

trans-4,4'-Dichloro-1,1',2,2',3,3'-tetrathiadiazafulvalene (DC-TAF) and Its 1:1 Radical Cation Salts [DC-TAF][X]: Preparation and Solid-State Properties of BF₄⁻, ClO₄⁻, and FSO₃⁻ Derivatives

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Abstract: Reductive coupling of 4,5-dichloro-1,2,3-dithiazolylium chloride yields *trans*-4,4'-dichloro-1,1',2,2',3,3'-tetrathiadiazafulvalene (DC-TAF), the first example of this heterofulvalene system. *Ab initio* molecular orbital (B3LYP/6-31G**) calculations on prototypal TAF confirm that the closed shell ¹A_g state lies 22 kcal mol⁻¹ below the ³B_u diradical triplet. Cyclic voltammetry on DC-TAF reveals two reversible oxidation waves at 0.80 and 1.25 V (in CH₃CN, reference SCE). The ESR signal (*g* = 2.0117) of the radical cation [DC-TAF]⁺ (in SO₂(l)) exhibits a five-line hyperfine coupling pattern with *a*_N = 0.096 mT. DC-TAF forms a series of 1:1 radical ion salts [DC-TAF][X] by electrooxidation in the presence of tetrahedral counterions (X⁻ = BF₄⁻, ClO₄⁻, FSO₃⁻). The crystal structures of these salts are isomorphous, monoclinic space group P2₁/*n*, and consist of one-dimensional ladder-like arrays of [DC-TAF]⁺ radical cations bridged by S - - S contacts ranging from 3.5 to 3.7 Å. Variable-temperature conductivity and magnetic measurements on [DC-TAF][ClO₄] indicate Mott insulator behavior, with a measured band gap of 0.30 eV.

Introduction

In the pursuit of new molecular magnetic and conductive materials attention is being focused on the design and synthesis of new heterocyclic radicals and radical ions. While neutral radical materials hold appeal because they obviate the need for counterions,² radical ion based compounds are generally easier to prepare, as the π-donors (or π-acceptors) from which they are generated are air stable, closed shell systems. Many organic π-donors have been investigated, but most have been based on the classical tetrathiafulvalene (TTF) framework; relatively few attempts have been made to break away from the TTF-based design paradigm.^{3–5} Purely inorganic rings, such as binary sulfur nitrogen (i.e., S_xN_y) systems,⁶ are noticeably absent from the group of non-TTF-type donors, in part because their redox chemistry, while rich, is not electrochemically reversible.⁷ Mixed organic/inorganic (i.e., C_xS_yN_z) donors can, however, afford more favorable redox chemistry, while still allowing the close intermolecular interactions which are characteristic of binary S_xN_y systems.

Within this context we have been pursuing the synthesis and characterization of bifunctional 1,2,3-dithiazoles, or bis(1,2,3-DTA)s, in which two 1,2,3-dithiazole residues⁸ are bridged by one or more aromatic rings, as in the benzo- and naphtho-bridged derivatives **1**, **2**, and **3**.^{9–11} These systems are strongly antiaromatic, and easily oxidized to stable, highly delocalized radical cations. As such they hold considerable potential as building blocks for radical ion conductors. Indeed we have already demonstrated that both **2** and **3** are capable of forming charge-transfer (CT) salts with a variety of stoichiometries, structures, and conductivities.

Recently, while investigating the chemistry and structures of simple 1,2,3-DTA radicals **4**, we discovered that the reduction of 4,5-dichloro-1,2,3-dithiazolylium chloride ([4][Cl], R_{4,5} = Cl), commonly referred to as Appel's salt,¹² affords not the expected radical, but the novel 4,4'-dichloro-5,5'-bridged 1,1',2,2',3,3'-tetrathiadiazafulvalene (**5A**, R = Cl), or DC-TAF.¹³ While a diradical formulation **5B** can be envisaged for DC-TAF,¹⁴ its ground state is closed shell. However, like the bridged systems **1**, **2**, and **3**, DC-TAF can be oxidized, both chemically and electrochemically, to a stable radical cation [DC-TAF]⁺. To investigate the potential of DC-TAF as a template or building block for radical ion molecular conductors, we have explored

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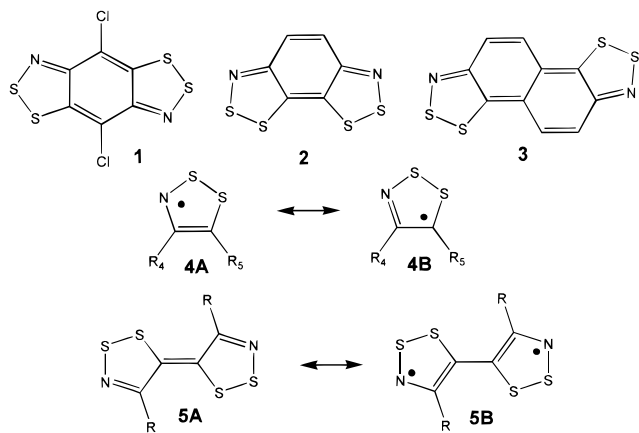
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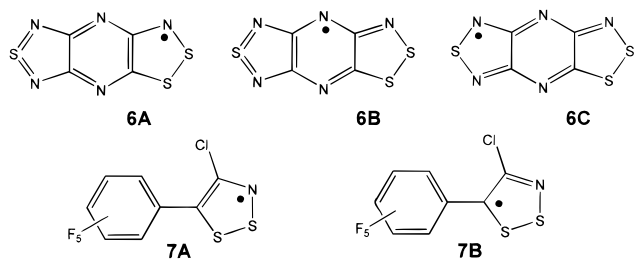
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its charge-transfer chemistry by electrooxidation methods. Herein we provide a full account of the synthesis of DC-TAF, address the spin state issue regarding its electronic structure, and describe the preparation and structural characterization of its 1:1 radical ion salts [DC-TAF][X] ($X^- = \text{BF}_4^-, \text{ClO}_4^-, \text{and } \text{FSO}_3^-$). Transport property (magnetic susceptibility and single-crystal conductivity) measurements on [DC-TAF][ClO₄] are also reported.

