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Preparation and Solid State Characterization of Isostructural Bifunctional 1,2,3,5-Dithiadiazolyls with Benzene, Bithiophene, and Piperazine Spacers

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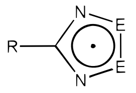
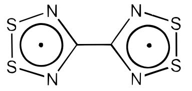
The preparation of the bis(1,2,3,5-dithiadiazolyl) radicals $[S_2N_2C]-X-[CN_2S_2]$, where X is a heterocyclic bridging group (X = piperazine, thiophene, bithiophene) is described. Crystal structures of the piperazine- and bithiophene-bridged diradicals have been determined by single-crystal X-ray diffraction. The two compounds are isostructural, belonging to the monoclinic space group $P2_1/n$; for the piperazine derivative $a = 5.9913(6)$ Å, $b = 19.1958(16)$ Å, $c = 9.1244(6)$ Å, $\beta = 100.314(7)°$, and $Z = 4$. For the bithiophene derivative $a = 5.9907(17)$ Å, $b = 24.272(3)$ Å, $c = 9.1740(14)$ Å, $\beta = 102.961(18)°$, and $Z = 4$. The diradicals associate as cofacial dimers which adopt a herringbone packing pattern analogous to that observed previously for the 1,4-phenylene-bridged derivative. In all three structures the herringbone arrays are characterized by a series of close interdimer S---S contacts along the spine. Consistently, the results of extended Hückel band structure calculations indicate highly developed two-dimensional electronic structures.

Introduction

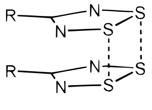
The molecular and solid state structures of heterocyclic thiazyl and selenazyl radicals have been intensively studied in recent years.[2] Derivatives of the 1,2,3,5-dithiadiazolyl radical **1** (E = S) and their selenium analogues (E = Se) have received particular attention. In part, this activity can be attributed to the potential use of these materials in the design of single-component molecular conductors.[3] With this concept in mind and with a view to designing molecules with particular solid state properties, we and others have prepared and structurally characterized a wide range of mono-, di-, and trifunctional radicals. Although solid state structures containing discrete (but isolated) radicals can be made,[4] most derivatives crystallize as diamagnetic dimers, e.g., **2** (**A**, **B**, and **C**). Such association can be understood, within a solid state context, as a natural consequence of the tendency of any electronic system based upon a half-filled energy band to undergo a charge density wave driven or Peierls distortion.[5] However, distorted structures consisting of tightly packed stacks of dimers can, in principle, still display good semiconductive behavior. However, early structural studies on monofunctional sulfur (R = NMe_2, Me, Ph, CF_3)[6] and selenium (R = Ph)[7] derivatives failed to show the desired stacking of molecular plates. We therefore investigated the structural consequences of the attachment of cyanophenyl[8] groups in the 4-position. As observed elsewhere,[9] the incorporation of the nitrile group leads to a solid state packing pattern in which individual molecules are linked by CN---S (or CN---Se) bridges; under favorable circumstances, stacked structures can prevail. More recent work on the prototypal derivative **1** (R = H) has revealed that it is polymorphic, but in both phases the dimers form one-dimensional stacks.[10] A stacked arrangement of dimers has also been found for the "back-to-back" diradical **3**.[11]



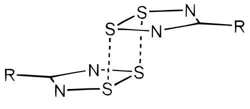
1 (E = S, Se)



3



2A



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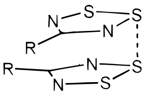

2C

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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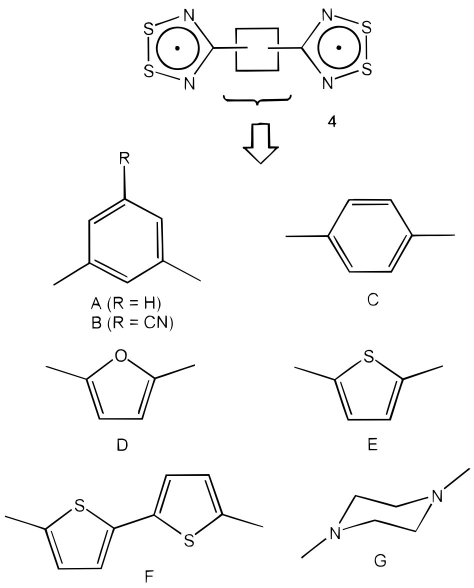
Difunctional radicals with 1,3- and 1,4-phenylene spacer groups, i.e., **4** (**A**, **B**, and **C**), have also been prepared,[12−15] as have triradicals linked by 1,3,5-benzenetriyl and 2,4,6-triazinetriyl spacers,[16] with the intent of increasing the number and magnitude of close intermolecular S---S interactions. Certainly, in the case of the selenium counterparts to **4** (**A**, **B**, and **C**), conductivity is notably improved relative to that of monofunctional systems. The packing patterns exhibited by **4A**/**4B** and **4C** are, however, quite different. While the 1,3-derivatives **4A** and **4B** adopt stacked structures with a zigzag arrangement of dimer contacts, the 1,4-compound **4C** consists of dimers locked into a tight herringbone pattern. For the selenium analogue of **4A**, a second phase, containing interlocking dimers rather than molecular stacks, has also been identified.[17] Interestingly, and despite the absence of stacking in **4C**, electronic interactions are highly developed, and its selenium analogue displays remarkably high conductivity.



