

Mixed Radical/Iodine Charge-Transfer Salts of Dithiadiazolyl Diradicals. Structural Characterization of the Pyridine-Bridged 2:1 Salt 2,6-[$(\text{S}_2\text{N}_2\text{C})\text{C}_5\text{H}_3\text{N}(\text{CN}_2\text{S}_2)]_2\text{[I]}$

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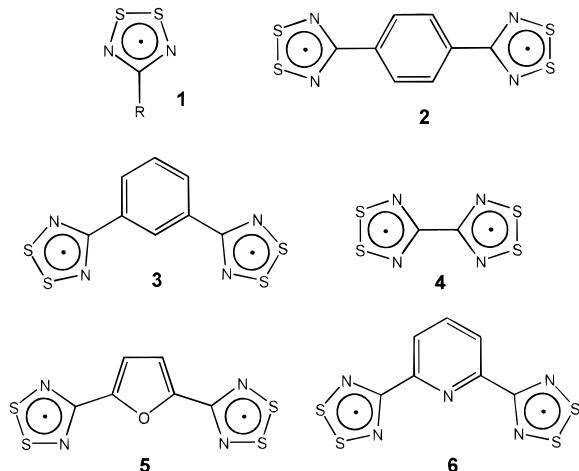
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Cosublimation of 2,5-furanbis(1,2,3,5-dithiadiazolyl) [F-2,5-S] and iodine affords 1:1 and 2:1 charge-transfer salts, [F-2,5-S][I] and [F-2,5-S]₂[I]. Cosublimation of 2,6-pyridinebis(1,2,3,5-dithiadiazolyl) [P-2,6-S] and iodine affords uniquely the 2:1 charge-transfer salt [P-2,6-S]₂[I]. Crystals of the latter belong to the space group $P2_1/c$, $a = 3.434(3)$, $b = 9.8914(9)$, $c = 30.803(4)$ Å, $\beta = 91.52(3)$ °, $V = 1045.9(9)$ Å³, $Z = 2$. The structure consists of [P-2,6-S] molecules stacked along the x direction. Pairs of stacks are linked head-on through iodine atoms, which themselves form disordered stacks running parallel to x . The internal structural parameters of the two CN₂S₂ rings within each molecule suggest that one (linked to iodine) is formally uncharged, while the other is partially oxidized. This latter ring is heavily coordinated through S–N linkages to neighboring CN₂S₂ rings and pyridine. Magnetic susceptibility measurements on [P-2,6-S]₂[I] indicate that it is diamagnetic below 220 K.

Introduction

Our studies of molecular conductors based on the use of neutral π -radicals,² notably 1,2,3,5-dithiadiazolyls and their selenium analogues, have recently been directed toward the design of charge-transfer (CT) salts with halogen acceptors.³ A variety of structures based on monofunctional derivatives **1** ($R = H, Ph$, Chart 1) have been reported,^{4,5} as have several materials based on the benzene-bridged diradicals^{6,7} [1,4-S] **2** and [1,3-S] **3** and the back-to-back diradical **4**.⁸ In the case of **2** and **3** the structures of the iodine CT salts, of nominal composition [1,4-S][I] and [1,3-S][I], consist of perfectly superimposed and evenly spaced molecular units, inter-

Chart 1



⁸ Abstract published in *Advance ACS Abstracts*, October 1, 1996.
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(2) Cordes, A. W.; Haddon, R. C.; Oakley, R. T. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; p 295.

(3) Cordes, A. W.; Haddon, R. C.; Oakley, R. T. *Adv. Mater.* **1994**, 6, 798.

(4) Bryan, C. D.; Cordes, A. W.; Haddon, R. C.; Glarum, S. H.; Hicks, S. H.; Kennepohl, D. K.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Schneemeyer, L. F.; Scott, S. R.; Waszczak, J. V. *J. Am. Chem. Soc.* **1994**, 116, 1205.

(5) Bryan, C. D.; Cordes, A. W.; Haddon, R. C.; Hicks, R. G.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Scott, S. R. *Chem. Mater.* **1994**, 6, 508.

(6) Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S. H.; Haddon, R. C.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *J. Am. Chem. Soc.* **1995**, 117, 6880.