Results and Discussion

Synthesis. Many 1,2,3-dithiazolyl radicals **4** have been characterized by ESR spectroscopy.^{15,16} In his pioneering work on these materials Mayer demonstrated that solids exhibiting persistent ESR signals could be isolated when electron-withdrawing (e.g., acyl) groups were attached at the 5-position, or when the radical was fused to an aromatic residue. None of these early examples was structurally characterized. Recently, however, we prepared and characterized two neutral 1,2,3-dithiazolyl radicals, the tricyclic system **6**, and the monocyclic 5-pentafluorophenyl derivative **7**.^{17,18} The remarkable thermal stability of **6** (it sublimes without decomposition at 150 °C/10⁻² Torr) can be attributed to its highly delocalized spin distribution, i.e., **6A**, **6B**, and **6C**. Compound **7** is thermally less stable, but the combined electronic and steric influence of the pentafluorophenyl substituent is sufficient to suppress C–C bond formation at the 5-position. This material associates weakly and reversibly via the 1-sulfur positions.



In light of these observations, the redox chemistry of 4,5-dichloro-1,2,3-dithiazolylum chloride (Appel's salt) posed an

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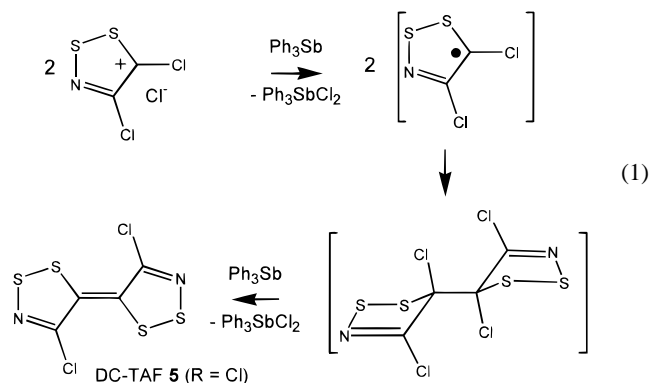
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Table 1. Total Energies^a (hartree) for **4** and **5** (R = H) as a Function of Oxidation State^b

compd	state	energy	compd	state	energy
4	(² A'')	-928.49605 (0.00)	5	¹ A _g	-1855.82915 (0.00)
[4] ⁺	(¹ A')	-928.238817 (7.00)	5	³ B _u	-1855.79448 (0.94)
			[5] ⁺	² B _u	-1855.57555 (6.90)
			[5] ²⁺	¹ A _g	-1855.14347 (18.66)

^a Energies of B3LYP/6-31G** optimized geometries in C_s (**4**) and C_{2h} (**5**). Relative energies (eV) for each manifold are in parentheses.

intriguing question. Could a simple dichloro-1,2,3-DTA radical be isolated, or even observed, or would it associate at carbon, as do 3-chlorodithiolylum salts upon reduction, to yield DC-TAF **5** (R = Cl)? To explore these possibilities we examined the reduction of Appel's salt in a variety of solvents, using either zinc metal or triphenylantimony as reducing agent. Organic solvents (CH₃CN, CH₂Cl₂) were generally ineffective, affording very low yields of **5**, regardless of the choice of reducing agent. The most successful procedure employed liquid sulfur dioxide at ca. -70 °C as solvent, with Ph₃Sb as reductant. When 2 equiv of Ph₃Sb were used, neutral DC-TAF could be isolated in 30% overall yield (eq 1). When only 1 equiv was used, the black



solid isolated displayed an infrared spectrum characteristic of the radical cation salt [DC-TAF][Cl]. Attempts to observe an ESR signal corresponding to a transient dichloro-1,2,3-DTA radical, by carrying out the reduction in an ESR cell at -70 °C, were always thwarted by the rapid emergence of the ESR signal corresponding to [DC-TAF]⁺. Only the *trans* isomer of DC-TAF has been isolated; we have no evidence to suggest the existence of the corresponding *cis* isomer. Presumably steric repulsion between adjacent chlorines militates against the latter configuration.

Electronic Structure. When dissolved in organic media DC-TAF exhibits a strong visible absorption maximum near 565 nm. These deep purple solutions are, however, diamagnetic, and X-ray crystallographic analysis of DC-TAF has revealed a molecular structure consistent with a fulvalene rather than a diradical formulation for the electronic ground state. To assess the energetic proximity of these two states, we have performed a series of density functional theory (DFT) calculations at the B3LYP/6-31G** level on prototypal TAF **5** (R = H) and its parent 1,2,3-DTA radical **4** (R_{4,5} = H). The energies of these species, in different oxidation states, along with computed bond lengths and charges as a function of oxidation state, are summarized in Tables 1–3. Computed spin densities and ¹⁴N isotropic hyperfine coupling constants for the neutral radical **4** and the radical cation [**5**]⁺ are collected in Table 4.