This structural dichotomy displayed by bridged diradicals, herringbone *vs* molecular stacks, poses an interesting architectural question. What are the electronic factors that control the energetic balance between these two morphologies? Clearly, for any compound, the factors favoring one mode of crystal packing over another are both complex and subtle.[18] In dithiadiazolyl derivatives, the structures are laced together with complex arrays of intermolecular S---N and S---S interactions, and the energetic consequences of these and other effects are difficult to assess, let alone predict, with any confidence. The polymorphism noted for several derivatives illustrates the close energetic balance between different structural types. As a step toward the rationalization of the relationship between molecular and solid state structures, we have been studying the effects on solid state architecture of minor modifications in the molecular “building blocks”. We have concentrated our efforts on variants of the benzene-bridged diradicals **4** (**A**, **B**, and **C**). In an earlier paper we described the preparation and structure of the 2,5-furandiyl-bridged diradical **4D**.[19] Herein we extend that work to include the synthesis of the diradicals **4** (**E**, **F**, and **G**), in which the bridging groups are thiophene, bithiophene, and piperazine. Compounds **4F** and **4G** are isostructural with **4C**, and the availability of this isostructural set allows a closer examination of the dominant intermolecular interactions which favor this packing mode. The electronic structures of **4F** and **4G** are compared to that of **4C** by means of extended Hückel band calculations. The results of preliminary studies on the use of these materials in the design of thin-film transistors is also reported.

Results and Discussion

Synthesis. In selecting new variants of the bridged diradicals noted above, we sought bridging or spacer groups which might perturb the electronic structure of the molecule *without* changing the crystal structure of the solid. In the case of the piperazine derivative **4G**, we wished to investigate the consequences of a strongly electron releasing group at the 4-position of the heterocyclic ring.[20] For the thiophene- and bithiophene-bridged materials **4E** and **4F**, the electronic effect of the ligand on the radical was again considered important, along with the possibility that the ligand itself might promote electron delocalization through the solid state structure. The importance of such effects on the properties of oligothiophenes[21] has been widely studied and is discussed in more detail below.

The synthesis of the thiophene- and bithiophene-bridged diradicals **4** (**E** and **F**) was based on the amidine technology that we have used extensively in the past.[7,10−15] Thus the dicyano derivatives **5** (**E** and **F**) were converted into the corresponding bifunctional amidines **6** by treatment with lithium bis(trimethylsilyl)amide, followed by treatment of the intermediate *N*-lithio material with chlorotrimethylsilane. These amidines were then condensed with sulfur dichloride[22] to afford the bis(dithiadiazolylium chloride) salts [**7**]Cl_2, which were reduced

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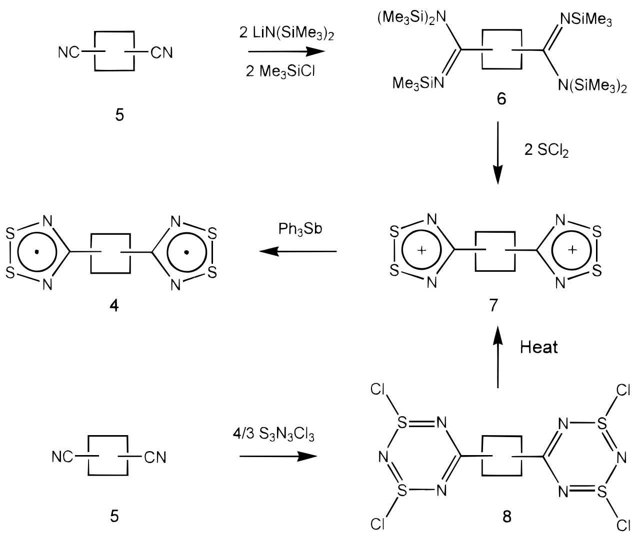

with triphenylantimony to the diradicals **4**. The latter were purified by fractional sublimation *in vacuo* in a gradient tube furnace.

The preparation of the piperazine-bridged diradical **4G** caused some difficulty. To our surprise, and in contrast to the reaction of *N*,*N*-dimethylguanidine with SCl_2, which affords 4-(dimethylamino)-1,2,3,5-dithiadiazolylium chloride in good yield, diguanylpiperazine dihydrochloride[23] does not react with SCl_2.[24] We have therefore taken advantage of the known cycloaddition chemistry of $S_3N_3Cl_3$ with simple dialkylcyanamides to afford dichlorodithiatriazines; the latter can then be thermally converted to dithiadiazolylium salts.[25] Accordingly we were able to react *N*,*N*′-dicyanopiperazine **5G** with $S_3N_3Cl_3$ in benzonitrile to generate, as an intermediate, the bis(dichlorodithiatriazine) **8G**. Heating this intermediate at *ca.* 150 °C effected its conversion to the bis(dithiadiazolylium) salt [**7G**]Cl_2, which was converted, by metathesis with $NOSbF_6$, to the corresponding hexafluoroantimonate salt [**7G**]$[SbF_6]_2$ for characterization purposes. The crude dichloride salt could be reduced directly to the diradical **4G**, which was purified as above by fractional sublimation *in vacuo*.

Crystal Structures. Of the three new diradicals **4** (**E**, **F**, and **G**) reported here only two (**F** and **G**) were amenable to single-crystal X-ray work. In contrast to the furan-based material **4D**, which grows as orthorhombic blocks well suited to X-ray analysis, the thiophene compound **4E** sublimes as fibrous, asbestos-like crystals which rendered structural analysis quite impossible. Likewise one of the two phases of **4G** grows as highly twinned microcrystals, and although several crystals were mounted, none diffracted X-rays. By contrast the block-like phase of **4G** provided extremely good X-ray data, as did the single phase observed for **4F**. Atomic coordinates for the two structures reported are compiled in Tables 1 and 2.