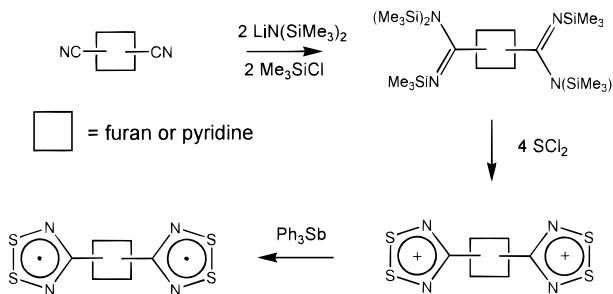
(7) Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S. H.; Haddon, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Schneemeyer, L. F.; Waszczak, J. V. *Nature* **1993**, 365, 821.

(8) Bryan, C. D.; Cordes, A. W.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; MacKinnon, C. D.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *J. Am. Chem. Soc.* **1996**, 118, 330.

spersed with columns of disordered iodines. Both materials exhibit metallic conductivity at ambient temperatures, but at lower temperatures (190 and 270 K, respectively) charge density wave (CDW) driven instabilities cause the structures to collapse into semiconducting states. The selenium variants [1,4-Se][I] and [1,3-Se][I] have also been characterized, and while these show improved conductivities at room temperature, they still display relatively high metal–insulator transitions T_{MI} .⁹ The susceptibility of the uniformly spaced stacks to undergo these CDW-driven distortions is readily

(9) Bryan, C. D.; Cordes, A. W.; George, N. A.; Haddon, R. C.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *Chem. Mater.* **1996**, 8, 762.

Scheme 1



attributed to their rather one-dimensional electronic structures.

Modifications of the molecular building blocks may afford solid-state arrangements with more lateral (cross-stack) as well as longitudinal (along stack) intermolecular interactions. These should be more resistant to metal–insulator transitions. To this end we are investigating variations on the basic structural unit of these diradicals. As a first step we have explored the use of aromatic heterocyclic spacers which provide molecular species similar to the [1,3-S] derivative **3**. In this paper we describe the iodine charge-transfer chemistry of diradicals bridged by 2,5-furan and 2,6-pyridine spacers, i.e., ([F-2,5-S]) **5**¹⁰ and ([P-2,6-S]) **6**. The structure of the salt [P-2,6-S]₂[I], the first 2:1 CT salt of a bis(dithiadiazolyl), is also reported. The results illustrate that seemingly subtle molecular modifications can not only induce major solid-state changes. The introduction of heteroatoms on the spacer group can also affect the preferred stoichiometry of the resulting CT salt.

Results and Discussion

Preparation of Diradicals. The diradicals [F-2,5-S] and [P-2,6-S] were prepared by condensation of the respective persilylated bis(amidines) with sulfur dichloride and reduction of the resultant dithiadiazolylum salts.¹⁰ The necessary amidines were generated from the corresponding dinitriles by treatment with lithium hexamethyldisilylamide followed by quenching with chlorotrimethylsilane (see Scheme 1). The diradicals were purified as their dimers by vacuum sublimation in a gradient tube sublimator. Yields ranged from 25 to 40%.

Reactions with Iodine. The reactions of [F-2,5-S] and [P-2,6-S] with iodine were performed by sealing in *vacuo* equivalent quantities of the diradical and iodine in glass tubes. In a typical experiment the tube was heated to ca. 150 °C, whereupon the initially formed “purple haze” of iodine slowly dispersed as the CT salt was formed. After 12–24 h the tube was cooled and opened, and the residual black solid repacked and sealed into a clean, evacuated tube. The tube was then returned to the furnace, and a temperature ramp applied along the tube so as to promote sublimation along the gradient.

In the case of [F-2,5-S], a crystalline sublimate was obtained with a gradient set at 170–130 °C, but this was accompanied by some decomposition, as indicated by a increase in the intensity of iodine vapor in the sublimation tube. Nevertheless, sufficient material, in