The computed energies (Table 1) on prototypal TAF confirm that the ¹A_g state is more stable than the triplet ³B_u state. The well-defined (21.8 kcal mol⁻¹) separation of the high and low-

Table 2. Summary of Bond Lengths (Å) and Mulliken Atomic Charges (q) for **4** and **[4]⁺** ($R_{4,5} = H$)^a

state	bond lengths		charges	
	4 (² A')'	[4]⁺ (¹ A')	4 (² A')'	[4]⁺ (¹ A')
S-S	2.154	2.099	$q_{S(C)}$	0.099
S-N	1.665	1.602	$q_{S(N)}$	0.274
S-C	1.744	1.681	q_N	-0.470
N-C	1.334	1.324	$q_{C(N)}$	0.128
C-C	1.386	1.409	$q_{C(S)}$	-0.317

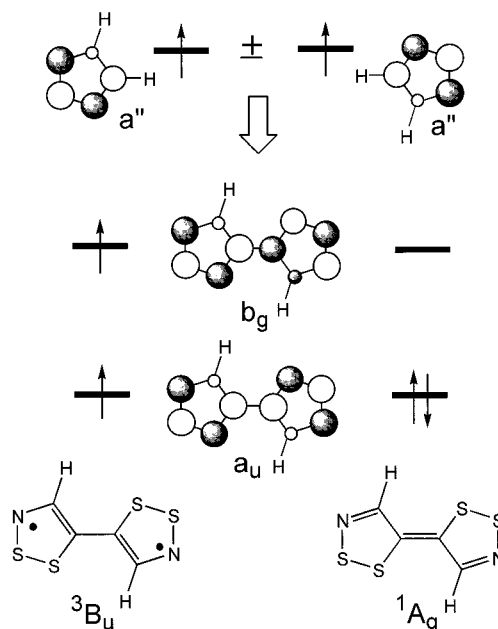
^a B3LYP/6-31G** optimized geometries in C_s symmetry.**Table 3.** Summary of Bond Lengths (Å) and Mulliken Atomic Charges (q) for **5**, **[5]⁺**, and **[5]²⁺** ($R = H$)^a

	compound (state)			
	5 (¹ A _g)	5 (³ B _u)	[5]⁺ (² A _u)	[5]²⁺ (¹ A _g)
S-S	2.157	2.138	2.120	2.093
S-N	1.670	1.661	1.631	1.594
S-C	1.789	1.766	1.746	1.716
N-C	1.290	1.337	1.302	1.320
(N)C-C(S)	1.452	1.392	1.439	1.423
(C)C-C(C)	1.373	1.455	1.413	1.468
$q_{S(C)}$	0.068	0.111	0.254	0.419
$q_{S(N)}$	0.276	0.303	0.479	0.680
$q(N)$	-0.450	-0.485	-0.397	-0.335
$q_{C(N)}$	0.133	0.101	0.148	0.167
$q_{C(S)}$	-0.176	-0.171	-0.178	-0.174

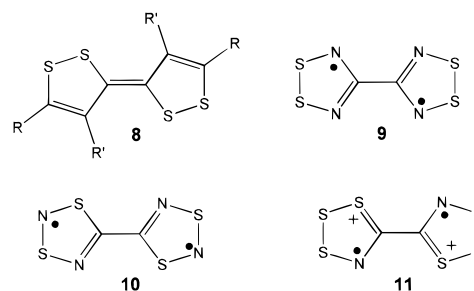
^a B3LYP/6-31G** optimized geometries in C_{2h} symmetry.**Table 4.** Calculated (B3LYP/6-31G**) Spin Densities (ρ) and ¹⁴N Isotropic Hyperfine Coupling Constants a_N (mT) for **4** ($R_{4,5} = H$) and **[5]⁺** ($R = H$)

	ρ_N	$\rho_{S(C)}$	$\rho_{S(N)}$	$\rho_{C(N)}$	$\rho_{C(S)}$	a_N
4	0.385	0.192	0.193	-0.160	0.404	0.695
[5]⁺	0.056	0.200	0.177	-0.03	0.101	0.109

spin states parallels the behavior of 1,1',2,2'-tetrathiafulvalenes **8**,¹⁹ and the origins of this splitting can be traced back to the electronic structure of the parent radical **4**. As is illustrated in Figure 1 the frontier orbitals of TAF can be generated by combining (in-phase and out-of-phase) the singly occupied molecular orbitals (SOMOs) of two 1,2,3-DTA radicals. Accordingly the relative stabilities of the low-spin fulvalene structure **5A** and the high-spin triplet **5B** depend on the degree of orbital interactions between the bridgehead carbons. The heavy localization of spin density on the 5-carbon of 1,2,3-DTA (Table 4), as prescribed by resonance structure **4B**, not only signals the proclivity of these radicals to associate through carbon, but also heralds the strong SOMO mixing that will occur in the fused system **5**. This is in sharp contrast to bis(1,2,3,5-dithiadiazolyl) **9**,²⁰ which is perfectly disjoint, i.e., the SOMOs of the separate radicals are nodal at carbon, and the frontier orbitals of the fused system are degenerate.^{21,22} As a consequence the ground state of **9** is diradical. Less clear-cut situations are found for bis(1,3,2,4-dithiadiazolyl) **10**²³ and the bis(1,2,3-

**Figure 1.** Combination of SOMOs of two 1,2,3-DTA radicals **4** ($R = H$) to afford the frontier orbitals of singlet and triplet TAF **5** ($R = H$).

dithiolylium) dication **11**.²⁴ While neither of these systems is formally disjoint, orbital interactions between the bridgehead carbons are weak, and open shell ground states prevail.