Table 1. Non-Hydrogen Atomic Parameters and B_{eq} Values for **4F**[a]

	x	y	z	B_{eq}, Å^2
S1	0.6351(2)	0.34196(7)	0.06280(16)	4.29(6)
S2	0.3466(3)	0.33911(6)	0.15608(15)	4.16(6)
S3	0.3801(2)	0.49248(6)	−0.23917(14)	3.50(6)
S4	−0.0756(2)	0.61734(6)	−0.48834(14)	3.37(5)
S5	−0.3928(3)	0.74897(6)	−0.83562(16)	4.45(7)
S6	−0.1135(3)	0.75204(6)	−0.93843(17)	4.48(6)
N1	0.5356(7)	0.39182(19)	−0.0527(5)	3.80(19)
N2	0.2084(8)	0.38736(19)	0.0503(5)	3.8(2)
N3	−0.2755(8)	0.7038(2)	−0.7109(5)	4.2(2)
N4	0.0342(7)	0.7073(2)	−0.8267(5)	4.3(2)
C1	0.3289(8)	0.4094(2)	−0.0436(5)	3.1(2)
C2	0.2247(8)	0.4548(2)	−0.1381(5)	3.04(19)
C3	0.0042(8)	0.4736(2)	−0.1607(6)	3.6(2)
C4	−0.0361(8)	0.5174(2)	−0.2595(6)	3.5(2)
C5	0.1469(8)	0.5334(2)	−0.3121(5)	3.10(19)
C6	0.1591(7)	0.5751(2)	−0.4248(5)	2.92(18)
C7	0.3236(8)	0.5855(2)	−0.4981(6)	3.6(2)
C8	0.2691(8)	0.6262(2)	−0.6070(6)	3.6(2)
C9	0.0543(8)	0.6480(2)	−0.6168(5)	3.20(19)
C10	−0.0664(8)	0.6880(2)	−0.7217(5)	3.6(2)

[a] Esds refer to the last digit printed. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table 2. Non-Hydrogen Atomic Parameters and B_{eq} Values for **4G**[a]

	x	y	z	B_{eq}, Å^2
S1	−0.06823(9)	−0.13898(3)	0.10882(6)	2.57(3)
S2	0.22732(10)	−0.14281(3)	0.01681(6)	2.50(3)
S3	0.87091(9)	0.25516(3)	0.67295(6)	2.33(3)
S4	0.57845(9)	0.25826(3)	0.76574(6)	2.38(2)
N1	0.0138(3)	−0.07169(10)	0.21325(19)	2.39(7)
N2	0.3454(3)	−0.07661(9)	0.10929(18)	2.36(7)
N3	0.7674(3)	0.20003(10)	0.54184(18)	2.25(7)
N4	0.4357(3)	0.20440(10)	0.64602(19)	2.38(7)
N5	0.3054(3)	0.00808(9)	0.28748(16)	1.73(6)
N6	0.4466(3)	0.13611(8)	0.43530(16)	1.65(6)
C1	0.2193(3)	−0.04786(10)	0.2012(2)	1.79(7)
C2	0.5532(3)	0.18072(10)	0.54397(19)	1.69(7)
C3	0.1435(3)	0.05174(10)	0.3474(2)	1.83(8)
C4	0.2604(3)	0.09465(11)	0.4768(2)	1.69(7)
C5	0.4829(3)	0.04949(11)	0.2389(2)	1.87(7)
C6	0.6040(3)	0.09336(10)	0.3654(2)	1.76(8)

[a] Esds refer to the last digit printed. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

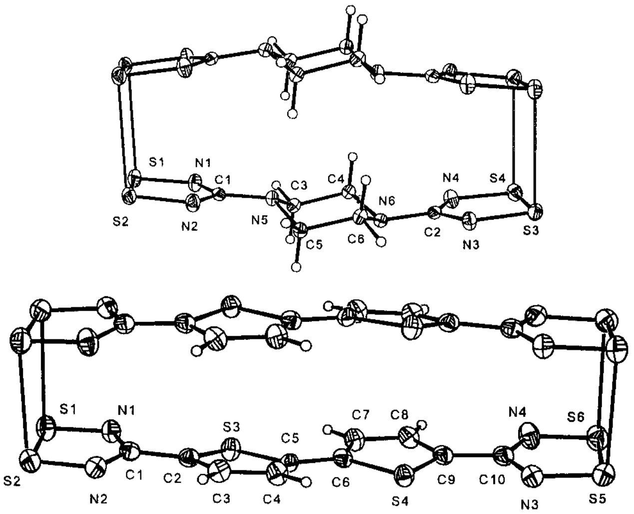

Figure 1. ORTEP drawings of **4G** (above) and **4F** (below), showing atom numbering.

Crystals of **4F** and of the α-phase of **4G** both belong to the monoclinic space group $P2_1/n$ and are isostructural with crystals of the dimer of the 1,4-phenylene-bridged material **4C**. The molecular units in all three structures consist of centrosymmetric dimers linked at both ends by long intrannular S---S contacts. ORTEP drawings of single dimer units, showing atom-numbering schemes, are shown in Figure 1. Internal S−S and S−N distances within the dithiadiazolyl rings (Table 3) are consistent with those seen elsewhere.

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(22) In most cases, an excess of sulfur dichloride is used to ensure ring closure. However, with the bithiophene-bridged material the amount of sulfur dichloride was restricted to the stoichiometric amount. The use of excess quantities led to chlorination of the thiophene rings, as indicated by mass spectrometry.