Table 1. Atomic Parameters *x*, *y*, *z*, *B*_{eq} and Iodine Occupancy for [P-2,6-S]₂[I]^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}	occup
I1	0.5000	0.5000	0.0000	2.59(14)	0.3974
I2	1.3597(8)	0.5013(6)	0.0001(2)	2.59(14)	0.3013
S1	0.3077(11)	0.0820(2)	0.2128(1)	4.36(13)	
S2	0.3210(8)	0.2889(2)	0.2041(1)	3.11(11)	
S3	0.3421(10)	0.6662(3)	0.4686(1)	4.18(13)	
S4	0.3489(9)	0.7571(2)	0.4077(1)	3.66(12)	
N1	0.261(3)	0.0931(7)	0.2644(3)	3.4(4)	
N2	0.282(2)	0.3249(7)	0.2549(2)	2.4(3)	
N3	0.287(3)	0.5140(7)	0.4492(2)	3.3(3)	
N4	0.295(3)	0.6153(8)	0.3809(2)	3.2(4)	
N5	0.252(2)	0.3567(7)	0.3447(2)	2.1(3)	
C1	0.253(3)	0.2161(8)	0.2815(3)	2.4(3)	
C2	0.194(2)	0.2326(8)	0.3274(3)	1.9(3)	
C3	0.087(3)	0.1224(9)	0.3526(3)	3.0(4)	
C4	0.024(3)	0.1399(10)	0.3961(3)	3.1(4)	
C5	0.085(3)	0.2640(10)	0.4130(3)	3.0(4)	
C6	0.197(3)	0.3715(9)	0.3875(3)	2.4(3)	
C7	0.268(3)	0.5072(9)	0.4067(3)	2.7(4)	
H3	0.058	0.036	0.340	3.8	
H4	-0.059	0.067	0.414	3.8	
H5	0.049	0.278	0.443	3.8	

^a ESDs refer to the last digit printed. ^b *B*_{eq} is the mean of the principal axes of the thermal ellipsoid.

the form of lustrous but irregular flakes, were obtained to allow an analysis, which confirmed the 1:1 formulation [F-2,5-S]₂[I]. The unsublimed residue was recharged into an evacuated tube, and a smaller, second crop of sublimate was collected. The residue from this sublimation, when repacked into a fresh tube, did not afford any sublimate at 170 °C. However, upon raising the temperature of the hot zone from 170 to 190 °C, large well-formed needles of composition [F-2,5-S]₂[I] were obtained. A similar study of the reaction of the pyridine based diradical with iodine afforded no indication of a sublimable 1:1 material. Under more forcing conditions, i.e., a temperature ramp of 200–140 °C, long needles of the 2:1 salt [P-2,6-S]₂[I] were obtained.

Crystal Structures. Numerous crystals of both [F-2,5-S]₂[I] and [F-2,5-S]₂[I] were mounted for crystallographic studies, and data sets collected on the best of these. For all these attempts the poor quality of sublimed crystals, coupled with a severe twinning problem, precluded a satisfactory refinement. For the 1:1 material the unit-cell dimensions and a partial structure were enough to show that the compound has the same packing arrangement as the [1,3-S]₂[I] derivative. In the slightly better situation for the 2:1 salt [F-2,5-S]₂[I] all the atoms could be located, but the data would not support a refinement below 10%. This was sufficient, however, to show that the crystals are isostructural with [P-2,6-S]₂[I] described below.¹¹

While the needlelike crystals of the [P-2,6-S]₂[I] compound also suffered from twinning problems, we were eventually able to achieve a satisfactory refinement. The crystals belong to the monoclinic space group *P*2₁/c, atom coordinates are provided in Table 1, while pertinent intra- and intermolecular distances are compiled in Tables 2 and 3. The crystal structure consists of stacks of [P-2,6-S] molecules bridged by stacks of disordered iodine atoms; the stacks run in the *x* direction, with an interstack separation (at room temperature) of 3.343(3) Å. The packing of these stacks within

(10) Cordes, A. W.; Chamchoumis, C. M.; Hicks, R. G.; Oakley, R. T.; Young, K. M.; Haddon, R. C. *Can. J. Chem.* **1992**, 70, 919.

(11) For [F-2,5-S]₂[I], *a* = 3.4139(5); *b* = 29.783(3), *c* = 10.130(3) Å, β = 90.63(2)°, *P*2₁/n, *Z* = 2.

Table 2. Selected Intramolecular Distances (Å) in $[P\text{-}2,6\text{-S}]_2\text{[I]}^a$

S1–S2 ring	S3–S4 ring		
S(1)–S(2)	2.065(3)	S(3)–S(4)	2.082(4)
S(1)–N(1)	1.607(9)	S(3)–N(3)	1.629(8)
S(2)–N(2)	1.613(8)	S(4)–N(4)	1.635(8)
N(1)–C(1)	1.325(11)	N(3)–C(7)	1.313(12)
N(2)–C(1)	1.358(10)	N(4)–C(7)	1.335(12)

^a ESDs refer to the last digit printed.