Given that the ground state of **5** is closed shell, both the computed charge distribution and geometry of its triplet state can be traced back to those of the parent radical **4** (Tables 2 and 3). Likewise the structural changes accompanying the oxidation of **5** to **[5]²⁺** parallels those encountered upon the oxidation of **4** to **[4]⁺**. In both cases the structural evolution, i.e., the shortening of the S-S, S-N, and S-C bonds, can be easily understood in terms of the antibonding properties of the a' SOMO of **4** and the occupied a_u frontier orbital of **5** (Figure 1). The radical cation **[5]⁺** represents a compromise, in structure and charge distribution, between the two limiting extremes. The spin distribution summarized in Table 4 reveals a more diluted spin density on all sites of **[5]⁺** in comparison to **4**, but particularly at the 4-carbons. We conclude from this latter result that the charge and spin distributions in derivatives of TAF, e.g., DC-TAF, should not be strongly influenced by substituent effects.

Cyclic Voltammetry and ESR Spectrum. Like compounds **1**, **2**, and **3**, and in accord with the computational results provided above, DC-TAF **5** ($R = Cl$) can be oxidized to a stable radical cation and closed shell dication. The energetics of these processes have been tracked by cyclic voltammetry on solutions

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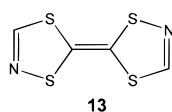
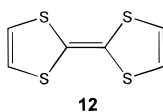
Table 5. Redox Potentials^a and ESR Data for Bis(1,2,3-DTA)s

	compound			
	5 (R = Cl)	1	2	3
$E_{1/2}^{(0/+)}$	0.80	0.93	0.61	0.41
$E_{1/2}^{(+/2+)}$	1.25	1.5 ^b	1.10	0.66
ΔE	0.45	0.57	0.49	0.25
$E_{pc}^{(0/-)}$	-1.11	-0.95	-0.98	-1.06
a_N^c	0.096	0.201	0.161	0.235
g -value	2.0117	2.0114	2.0117	2.0106

^a Volts vs SCE, in CH₃CN. ^b Irreversible; the anodic peak potential E_{pa} is cited. ^c In mT, for radical cation.

**Figure 2.** X-band ESR spectrum of [DC-TAF][ClO₄] in SO₂(l). Sweep width = 2 mT.

of DC-TAF in CH₃CN (with [Bu₄N][PF₆] as supporting electrolyte). Two reversible one-electron waves (Table 5) are observed, as well as a single irreversible reduction wave. The half-wave potential for oxidation of DC-TAF is more anodic than that observed for TTF **12**,^{25,26} as expected from the electronegativity of nitrogen, and close to the oxidation potentials found for the isomeric tetrathiadiazafulvalene **13**.²⁷ However, despite the variations in half-wave potentials, the overall cell potentials ΔE ($\Delta E = E^{(+/2+)} - E^{(0/+)}$) for the disproportionation of the radical cations of all three fulvalenes (**5**, **12**, and **13**) are comparable.



The ESR spectrum ($g = 2.0117$) of the radical cation [DC-TAF]⁺, recorded on solutions of its perchlorate salt, prepared electrochemically (*vide infra*), consists of a pentet with a 1:2:3:2:1 hyperfine pattern ($a_N = 0.096$ mT) characteristic of coupling to two equivalent nitrogens (Figure 2). In simple 1,2,3-DTA radicals hyperfine coupling constants to ¹⁴N are generally in the range of 0.5–0.7 mT, and in this light the value of 0.695 mT predicted for **4** ($R_{4,5} = H$) is satisfying. In the radical cations of **1**, **2**, and **3** the hyperfine coupling constant a_N is reduced, as expected from the more delocalized SOMO. In [DC-TAF]⁺ the a_N value is smaller still, in remarkably good agreement with that computed for [proto-TAF]⁺, and indicative of greater spin density on sulfur. There is no indication of hyperfine coupling to chlorine, also in accord with the computational results, which places very low-spin density on the 4-carbon positions.