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Table 3. Summary of Mean Intra- and Intermolecular Distances (Å) in **4C**, **4F**, and **4G**[a]

	4C	**4F**	**4G**
	Intramolecular Distances		
S-S	2.099(9)	2.0965(36)	2.086(23)
S-N	1.638(22)	1.624(26)	1.627(17)
	Intermolecular S---S Contacts		
d1	3.117(4)	3.157(2)	3.0810(8)
d2	3.124(4)	3.095(2)	3.0620(8)
d3	3.558(4)	3.465(2)	3.5154(8)
d4	3.441(4)	3.446(2)	3.5422(8)
d5		3.606(6)	
d6		3.907(2)	
d7		3.826(2)	

[a] Values in parentheses are the greater of the range or the esd.

In the case of **4G**, the two piperazine rings are nested together as stacked chairs, as a result of which one nitrogen (N5) is pyramidalized *endo* to the dimer unit while the other (N6) is *exo*-pyramidalized. In contrast to the structure of the dimer of **1** (E = S, R = NMe_2), where the exocyclic nitrogen is perfectly sp^2-hybridized, both N5 and N6 are far from planar. Cyclic constraints enforce tighter endocyclic angles at nitrogen (C3−N5−C5 = 111.73(16)°, C4−N6−C6 = 112.46(15)°), and the angle sums are 346.9° (N5) and 341.6° (N6). These correspond to POAV[26] pyramidalization angles $\theta_{\sigma\pi}$ of 9.1 and 8.9° (where 0 and 19.47° are respectively the pyramidalization angles for pure planar and tetrahedral geometries). The cofacial dimerization mode in **4F** forces the two bithiophene units into close proximity. This effect is attenuated slightly by torsion (14.4°) of the two thiophene rings about the connecting C5−C6 bonds, so that the S3---S4′ interaction (d7) is increased to 3.826(2) Å.

Like **4C**, the crystal structures of both **4F** and **4G** consist of herringbone arrays of closely interlocked dimers (Figures 2 and 3). In all three structures, the intradimer S−S bonds (d1, d2) as well as the interdimer S---S separations (d3, d4) along the herringbone arrays fall into similar groups (Table 3). In **4C**, there were several additional S---S contacts near the van der Waals separation (3.6 Å)[27] between adjacent layers of herringbone sheets. While similar arrangements of contacts are found for both **4F** and **4G**, all of the interlayer contacts are well outside the expected van der Waals limit. In the case of **4F**, there are, in addition to the interdimer and interthiophene S---S contacts already noted, two interactions (d5, d6) that span the dimers and thiophene rings. The influence of the latter interactions on the electronic structure and properties of this material is discussed below.

Band Structures. The characterization of the three isostructural materials **4** (**C**, **F**, and **G**) provides a unique opportunity to compare the effects of subtle variations in intermolecular separations on electronic structure and physical properties. Accordingly we have carried out a comparative analysis, using the extended Hückel or tight-binding approximation, of the electronic band structures of the three compounds. As noted above, S---S contacts between the herringbone sheets in **4F** and **4G** are well outside the expected van der Waals separation, so that dispersion effects from interactions between these layers are expected to be diminished with respect to those seen in **4C**. However, in contrast to **4G**, the bridging unit in **4C** and **4F** may play a significant electronic role.

Figure 4 illustrates, for the three compounds **4C**, **4F**, and **4G**, the dispersion of the four highest lying occupied crystal orbitals and four lowest unoccupied crystal orbitals along the three principal directions of reciprocal space. As observed earlier for **4C**, the directions of largest dispersion for all three structures are along *a** and *c**. In these monoclinic cells it is difficult to correlate dispersion effects directly with real-space interactions, but qualitatively they can be related to the strong network of S---S interactions along the "spine" of the herringbone array. Likewise, the near absence of dispersion along *b** is consistent with the paucity of extended interactions across the herringbone network. Given these common features, the three structures do exhibit important differences. The conduction levels are much lower in **4C** and **4F** lying than in **4G**, and the band gaps are consequently smaller. This we attribute to the interactions (noted above) between the heterocyclic ring and the π-system of the aromatic bridging unit; in the case of **4F**, the saturated piperazine bridge offers no opportunity for electron delocalization. Closer comparison of **4C** and **4F** reveals slightly larger dispersion for the former, perhaps consistent with the closer contacts found between that herringbone layers. The replacement the benzene bridge in **4C** with a bithiophene bridge in **4F** also leads to a reversal in the sense of dispersion along *c**, so that while **4C** is a predicted to be direct band gap material, the results suggest that **4F** is an indirect band gap material.