Table 3. Selected Lateral Intermolecular S–S and S–N Distances (Å) in $[P\text{-}2,6\text{-S}]_2\text{[I]}^a$

S1–N2'	3.060(7)	at	1.000–x	-0.500+y	0.500–z
S1–N2'	3.415(8)	at	–x	-0.500+y	0.500–z
S1–N4'	3.242(7)	at	1.000–x	-0.500+y	0.500–z
d_1 S1–N5'	3.246(7)	at	1.000–x	-0.500+y	0.500–z
d_1 S1–N5'	3.408(7)	at	–x	-0.500+y	0.500–z
d_2 S2–S4'	3.668(4)	at	1.000–x	-0.500+y	0.500–z
d_2 S2–N4'	3.426(8)	at	1.000–x	-0.500+y	0.500–z
d_3 S3–S3'	3.952(5)	at	1.000–x	1.000–y	1.000–z
S3–N3'	3.322(8)	at	1.000–x	1.000–y	1.000–z

^a ESDs refer to the last digit printed. Contacts d_1 – d_3 are illustrated in Figure 1.

the *yz* plane is illustrated in Figure 1. Figure 2 shows a side view of [P-2,6-S] molecules along the stacking direction.

The two CN_2S_2 rings within each [P-2,6-S] unit have very different environments. Pairs of S3–S4 rings are linked by bridging iodines, with S–I contacts ranging from 3.428(7) to 3.842(6) Å. By contrast the S1–S2 rings are well separated from the iodines but exhibit a series of S–S and S–N contacts (Figure 1) from neighboring CN_2S_2 and pyridine rings. To the extent that charge transfer occurs from iodine to the [P-2,6-S] molecule, it would be reasonable to suppose that the charge-transfer process would be between iodine and the CN_2S_2 ring to which it is coordinated. However, a close inspection of the structural features of the two CN_2S_2 rings suggests that this is not the case.

In the past we⁶ and others¹² have probed the degree of charge transfer in dithiadiazolyl CT salts by comparing the internal S–S and S–N distances with those found in fully reduced and fully oxidized structures. The variations are small, the differences between fully oxidized cations and neutral rings being no more than 0.1 Å. In iodine CT salts charge transfer is incomplete, and internal structural parameters are, as expected, intermediate between those found for neutral and +1ve charge rings. In [1,4-S][I], for example, the charge distribution was established (by low-temperature crystallography) as $[\text{CN}_2\text{S}_2]^{1/4+} [\text{I}]^{1/4-}$, i.e., each CN_2S_2 ring carries a $1/4$ +ve charge. Consistently the internal S–S and S–N distances in both CN_2S_2 rings are closer to those found for neutral rings than for cations. In the present case, the two CN_2S_2 rings (S1–S2) and (S3–S4) are not in identical environments, and there are structural differences. Given that the differences are small (within 3 or 4 standard deviations), and should therefore be viewed with caution, comparison of the trends in S–S and S–N distances reveals that the longer S–S and S–N distances (formally to be associated with a lower oxidation state) are found in the S3–

(12) (a) Banister, A. J.; Hansford, M. I.; Hauptman, Z. V.; Luke, A. W.; Wait, S. T.; Clegg, W.; Jorgenson, K. A. *J. Chem. Soc., Dalton Trans.* **1990**, 2793. (b) Banister, A. J.; Rawson, J. M.; Lavender, I. *Adv. Heterocycl. Chem.* **1995**, 62, 137.

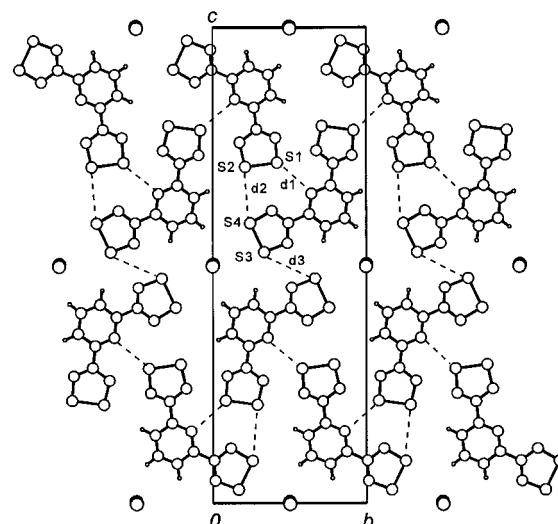


Figure 1. Packing pattern of $[P\text{-}2,6\text{-S}]_2\text{[I]}$ in the *yz* plane.