In summary, while the oxidation of DC-TAF requires more forcing conditions than those observed for classical TTF-type materials, the ensuing radical cation is extremely stable, and

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Table 6. Crystal Data

formula	S ₄ Cl ₂ F ₄ BN ₂ C ₄	S ₄ Cl ₃ O ₄ N ₂ C ₄	S ₅ Cl ₂ FO ₃ N ₂ C ₄
fw	362.00	374.65	358.26
a , Å	7.2873(17)	7.3684(14)	7.3774(11)
b , Å	13.992(2)	14.0572(19)	14.1757(18)
c , Å	10.872(4)	10.942(2)	10.942(2)
β , deg	92.45(2)	91.937(17)	91.732(15)
V , Å ³	1107.6(5)	1132.6(4)	1143.8(3)
ρ (calcd), g cm ⁻³	2.17	2.20	2.08
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4
F_{000}	711.1	743.6	711.5
radiation	Mo K α , graphite monochromated	Mo K α , graphite monochromated	Mo K α , graphite monochromated
γ , Å	0.7107	0.7107	0.7107
temp, K	293	293	293
μ , mm ⁻¹	1.34	1.52	1.45
no. of refls in refinement $I > 1.0\sigma(I)$	1449	1413	1454
$R(F)$, $R_w(F)^a$	0.039, 0.046	0.044, 0.049	0.047, 0.054

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

exhibits substantial spin density on sulfur. These factors, taken together with the small difference ΔE in the first and second oxidation potentials, which is reminiscent of the corresponding difference for TTF, signals a relatively low Coulombic barrier to charge transfer in the solid state,²⁸ and provides encouragement for the pursuit of DC-TAF and related compounds as building blocks for radical ion conductors.

Charge-Transfer Salts. As expected from the electrochemical results, chemical oxidation of DC-TAF requires forcing conditions. Unlike TTF-based materials, DC-TAF fails to form CT complexes with TCNE, TCNQ, and chloranil, and does not react with iodine. It does, however, react cleanly with bromine, to give a 1:1 bromide salt [DC-TAF][Br], but we have been unable to recrystallize this material for more detailed study. To pursue the potential of DC-TAF as a building block for radical ion conductors we have carried out a systematic study of its response to electrooxidation in the presence of simple tetrahedral inorganic counterions, the latter introduced as ca. 0.1 M solutions of their tetra-*n*-butylammonium salts. We have tested several solvents and a range of current densities, and to date the most effective combination is pure 1,2-dichloroethane with currents of 1–5 μ A. While large tetrahedral anions (FeCl₄⁻, GaCl₄⁻) failed to deposit any product under these conditions, the medium-to-small anions FSO₃⁻, ClO₄⁻, and BF₄⁻ afforded well-formed crystalline material on the anode within a few days. Only one morphology has been observed for all three CT salts, with the stoichiometry of 1:1, i.e., [DC-TAF][X] (X⁻ = FSO₃⁻, ClO₄⁻, and BF₄⁻). The structural features of these materials are described below.

Crystal data for the three CT salts are compiled in Table 6. Their mean internal structural parameters are summarized in Table 7, and a listing of pertinent intermolecular S...S contacts is provided in Table 8. The three compounds are isomorphous, belonging to the space group $P2_1/n$. Two representative views of the BF₄⁻ salt are shown in Figures 3 and 4. Comparison of the internal structural features of the [DC-TAF]⁺ radical cation with those of the parent DC-TAF mirror the subtle changes predicted by the *ab initio* calculations. In accord with the phase properties of the HOMO shown in Figure 1, oxidation of DC-TAF causes a lengthening of the central C–C bond and a shortening of the S–S, S–N, and S–C bonds.

When viewed down the y direction (Figure 3), the crystal structures of [DC-TAF][X] consist of layers of [DC-TAF]⁺

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Table 7. Mean Internal Structural Parameters in DC-TAF 5 (R = Cl) and Its CT Salts^a

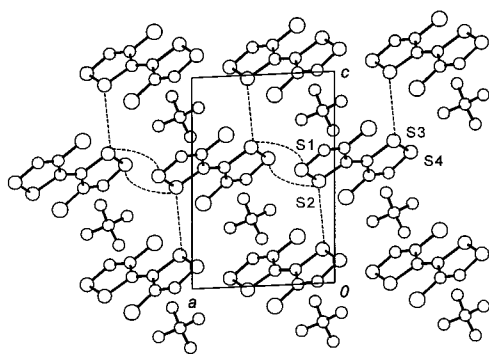
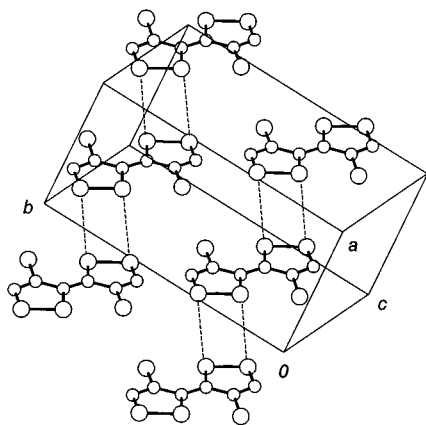
	[DC-TAF][X], X =			
	[DC-TAF]	BF ₄ ⁻	ClO ₄ ⁻	FSO ₃ ⁻
S-S	2.0759(15)	2.050(5)	2.059(14)	2.045(8)
S-N	1.657(4)	1.622(5)	1.615(5)	1.622(10)
S-C	1.768(4)	1.726(4)	1.727(5)	1.730(7)
N-C	1.276(6)	1.286(14)	1.303(7)	1.290(19)
(N)C-C(S)	1.458(5)	1.438(8)	1.437(7)	1.442(8)
(C)C-C(C)	1.383(7)	1.410(5)	1.405(7)	1.401(7)

^a The number in parentheses is the greater of the ESD or range.