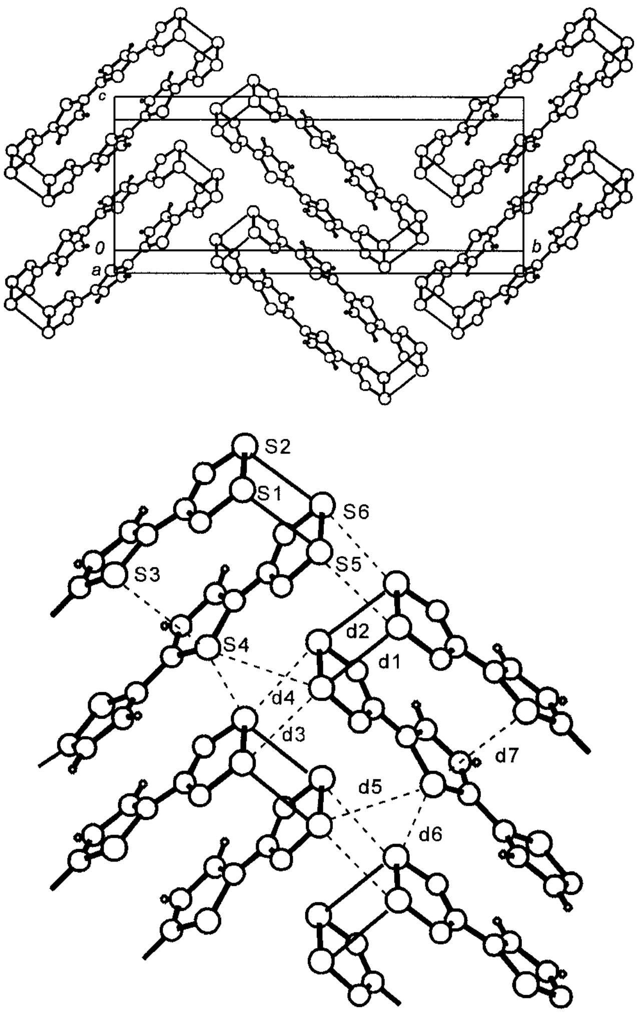

Figure 2. Crystal packing of **4F**. Intermolecular contacts (d1−d7) are listed in Table 3.

Transistor Applications. The strong two-dimensional dispersion of the valence band of **4** (**C**, **F**, and **G**), which rivals if not surpasses that observed for oligothiophenes, prompted us to investigate the potential use of these diradical dimers in thin-film transistors.[21,28] Because of the tendency of **4G** to sublime in (at least) two phases, we restricted our preliminary studies to thin films of **4C** and **4F**. Both materials are highly resistive.

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(26) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.
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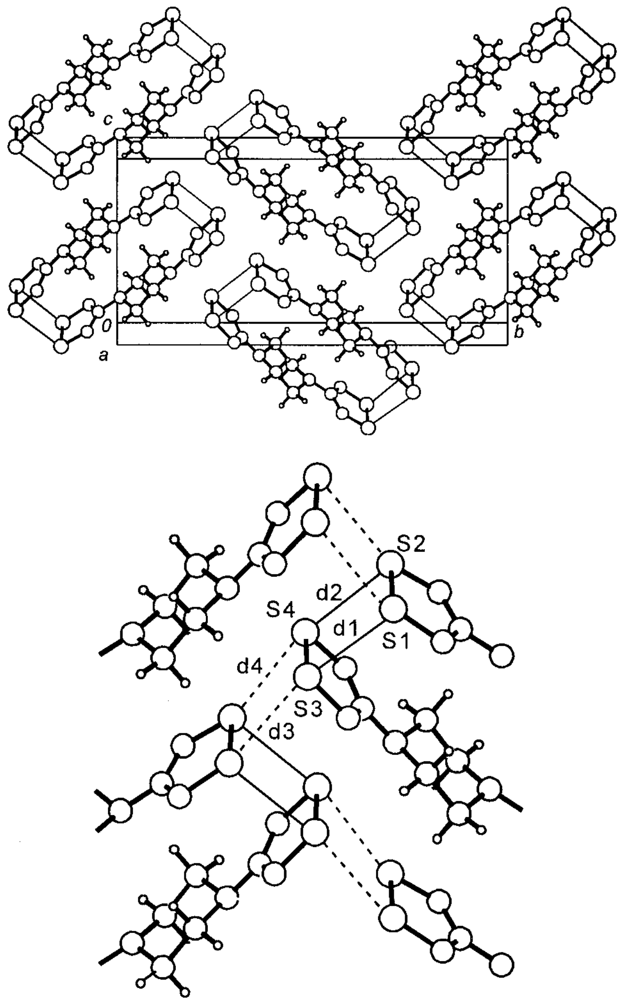

Figure 3. Crystal packing of **4G**. Intermolecular contacts (d1−d4) are listed in Table 3.

The benzene-bridged material **4C** showed no field effect, but the bithiophene derivative **4F**, despite a high threshold voltage, showed a field effect mobility of *ca.* 10^{-6} cm^2 V^{-1} s^{-1}. Additional transport property measurements on these and related materials are underway.

Experimental Section

Starting Materials and General Procedures. The compounds piperazine, cyanogen bromide, triphenylantimony, and chlorotrimethylsilane were obtained commercially (Aldrich), as was nitrosyl hexafluoroantimonate (Strem). Dicyanothiophene[29] was prepared from the reaction of dibromothiophene (Aldrich) with anhydrous CuCN (Aldrich) in quinoline. 2,2′-Bithiophene-5,5′-dicarbonitrile[30] was prepared by reductive coupling of 2-bromo-5-cyanothiophene[31] with copper bronze (Aldrich) and recrystallized from chlorobenzene before use. Acetonitrile (Fisher HPLC grade) and benzonitrile (Aldrich) were purified by distillation from P_2O_5, toluene (Fisher) was purified by distillation from sodium, and chlorobenzene (Fisher) was purified by distillation from P_2O_5. Sulfur dichloride was prepared by direct chlorination of sulfur monochloride (in the presence of trace Fe(III)) and redistilled before use, and $LiN(SiMe_3)_2$ (Aldrich) was converted into its monoetherate in order to facilitate amidine synthesis.[32] All reactions were performed under an atmosphere of nitrogen. Fractional sublimations of diradicals were performed in an ATS series 3210 three-zone tube furnace, linked to a series 1400 temperature control system. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Infrared spectra were recorded (at 2 cm^{-1} resolution on Nujol mulls) with a Nicolet 20SX/C infrared spectrometer. Mass spectra were recorded on a Kratos MS890 mass spectrometer, and ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 spectrometer.