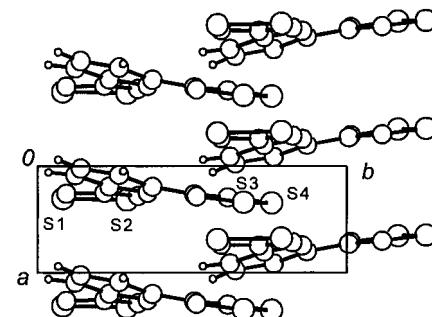


Figure 2. Stacks of [P-2,6-S] molecules along the *x* direction. Disordered iodine atoms are omitted for clarity.

S4 ring, the one coordinated to iodine. Indeed the structural parameters of the S3–S4 ring are virtually identical with those observed in the dimers of neutral radicals [1,4-S]¹³ and [1,3-S].¹⁴ By contrast, the S1–S2 ring exhibits S–S and S–N distances very similar to those observed in [1,3-S][I] and [1,4-S][I],⁶ i.e., they are consistent with a partially oxidized ring. Indeed the structural similarity of the S1–S2 ring observed here to the those found in [1,4-S][I] suggests a comparable degree of charge transfer.

The only other known structure possessing two rings with different oxidation states is [1,4-S][Br]. However, in this latter case the charged and uncharged rings are coordinated in different orientations to the same bromide ion. Charge transfer is also complete in [1,4-S][Br], i.e., bromine is fully reduced.⁶

Magnetic and Conductivity Measurements. In previous studies of the transport properties of dithiadiazoyls and their CT salts we have examined both conductivity and magnetic susceptibility characteristics as a function of temperature. The former require, for four-probe measurements, reasonably large, well-formed crystals, while the latter can be performed on bulk poly- or microcrystalline samples. For the iodine CT salts reported here, we have been restricted, by crystal size

(13) Cordes, A. W.; Haddon, R. C.; Oakley, R. T.; Schneemeyer, L. F.; Waszczak, K. A.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, 113, 582.

(14) (a) Andrews, M. P.; Cordes, A. W.; Douglass, D. C.; Fleming, R. M.; Glarum, S. H.; Haddon, R. C.; Marsh, P.; Oakley, R. T.; Palstra, T. T. M.; Schneemeyer, L. F.; Trucks, G. W.; Tycko, R. R.; Waszczak, J. V.; Warren, W. W.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, 113, 3559.

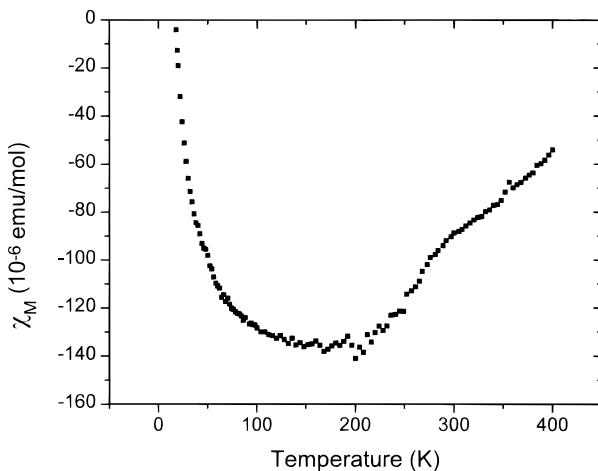


Figure 3. Magnetic susceptibility of $[P-2,6-S]_2[I]$ as a function of temperature.

and quality, to information obtained from the magnetic measurements on $[P-2,6-S][I]$. The data, as illustrated in Figure 3, provide a clear picture of the electronic structure of the compound as a function of temperature. The material is basically diamagnetic at low temperature, as seen for the 1:1 salts of $[1,3-S]$ and $[1,4-S]$; a Curie fit to the data leads to a susceptibility of $-153 \text{ cgs ppm mol}^{-1}$ for the diamagnetic term, in good agreement with estimates based on the Pascal scheme. The concentration of unpaired spins was found to be 0.7%. Paramagnetism develops above 220 K and continues to climb steadily with increasing temperature up to 400 K, the limit of the experiment. Overall, this behavior is very similar to that of the 1:1 iodine CT salts of $[1,3-S]$ and $[1,4-S]$, except that the onset in paramagnetism, which was earlier associated with a transition from a semiconducting to a metallic phase, occurs at a higher temperature in the present case. Pressed pellet conductivity measurements on $[P-2,6-S][I]$ at room temperature indicate a conductivity near $10^{-2} \text{ S cm}^{-1}$, a value somewhat lower than found for $[1,3-S][I]$. Taken together with the magnetic data, we interpret this as an indication that, at room temperature, the compound lies near the T_{MI} transition. In the absence of definitive structural information on either the 1:1 or 2:1 iodine CT salts of $[F-2,6-S]$, we have not pursued detailed transport property measurements. The 1:1 material is a good conductor at room temperature with a pressed pellet conductivity near 10 S cm^{-1} , as expected from its structural resemblance to $[1,3-S][I]$. The 2:1 material is a semiconductor with a pressed pellet conductivity near $10^{-5} \text{ S cm}^{-1}$.