Table 8. Intermolecular Contacts (Å) in [DC-TAF][X] (X⁻ = BF₄⁻, ClO₄⁻, FSO₃⁻)^a

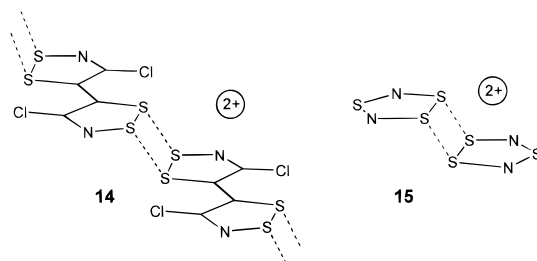
X ⁻	BF ₄ ⁻	ClO ₄ ⁻	FSO ₃ ⁻
S1--S3'	3.605(2)	3.641(2)	3.688(2)
S2--S3'	3.535(2)	3.563(2)	3.524(2)
S2--S4'	3.636(2)	3.670(2)	3.659(2)

^a ESDs are in parentheses.

**Figure 3.** Crystal structure of [DC-TAF][BF₄].**Figure 4.** Ladder-like arrays of radical cations in [DC-TAF][BF₄] (anions omitted for clarity).

radical cations interspersed by X⁻ anions. Molecules in adjacent layers are linked, up and down, by intermolecular S2--S3' contacts (Table 8) which are close to the van der Waals separation for two sulfurs.²⁹ Within the layers, molecules are connected on both sides by S1--S3' and S2--S4' contacts which again are near the van der Waals limit. When the structure is rotated, and the anions removed (for clarity), the layers of radical cations take on the appearance of a ladder-like structure (Figure 2). Given that the bridging interactions are significantly longer (one electron, as opposed to two, is shared between the two radical ions), the locally centrosymmetric arrangement of the bridged five-membered rings **14** is reminiscent of the dimers

15 commonly observed in salts of the well-known [S₃N₂]⁺ radical cation.³⁰



Conductivity and Magnetic Susceptibility. Within the context of a simple band model the electronic structures of the 1:1 [DC-TAF][X] salts reported here can be described in terms of an exactly half-filled energy band. However, the ladder-like arrays of TAF⁺ radical ions are linked only weakly by S--S contacts close to the van der Waals separation, and the bandwidth arising from such a structure is expected to be small, perhaps insufficient to offset the high Coulombic barrier to charge transfer associated with a half-filled energy band. Consistently, preliminary pressed pellet measurements on all three CT salts [DC-TAF][X] (X⁻ = FSO₃⁻, ClO₄⁻, and BF₄⁻) indicated room-temperature conductivities in the region of 10⁻¹ to 10⁻³ S cm⁻¹. These values are consistent with semiconductive (Mott insulator) behavior. By comparison, in the iodide CT salt of **9**, where the degree of band filling is moved away from the half-filled level, and the bandwidth is considerably larger, the room-temperature conductivity is >10² S cm⁻¹.²⁰

To probe these issues in greater detail, we carried out variable-temperature single-crystal conductivity measurements on [DC-TAF][ClO₄⁻], which affords the best crystals of the three salts. The results of these measurements (plotted in terms of resistivity) are illustrated in Figure 5. On the basis of both two-probe and four-probe measurements, the conductivity of [DC-TAF][ClO₄⁻] at room temperature is close to 10¹ S cm⁻¹, and the temperature dependence confirms that the conductivity is activated, with an estimated band gap E_g ($E_g = 2\Delta$) of 0.30 eV. The results of variable-temperature magnetic susceptibility measurements (Figure 6), plotted in terms of the effective fraction of Curie spins, also point to thermal generation of free spins, as expected from a Mott insulator material.

Summary and Conclusions

Heterocyclic thiazyl radicals hold much appeal as molecular building blocks in the design of new molecular magnetic and conductive materials. One of the *raison d'être* behind using these molecules rather than purely carbon-based rings is that the incorporation of heteroatoms reduces the possibility of C-C bond formation. However, in the 1,2,3-dithiazolyl system **4** spin density on the 5-carbon is significant, and in the absence of steric hindrance¹⁸ or delocalization effects¹⁷ C-C bond formation can occur. Herein we have shown how this tendency to self-associate through carbon can be used to advantage, allowing access to the novel tetrathiadiazafulvalene (TAF) ring system **5**. We have also shown that, in contrast to the bifunctional dithiadiazolyls **9** and **10**, TAFs exhibit closed shell **5A** rather than biradical **5B** ground states, again as a result of strong interannular interactions across the bridgehead C-C bond.

While direct applications of TAFs in magnetic materials¹⁴ are unlikely, they are, like other bifunctional 1,2,3-DTAs, excel-

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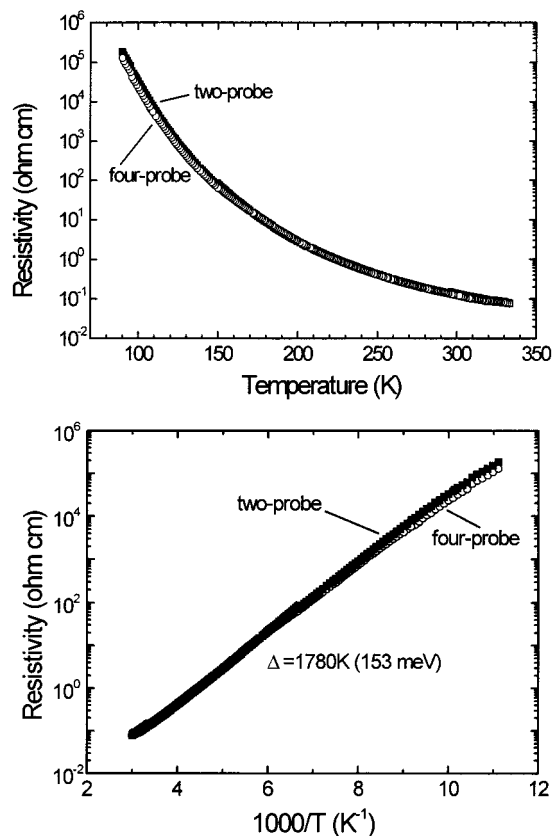