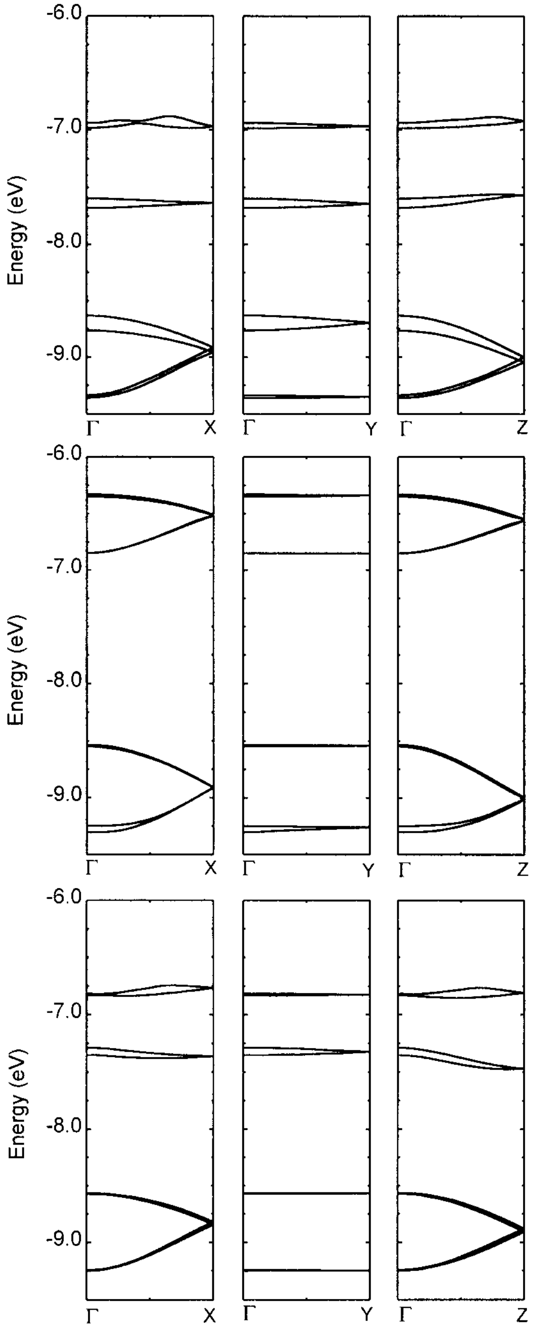

Figure 4. Band structures of **4C** (top), **4G** (middle), and **4F** (bottom). Orbital dispersions are plotted (along the three principal directions of reciprocal space) for the two highest occupied and two lowest unoccupied crystal orbitals.

Preparation of *N,N,N′,N″,N″,N‴*-Hexakis(trimethylsilyl)thiophene-2,5-dicarboximidamide, 6E. Solid $LiN(SiMe_3)_2{\cdot}Et_2O$ (24.1 g, 100 mmol) was added to a solution of 2,5-dicyanothiophene (6.71 g, 50.0 mmol) in 125 mL of toluene. The resultant mixture was stirred at room temperature for 48 h, i.e., until the initially formed precipitate had dispersed to afford a dark brown solution. Neat Me_3SiCl (13 mL, 100 mmol) was then added and the mixture gently refluxed for 4 h. The mixture was then cooled and filtered, and the filtrate was concentrated *in vacuo* to about half its original volume. The remaining solution was heated to *ca.* 80 °C and an equal volume of hot acetonitrile added.

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Upon cooling of the solution, off-white needles of the bis(amidine) **6E** were formed. The crude product was collected by filtration, washed with CH_3CN/toluene (3:1), and dried *in vacuo* (22 g, 73%). The product was recrystallized from 2:1 CH_3CN/toluene as colorless needles, mp 68−72 °C. Anal. Calcd for $C_{24}H_{56}N_4SSi_6$: C, 47.94; H, 9.39; N, 9.32. Found: C, 48.12; H, 8.96; N, 9.55. ^1H NMR (δ, $CDCl_3$): 6.98 (s, 2H), 0.122 (s, 54H). IR (2000−400 cm^{-1} region): 1632 (m), 1525 (w), 1250 (m), 1230 (m), 1197 (w), 1090 (w), 1057 (w), 1023 (w), 972 (m), 947 (w), 880 (m), 846 (s), 759 (w), 703 (w), 686 (w), 653 (w), 636 (w) cm^{-1}.

Preparation of 2,5-Thiophenediylbis(1,2,3,5-dithiadiazol-4-yl), 4E. A solution of sulfur dichloride (2.3 g, 22.3 mmol) in 5 mL of CH_3CN was added to a slurry of **6E** (3.00 g, 5.00 mmol) in 50 mL of CH_3CN, and the mixture was stirred and heated at gentle reflux for 2 h under nitrogen. After this time, the dark red precipitate of the crude bis(dithiadiazolylium chloride) [**7E**]Cl_2 was filtered off, washed with 2 × 20 mL of CH_3CN, and dried *in vacuo*. The crude salt was slurried in 50 mL of CH_3CN, solid triphenylantimony (2.00 g, 5.67 mmol) was added, and the mixture was then stirred and heated at gentle reflux for 1 h. The resulting black solid, crude 2,5-thiophenediylbis(dithiadiazol-4-yl) (as its dimer), was filtered off, washed with 2 × 20 mL of CH_3CN, and dried *in vacuo*. The crude solid was purified by gradient vacuum sublimation from 170 to 130 °C/10^{-3} Torr to afford extremely thin, fibrous black needles of the dimer of **4E** (0.52 g, 1.8 mmol, 36%), mp >250 °C. Anal. Calcd for $C_6H_2N_4S_5$: C, 24.82; H, 0.69; N, 19.29. Found: C, 24.72; H, 0.53; N, 19.42. Mass spectrum, *m/z* (EI, 70 eV): 290 (M^+, 100%), 244 ($[M - SN]^+$, 45%), 212 ($[M - S_2N]^+$, 85%), 166 ($NCC_4H_2SCNS^+$, 30%), 134 ($[NCC_4H_2SCN]^+$, 25%), 78 (S_2N^+, 28%), 64 (S_2^+, 15%). IR (2000−400 cm^{-1} region): 1540 (w), 1331 (w), 1240 (m), 1123 (w), 1106 (s), 1043 (w), 827 (w), 817 (m), 800 (m), 774 (s), 667 (m), 660 (m), 502 (s), 343 (w) cm^{-1}.