Summary

The seemingly minor modification of replacing one CH unit of $[1,3-S]$ **3** with a nitrogen atom, to afford $[P-2,6-S]$ (**6**), has a significant effect on charge-transfer chemistry. Whereas the former reacts with iodine to afford a 1:1 salt in which the molecules form infinite chains linked by bridging halogens, the latter forms a 2:1 salt in which only one CN_2S_2 ring of each molecule is coordinated to iodine. The nitrogen atom on the pyridine spacer group competes successfully as a coordinating base to the other CN_2S_2 ring, thereby precluding the need for a second bridging iodine. Similar although less dramatic effects were noted between the structures

of benzene-1,3,5-tris(dithiadiazolyl) and triazine-2,4,6-tris(dithiadiazolyl).¹⁵ Each molecule within the structure of $[P-2,6-S]_2[I]$ thus contains one isolated, formally neutral CN_2S_2 radical, while the other exists as an iodine CT salt. While the structural evidence on the iodine CT salts of $[F-2,5-S]$ is less complete, it is clear that two stoichiometries (2:1 and 1:1) are possible. In $[F-2,5-S]$ the oxygen atom of the furan ring presumably competes less effectively with iodine than does the pyridine nitrogen in $[P-2,6-S]$ as a coordinating base to the CN_2S_2 rings. Thus, while a 2:1 salt $[F-2,5-S]_2[I]$ can be produced, a 1:1 salt $[F-2,5-S][I]$ with the same packing arrangement as $[1,3-S][I]$ is also possible.

Compared to the stacked 1:1 iodine CT salts, the 2:1 material $[P-2,6-S]_2[I]$ is more susceptible to CDW instabilities; below room temperature the structure collapses into a diamagnetic semiconductor. We have no evidence as to the nature of the low-temperature superlattice, but one-dimensional distortion of the molecular stacks of the two distinct CN_2S_2 units (charged and neutral) to form a diamagnetic ground state is presumably associated with CDWs of different periodicities.

Experimental Section

Furan-2,5-dimethanol, pyridine-2,6-dicarboxylic acid, lithium hexamethyldisilylamide, sulfur dichloride, triphenylantimony, and iodine were all obtained commercially (Aldrich). Sulfur dichloride was redistilled at 1 atm ($=101.3 \text{ kPa}$) prior to use, and iodine was resublimed. Acetonitrile (Fisher HPLC grade) was purified by distillation from P_2O_5 . Furan-2,5-dicarbonitrile¹⁶ and pyridine-2,6-dicarbonitrile¹⁷ were prepared according to literature methods. All reactions were carried out under an atmosphere of nitrogen. The doping reactions were performed in an ATS series 3210 three-zone tube furnace, linked to a series 1400 temperature control system. Infrared spectra were recorded (at 2 cm^{-1} resolution on Nujol mulls) on a Nicolet 20SX/C infrared spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Furan-2,5-bis(dithiadiazolyl) $[F-2,5-S]$ was prepared as previously described by condensation of persilylated furan-2,5-bis(amidine) DIFURADS with SCl_2 and reduction of the so-formed furan-2,5-bis(dithiadiazolylum chloride) with triphenylantimony.¹⁰ Pyridine-2,6-bis(dithiadiazolyl) was prepared using the same procedure, starting from the persilylated pyridine-2,6-bis(amidine) DIPADS; details are provided below.