Figure 5. Two and four probe resistivity of [DC-TAF][ClO₄] as a function of temperature (above) and $1/T$ (below).

lent sources of stable radical cations, which can be used as building blocks for CT conductors. Although the ladder-like arrays observed for the three 1:1 CT salts [DC-TAF][X] ($X^- = \text{FSO}_3^-$, ClO_4^- , and BF_4^-) give rise only to semiconductive behavior, derivitization of the TAF framework may allow the design of materials with metallic and perhaps superconducting properties.

Experimental Section

General Procedures and Starting Materials. Sulfur monochloride, chloroacetonitrile, and triphenylantimony were obtained commercially (Aldrich). The electrolytes [*n*-Bu₄N][X], with $X^- = \text{BF}_4^-$, PF_6^- , and ClO_4^- , were also obtained commercially (Fluka), and used as received, while for $X^- = \text{GaCl}_4^-$ and FSO_3^- the materials were prepared and purified according to literature procedures.³¹ The solvents chlorobenzene (Fisher), dichloroethane (Fisher), and acetonitrile (Fisher HPLC grade) were commercial products and were dried by distillation from P₂O₅. Sulfur dioxide gas (Matheson) was also used as received. Melting points are uncorrected. Appel's salt was prepared as described in the literature,¹² with adogen 464 (Aldrich) used as a catalyst. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Infrared spectra were recorded (at 2 cm⁻¹ resolution on Nujol mulls) on a Nicolet Avatar infrared spectrometer. Low-resolution mass spectra (70 eV, EI, DEI and CI, DCI) were run on a Finnigan 4500 quadrupole mass spectrometer at the McMaster Regional Centre for Mass Spectrometry. The X-Band ESR spectrum of the radical cation of DC-TAF was recorded, using a Varian E-109 spectrometer with DPPH as a field marker, on a sample of its perchlorate salt, prepared electrochemically (vide infra) and dissolved in SO₂(l). UV-visible spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer.

Preparation of DC-TAF 5 (R = Cl). Sulfur dioxide (50 mL) was transferred on a vacuum line into an evacuated H-cell containing Appel's salt [4][Cl] (R_{4,5} = Cl, 2.08 g, 10.0 mmol) and triphenylan-

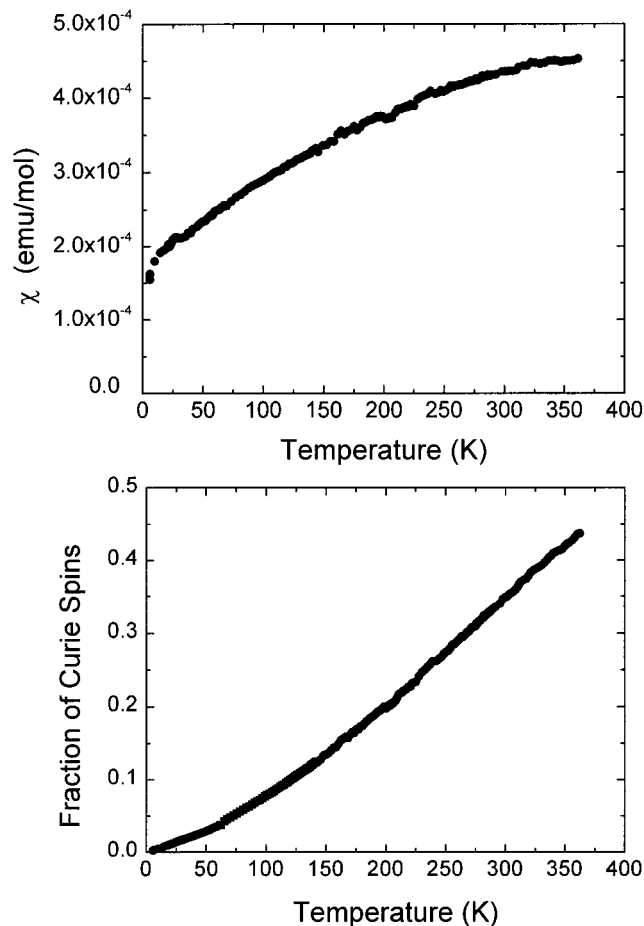


Figure 6. Magnetic susceptibility of [DC-TAF][ClO₄] as a function of temperature (above), after correction to diamagnetism ($=1.6734 \times 10^{-4} \text{ emu mol}^{-1}$), and effective fraction of Curie spins as a function of temperature (below).