Preparation of *N,N′,N″,N″,N‴*-Hexakis(trimethylsilyl)-2,2′-bithiophene-5,5′-dicarboximidamide, 6F. Solid $LiN(SiMe_3)_2 \cdot Et_2O$ (9.5 g, 40 mmol) was added to a slurry of 5,5′-dicyano-2,2′-bithiophene **5F** (4.25 g, 20 mmol) in 120 mL of toluene. This solution was stirred for 5 h at room temperature, after which Me_3SiCl (8 mL, 60 mmol) was added; the mixture was then gently warmed (70 °C) overnight. LiCl was filtered off and the solvent removed *in vacuo* to afford a brown oil. The oil was taken up in a 2:1 mixture of CH_3CN/toluene, and yellow crystals of **6F** (5.1 g, 7.5 mmol, 32%) appeared when the mixture was cooled to −20 °C. The product was recrystallized from 2:1 CH_3CN/toluene as yellow fibrous needles, mp 102−104 °C. ^1H NMR (δ, $CDCl_3$): 0.15 (Me_3Si, 27H), 7.03 (AB, thiophene, 4 H). IR (2000−400 cm^{-1} region): 1624 (s), 1519 (w), 1302 (m), 1256 (s), 1210 (s), 1183 (s), 1098 (m), 966 (s), 841 (s, br), 755 (m), 683 (m), 505 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{58}N_4S_2Si_6$: C, 49.21; H, 8.55; N, 8.20. Found: C, 48.97; H, 8.66; N, 8.12.

Preparation of 2,2′-Bithiophene-5,5′-diylbis(1,2,3,5-dithiadiazol-4-yl), 4F. A solution of SCl_2 (3.66 g, 36 mmol) in 10 mL of chlorobenzene was added dropwise to a solution of **6F** (6.0 g, 8.8 mmol) in 100 mL of chlorobenzene, and the mixture was heated for 1 h at 70 °C. The crude bis(dithiadiazolylium chloride) **[7F]**Cl_2 was filtered off, washed with 3 × 20 mL of CH_3CN, and dried *in vacuo*. This orange solid was immediately reduced with excess triphenylantimony (3.9 g, 11 mmol) in refluxing CH_3CN for 24 h. The black solid was filtered off, washed with CH_3CN, and dried *in vacuo*. This crude product was purified by fractional sublimation over several days in a gradient tube sublimator at 200−150 °C/10^{-3} Torr to afford lustrous black crystalline rods of the dimer of **4F** (0.35 g, 0.94 mmol, 11%), dec >250 °C. IR (1600−400 cm^{-1} region): 1526 (m), 1301 (m), 1245 (w), 1124 (w), 1109 (m), 1058 (w), 889 (w), 820 (m), 797 (s), 770 (s), 740 (m), 735 (m), 660 (m), 633 (w), 502 (m), 474 (w), 464 (w), 416 (w) cm^{-1}. Anal. Calcd for $C_{10}H_4N_4S_6$: C, 32.24; H, 1.08; N, 15.04. Found: C, 32.44; H, 1.20; N, 15.14. Mass spectrum, *m/z* (EI, 70 eV): 372 (M^+, 5%), 294 ($[M - S_2N]^+$, 15%), 216 ($[M - 2(S_2N)]^+$, 25%), 160 ($[C_4H_2S]_2^+$, 15%), 78 (S_2N^+, 10%, 64 (S_2, 100%).

Preparation of *N,N′*-Dicyanopiperazine, 5G. *N,N′*-Dicyanopiperazine was prepared by a modification of the literature method.[33] Piperazine (8.0 g, 93 mmol) and sodium acetate trihydrate (25.4 g, 190 mmol) were dissolved in 100 mL of ethanol at 0 °C. Cyanogen bromide (19.7 g, 190 mmol) was added to the yellow solution, generating heat and precipitating a white powder. After 1 h, this solid was filtered off and washed with water and ethanol. A second crop was recovered from the mother liquor. The two crops were combined and recrystallized from ethanol to give white flakes of *N,N′*-dicyanopiperazine, **5G** (10.5 g, 77.0 mmol, 83%). ^1H NMR (δ, $CDCl_3$): 3.32 (s, 8H).

