this material was identical to that of the product of the gas-phase reaction described above.

Preparation of \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\). In a typical experiment, iodine (510 mg, 4.04 mmol) and \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\) (220 mg, 1.21 mmol) were sealed in an evacuated (10⁻³ Torr) Pyrex tube. The end of the tube containing both reagents was heated initially to 70 °C and then slowly raised over a 3-week period to 90 °C, while the far end of the tube was similarly ramped from 45 to 60 °C. Lustrous dark copper rodlike crystals slowly formed at the far end. The mildly air-sensitive crystals were harvested and stored under an inert atmosphere (nitrogen or argon). The residue still appeared to contain significant amounts of material; however, leaving the sublimation tube sealed at 90 °C for longer periods of time resulted in decomposition to \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\) (yield 210 mg, 80%).

Yields were also led to decomposition to \([\text{C}_{6}\text{H}_{5}\text{CN}]_{2}\text{S}_2\text{I}_3\)·I₂. Yields were calculated structure factors (42 pages). Ordering information is available on any current masthead page.

### Band Structure Calculations

The band structure calculations were carried out with the EHMCC suite of programs using the parameters discussed previously. The phenyl groups were replaced by a hydrogen atom at the site of the ipso carbon, and the iodines were not included. The off-diagonal elements of the Hamiltonian matrix were calculated with the standard matrix elements.

### Supplementary Material Available

Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters for \([\text{PhCN}]_2\text{S}_2\)·[\(\text{I}_3\)] (E = S, Se) and \([\text{PhCN}]_2\text{S}_2\)·[\(\text{I}_3\)] (10 pages); observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

### Acknowledgment

Financial support at Guelph was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and at Arkansas by the National Science Foundation (EPSCOR program). C.D.B. acknowledges a DOE/ASTA Traineeship.