timony (3.88 g, 11.0 mmol), and the mixture was stirred and allowed to warm slowly (2 h) from -70°C to room temperature. The black solid so produced was filtered off and back-washed twice with liquid SO₂. The solvent was removed from the reactor, and the residual solid washed sequentially with 50 mL of CH₃CN, 50 mL of aqueous EtOH, and 50 mL of CH₂Cl₂. The remaining solid was then extracted with 4 × 80 mL of hot carbon disulfide, the deep purple extracts combined, and the solvent removed to leave crude DC-TAF 5 (R = Cl), which was recrystallized from toluene as black/purple needles (0.42 g, 1.5 mmol, 30%), mp 120–21 °C, $\gamma_{\text{max}}(\text{CH}_2\text{Cl}_2)$ 565 nm ($\epsilon = 1.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$). MS (*m/z*, %): 274 (M⁺, 100); 210 ([M-S₂]⁺, 30). IR (Nujol): 1487 (m), 1123 (vs), 877 (m), 791 (s), 767 (vs), 604 (w), 498 (w), 473 (s) cm⁻¹. Anal. Calcd for C₄N₂S₄Cl₂: C, 17.46; N, 10.18. Found: C, 17.57; N, 9.97.

Cyclic Voltammetry. Cyclic voltammetry was performed on a PAR 273A electrochemical system (EG&G Instruments) with scan rates of 50–100 mV s⁻¹ on solutions of DC-TAF containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate in CH₃CN (dried by distillation from P₂O₅). Potentials were scanned from -2.5 to 1.5 V with respect to the quasireference electrode in a single compartment cell fitted with Pt electrodes and referenced to the ferrocenium/ferrocene couple at 0.38 V vs SCE.³²

Electrocrystallizations. The electrocrystallization work employed standard H-cell techniques,³³ with samples of DC-TAF (10 mg) dissolved under nitrogen in 20 mL of solvent containing 0.02–0.05 M

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[*n*-Bu₄N][X] (X⁻ = BF₄⁻, FSO₃⁻, and ClO₄⁻). Currents ranged from 1 to 5 μA, with growth periods of 7–10 days. Crystals of all the CT salts were stable indefinitely in air. [DC-TAF][ClO₄]: >100 °C dec. **(WARNING: this material detonates upon heating to temperatures above 100 °C.)** IR (Nujol): 1167 (s), 1117 (s), 1104 (s), 1091 (s), 1059(s), 843 (m), 796 (s), 624 (m), 617 (m), 507 (w), 488 (w) cm⁻¹. Anal. Calcd for C₄N₂O₄S₄Cl₃: C, 12.82; N, 7.48. Found: C, 13.03, N, 7.32. [DC-TAF][FSO₃]: >220 °C dec. IR (Nujol): 1290 (s), 1253 (s), 1165 (s), 1065 (s), 842 (m), 798 (s), 724 (m), 625 (vw), 581 (w), 574 (w), 557 (vw), 510 (vw), 488 (vw) cm⁻¹. Anal. Calcd for C₄N₂O₃S₅-Cl₂F: C, 12.84; N, 7.48. Found: C, 13.06, N, 7.49. [DC-TAF][BF₄]: >220 °C dec. IR (Nujol): 1168 (s), 1125 (m), 1084 (s), 1050 (s), 1038 (m), 1010 (s), 844 (m), 797 (vs), 627 (w), 523 (vw), 517 (vw), 507 (w), 496 (w) cm⁻¹. Anal. Calcd for C₄N₂S₄Cl₂BF₄: C, 13.27; N, 7.74. Found: C, 13.40, N, 7.58.

X-ray Measurements. X-ray data were collected on an ENRAF-Nonius CAD-4 diffractometer with monochromated Mo K α radiation. Crystals were mounted on glass fibers with silicone or epoxy. Data were collected using a $\theta/2\theta$ technique. The structures were solved using direct methods and refined by full-matrix least squares which minimized $\sum w(\Delta F)^2$. In the crystal structure of [DC-TAF][FSO₃] the FSO₃⁻ ions were disordered. The disordered positions were indicated by difference maps, and the occupancies were determined by refinement.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured over the temperature range 5–350 K on a George Associates Faraday balance operating at 0.5 T.

Conductivity Measurements. Conductivity was measured in a helium variable-temperature probe using a LakeShore 340 temperature controller. A Keithley 236 unit was used as a voltage source and current meter, and two 6517A Keithley electrometers were used to measure the voltage drop between the potential leads in a four-probe configuration.

Ab Initio Calculations. All calculations were run on Pentium II workstations using the B3LYP DFT method, as contained in the Gaussian 98W suite of programs.³⁴ Geometries were optimized using a 6-31G** basis set, within the constraints of C_s (for **4**, R_{4,5} = H) and C_{2h} (for **5**, R = H) symmetry. Spin contamination was minimal, with S² = 0.7765 for **4** (R_{4,5} = H), 0.7607 for [**5**]⁺ (R = H), and 2.0200 for the triplet state of **5** (R = H).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the NSF/EPSCoR program (Grant No. EPS-9452895), the State of Arkansas, the Department of Energy (Grant No. DE-FG02-97ER45668), and the MRSEC program of the NSF (Award No. DMR-9809686) for financial support. We also acknowledge the NSERC for a postgraduate scholarship to K.E.P.

Supporting Information Available: Tables of crystal data, structure solution and refinement, bond lengths and angles, and anisotropic thermal parameters for the structures reported (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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