Table 4. Crystal Data

	4F	**4G**
formula	$C_{10}H_4N_4S_6$	$C_6H_8N_6S_4$
fw	372.5	292.4
a, Å	5.9907(17)	5.9913(6)
b, Å	24.272(3)	19.1958(16)
c, Å	9.1740(14)	9.1244(6)
β, deg	102.961(18)	100.314(7)
V, Å^3	1300.0(4)	1032.42(15)
ρ_{calcd}, g cm^{-3}	1.90	1.88
space group	$P2_1/n$	$P2_1/n$
Z	4	4
radiation	Mo Kα, graphite monochromated	Mo Kα, graphite monochromated
λ, Å	0.710 73	0.710 73
temp, K	293	293
μ, mm^{-1}	1.0	0.86
no. of data with $I > 3\sigma(I)$	1695	1591
R, R_w[a]	0.045, 0.081	0.024, 0.057

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

Preparation of *N,N′*-Piperazinediylbis(1,2,3,5-dithiadiazol-4-yl), 4G. Dicyanopiperazine (1.02 g, 7.5 mmol) was added to a slurry of $S_3N_3Cl_3$ (2.48 g, 10.1 mmol) in 70 mL of benzonitrile. The resulting solution was gently heated (to about 70 °C) under nitrogen for 2 h, during which a heavy orange-brown precipitate was produced. This intermediate **8G** (see Results and Discussion) was directly converted to the bis(dithiadiazolylium chloride) [**7G**]Cl_2 by heating the mixture to gentle reflux for an additional 2 h. The brown/black solid was filtered off, washed with 2 × 15 mL portions of acetonitrile, and dried *in vacuo*. IR (1600−500 cm^{-1} region): 1530 (s), 1298 (s), 1261 (m), 1125 (m), 1010 (s), 950 (w), 892 (m), 801 (w), 707 (w), 568 (w) cm^{-1}. Triphenylantimony (5.0 g, excess) was then added to a slurry of the crude dichloride in 100 mL of acetonitrile, and the mixture was refluxed under nitrogen for 12 h. The resulting black precipitate was filtered off, rinsed with acetonitrile, and dried *in vacuo*. The crude product was purified by fractional sublimation (over 3 days) at 170−120 °C/10^{-3} Torr to afford two crystalline phases, lustrous black blocks (α-phase) and spike-like clusters (β-phase) of the dimer of **4G** (yield 300 mg, 1.0 mmol, 14%). Anal. Calcd for $C_6H_8N_6S_4$: C, 24.61; H, 2.76; N, 28.74. Found: C, 24.66; H, 2.96; N, 29.00. Mass spectrum, *m/z* (EI, 70 eV): 292 (M^+, 72%), 214 ($[M - S_2N]^+$, 17%), 186 (43%), 132 (12%), 108 (12%), 78 (S_2N^+, 26%), 64 (S_2^+, 100%). α-Phase, dec >170 °C. IR (1600−500 cm^{-1} region): 1401 (m), 1286 (m), 1266 (s), 1162 (w), 1141 (w), 1119 (w), 1038 (w), 1001 (w), 879 (m), 808 (m), 781 (s), 708 (w), 511 (m) cm^{-1}. β-Phase, dec >150 °C. IR (1600−500 cm^{-1} region): 1300 (w), 1253 (w), 1172 (w), 1141 (w), 1127 (w), 1076 (w), 1011 (w), 879 (w), 857 (w), 808 (m), 781 (w), 725 (w), 521 (w) cm^{-1}.

Preparation of *N,N′*-Piperazinediylbis(1,2,3,5-dithiadiazol-4-ylium hexafluoroantimonate), [7G][SbF$_6$]$_2$. Nitrosyl hexafluoroantimonate (4.17 g, 16 mmol) was added to a slurry of crude [**7G**]Cl_2 (obtained from 1.0 g of dicyanopiperazine) in 50 mL of CH_3CN to afford a dark wine red solution. After 1 h, the solvent was removed *in vacuo* to leave a dark red semisolid. Addition of 35 mL of benzonitrile to the mixture provided a free-flowing granular solid in a dark red solution. The red solid was filtered off, washed with 2 × 10 mL portions of chlorobenzene and dried *in vacuo*. This crude material was recrystallized from 60 mL of a 1:1 PhCN/PhCl mixture to afford dark purple plates of *N,N′*-piperazinediylbis(1,2,3,5-dithiadiazol-4-ylium hexafluoroantimonate), [**7G**][SbF_6]$_2$ (1.35 g, 1.77 mmol, 23%), mp >

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250 °C. Anal. Calcd for $C_6H_8N_6S_4Sb_2F_{12}$: C, 9.43; H, 1.06; N, 11.00. Found: C, 9.77; H, 1.24; N, 11.23. IR (2000−400 cm^{-1} region): 1626 (w), 1577 (vs), 1300 (m), 1279 (s), 1159 (m), 1054 (w), 1008 (m), 986 (w), 932 (w), 918 (m), 820 (w), 776 (w), 710 (w), 664 (vs), 644 (m), 568 (m) cm^{-1}.

X-ray Measurements. All X-ray data were collected on an ENRAF-Nonius CAD-4 diffractometer with monochromated Mo Kα radiation. Crystals were mounted on a glass fiber with silicone grease. Data were collected using the $\theta-2\theta$ technique. The structures were solved using Direct methods and refined by full-matrix least-squares analysis which minimized $\sum w(\Delta F)^2$. A summary of crystallographic data is provided in Table 4.

Band Structure Calculations. The band structure calculations were carried out on a Pentium 166 personal computer with the EHMACC suite of programs[34] using the parameters discussed previously.[14,35] The off-diagonal elements of the Hamiltonian matrix were calculated with the standard weighting formula.[36]

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Supporting Information Available: Tables of crystal data, structure solution and refinement parameters, bond lengths and angles, hydrogen positional and isotropic thermal parameters, and anisotropic thermal parameters for **4F** and **4G** (7 pages). Ordering information is given on any current masthead page.

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