Preparation of $[P-2,6-S]$. The persilylated pyridine-2,6-bis(amidine) DIPADS was made (in 73% yield) by standard methods¹⁸ from lithium hexamethyldisilylamide and pyridine-2,6-dicarbonitrile followed by treatment of the intermediate lithium amidinate with chlorotrimethylsilane. The product, DIPADS, was recrystallized from acetonitrile/toluene as colorless needles, mp $101\text{--}105 \text{ }^{\circ}\text{C}$. Anal. Calcd for $C_{25}H_{57}N_5Si_6$: C, 50.36; H, 9.63; N, 11.75%. Found: C, 50.48; H, 9.39; N, 11.93%. Excess (5 mL) sulfur dichloride was added to a slurry of DIPADS (6.41 g, 10.8 mmol) in 100 mL of CH_3CN , and the resulting mixture heated at gentle reflux for 4 h. The yellow solid so formed was filtered off, washed with $2 \times 20 \text{ mL}$ CH_3CN , and dried in *vacuo*. This crude pyridine-2,6-bis(dithiadiazolylum chloride) was reduced with Ph_3Sb (4.14 g, 11.73 mmol) in 100 mL of refluxing CH_3CN for 4 h. The

(15) Cordes, A. W.; Haddon, R. C.; Hicks, R. G.; Kennepohl, D. K.; Oakley, R. T.; Schneemeyer, L. F.; Waszczak, J. V. *Inorg. Chem.* **1993**, *32*, 1554.

(16) (a) Oleinik, A. F.; Yu Novitskii, K. *Zh. Org. Khim.* **1970**, *6*, 2632. (b) El Hajj, T.; Masroua, A.; Martin, J.-C.; Descotes, G. *Bull. Soc. Chim. Fr.* **1987**, 855. (c) Morikiwa, S.; Teratake, Jpn. *Kohai Tokkyo Koho*, **63**, 19,963; *Chem. Abs.* **1979**, *91*, 39301c.

(17) Gorbyleva, O. I.; Evstratova, M. I.; Yakhontov, L. N. *Khim. Geterotsikl. Soedin.* **1983**, 1419; *Chem. Abs.* **1984**, *100*, 51419J.

(18) Boeré, R. T.; Hicks, R. T.; Oakley, R. T. *Inorg. Synth.* **1996**, *36*, 94.

resulting crude diradical was filtered off, washed with 2×20 mL of CH_3CN , and dried in vacuo. Pyridine-2,6-bis(dithiadiazolyl) [P-2,6-S] was purified, as its dimer, by gradient sublimation from $190\text{--}140\text{ }^\circ\text{C}/10^{-3}$ Torr as lustrous black needles, mp $251\text{--}254\text{ }^\circ\text{C}$. Yields were typically 30–40%. Anal. Calcd for $\text{C}_7\text{H}_3\text{N}_5\text{S}_4$: C, 29.46; H, 1.06; N, 24.54%. Found: C, 29.73; H, 1.01; N, 24.76%. IR ($1600\text{--}400\text{ cm}^{-1}$) 1303 (w), 1257 (m), 1157 (m), 1077 (m), 979 (m), 834 (m), 813 (m), 792 (s), 774 (m), 760 (s), 718 (m), 640 (m), 507 (m) cm^{-1} .

Preparation of [F-2,5-S][I] and [F-2,5-S]₂[I]. The following description is a summary of many similar reactions. [F-2,5-S] (0.50 mmol of the dimer) and an equimolar amount of I₂ (126 mg, 0.50 mmol) were sealed in an evacuated (10^{-3} Torr) Pyrex tube (25 mm \times 250 mm). The tube was then placed in a three-zone tube furnace with all three zones set at $130\text{ }^\circ\text{C}$. Over a period of several hours the initially intense purple color faded as the iodine was absorbed by the dimer to generate the CT salt. The tube was then cooled and opened, and the black residue repacked into a new tube which was then evacuated, sealed and set back into the furnace. The temperature along the tube was ramped from 170 to $130\text{ }^\circ\text{C}$ and the assembly left for periods ranging from 2 to 10 days. Black, heavily twinned flakes of the 1:1 salt [F-2,5-S][I] slowly grew in the cooler regions of the tube. Sublimation was usually incomplete because of a slow buildup of iodine pressure and the simultaneous appearance, in the unsublimed material, of more lustrous needles of the 2:1 salt [F-2,5-S]₂[I]. The tube was then removed from the furnace, cooled, and opened. The 1:1 salt was harvested and the crude unsublimed needles of the 2:1 salt repacked into a fresh, evacuated sealed tube. The new sublimer tube was then set in the furnace, and temperature ramp increased to $200\text{--}130\text{ }^\circ\text{C}$. Under these slightly more severe conditions the 2:1 salt sublimed along the tube, albeit on some occasions slightly contaminated by the 1:1 material. The combined yields of the two salts ranged from 30 to 60%. Both materials could be harvested in air but were stored in sealed tubes under argon. Anal. Calcd for $\text{C}_6\text{H}_2\text{N}_4\text{OS}_4\text{I}$: C, 17.96; H, 0.50; N, 13.96; I, 31.63%. Found: C, 18.11; H, 0.36; N, 13.80; I, 31.90%. Anal. Calcd for $\text{C}_{12}\text{H}_4\text{N}_8\text{O}_2\text{S}_8\text{I}$: C, 21.33; H, 0.60; N, 16.59; I, 18.78%. Found: C, 21.43; H, 0.74; N, 16.48; I, 19.85%.¹⁹ The IR spectrum of [F-2,5-S][I] was very poorly resolved because of scattering of the incident radiation by the sample; only bands at 1158 (w, br), 985 (m), 809 (w), and 511 (m) cm^{-1} were observed. The IR spectrum of [F-2,5-S]₂[I] was more clearly resolved and exhibited bands at 1592 (w), 1354 (m), 1226 (w), 1153 (w, br), 1015 (m), 984 (m), 830 (w), 803 (m), 765 (m, br), and 511 (m) cm^{-1} .

Preparation of [P-2,6-S]₂[I]. Attempts to prepare a 1:1 salt for [P-2,6-S] were unsuccessful. Although uptake of iodine, either by solid/vapor methods as described above or by solid/solution reaction, showed (by mass balance) that a 1:1

(19) The iodine analysis for the 2:1 CT salts was variable and irreproducible as a result of interference from sulfur. For each of these compounds the reported iodine data represents the best of many separate analyses. Repeated and accurate C, H and N data plus, in the case of [P-2,6-S]₂[I], the iodine occupancy from the X-ray work, confirmed the stoichiometry.

Table 4. Crystal Data for [P-2,6-S]₂[I]

formula	$\text{IS}_8\text{N}_{10}\text{C}_{14}\text{H}_6$
fw	348.83
crystal size, mm	$0.51 \times 0.11 \times 0.08$
crystal color	black
crystal mount	on glass fiber by epoxy
<i>a</i> , Å	3.434(3)
<i>b</i> , Å	9.8914(9)
<i>c</i> , Å	30.803(4)
β , deg	91.52(3)
<i>V</i> , Å ³	1045.9(9)
d(calcd), g cm ⁻³	2.22
space group	<i>P</i> 2 ₁ / <i>c</i>
Z	2
λ , Å	0.71073
temp, K	293
μ , mm ⁻¹	2.31
<i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i>) ^a	0.047, 0.081

$$^a R = \{\sum |F_o| - |F_c|\}/\{\sum |F_o|\}, R_w = \{\sum w|F_o| - |F_c|^2\}/\{\sum (w|F_o|^2)\}\}^{1/2}.$$

salt was formed, sublimation of such material invariably led to iodine release and the generation of a 2:1 material. Once this excess iodine vapor had been removed (as described above), the 2:1 material could sublimed along a $200\text{--}130\text{ }^\circ\text{C}$ gradient to afford black, lustrous needles. Anal. Calcd for $\text{C}_{14}\text{H}_6\text{N}_{10}\text{S}_8\text{I}$: C, 24.10; H, 0.87; N, 20.08, I, 18.19%. Found: C, 24.07; H, 0.65; N, 19.92; I, 19.03%.¹⁹ Dec $> 250\text{ }^\circ\text{C}$. IR ($1600\text{--}400\text{ cm}^{-1}$) 1577 (w), 1352 (m), 1166 (m), 1087 (w), 983 (w), 835 (w), 771 (s), 654 (m), 511 (w), 405 (w) cm^{-1} .

X-ray Measurements. All X-ray data were collected on an ENRAF-Nonius CAD-4 diffractometer with monochromated Mo K α radiation. Crystals of [P-2,6-S]₂[I] were mounted on a glass fiber with epoxy. Data were collected using the $\theta/2\theta$ technique. The structures were solved using direct methods and refined by full-matrix least-squares which minimized $\sum w(\Delta F)^2$. A summary of crystallographic data is provided in Table 4.

Magnetic Susceptibility Measurements. The magnetic susceptibility of [P-2,6-S]₂[I] as a function of temperature was measured using a SQUID magnetometer operating at 1 T.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, bond lengths and angles, anisotropic thermal parameters for [P-2,6-S]₂[I] (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfiche version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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