

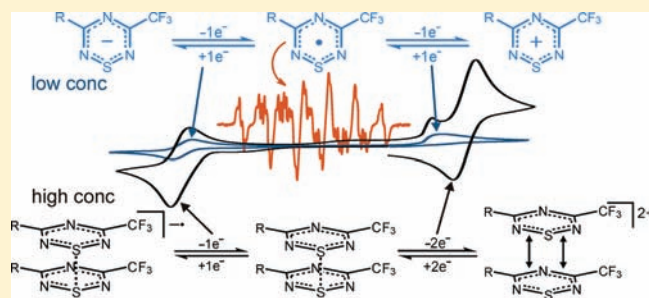
Unsymmetrical $1\lambda^3$ -1,2,4,6-Thiatriazinyls with Aryl and Trifluoromethyl Substituents: Synthesis, Crystal Structures, EPR Spectroscopy, and Voltammetry

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Supporting Information

ABSTRACT: A general synthetic route to 3-trifluoromethyl-5-aryl- $1\lambda^3$ -1,2,4,6-thiatriazinyl radicals was developed. X-ray structures were obtained for all five neutral radicals and show that they exist in the solid state as cofacial dimers linked by $S\cdots S$ contacts. X-ray structures were also obtained for two of the precursor chlorothiatriazines along with several aryl *N*-imidoylamidines, *p*-methoxybenzamidine, and *N*-chlorosulfonyl-*N,N'*-benzamidine. Cyclic voltammetric studies were performed on the $[R_2C_2N_3S]^{\bullet}$ radicals in CH_3CN and CH_2Cl_2 with $[^nBu_4N][PF_6]$ as the supporting electrolyte under vacuum conditions in an all-glass electrochemical cell. The results provide quasi-reversible formal potentials for the $[R_2C_2N_3S]^{-/0}$ process in the range of -0.61 to -0.47 V, irreversible peak potentials for the $[R_2C_2N_3S]^{0/+}$ process from 0.59 to 0.91 V at lower concentrations, and the appearance of a second, reversible oxidation process from 0.69 to 0.94 V at higher concentrations (versus the $Fc^{0/+}$ couple; Fc = ferrocene). This behavior was indicative of monomer–dimer equilibrium in solution, as ascertained from digital models of the voltammograms. There is a small but measurable trend in both the oxidation and reduction potentials with varying remote aryl substituents. EPR spectra were obtained for all five neutral radicals in CH_2Cl_2 solutions, which confirm the concentration of the unpaired electron density on the heterocyclic core. Trends were also seen in the hyperfine splitting constants a_N with varying remote aryl substituents. Calculations were performed for all three oxidation states of the $[R_2C_2N_3S]^{-/+}$ monomeric rings; the resulting theoretical redox energies correlate well with solution phase voltammetric data.



INTRODUCTION

There is strong continuing interest in the synthesis and structural chemistry of sulfur–nitrogen–carbon heterocyclic free radicals, with an emphasis on applications to the design of molecular conductors and molecular magnetism.¹ This interest extends to transition-metal coordination complexes that incorporate such radicals as ligands—including spin-active ligands.² We have contributed to the electrochemical characterization of the redox properties of this whole class of compounds and, in particular, have characterized by solution electrochemistry the influence of aryl ring substituents on 5-aryl-1,2,3,4-dithiadiazolyls.³

In order to extend our approach to a new class of C,N,S radicals, we have developed a general synthetic route to the asymmetrically substituted 3-trifluoromethyl-5-aryl- $1\lambda^3$ -1,2,4,6-thiatriazinyls (Chart 1). We recently communicated the utility of such thiatriazinyl radicals as novel π -donor ligands to the organometallic moiety $CpCr(CO)_2$;⁴ here, we elaborate the chemistry of these heterocyclic free radicals, including structural characterization of novel intermediates and several final products in the solid state by X-ray crystallography, solution EPR spectroscopy, and a detailed electrochemical investigation interpreted in light of DFT calculations.

RESULTS AND DISCUSSION

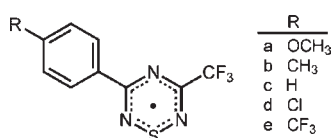
A primary goal of this work was the development of a more general route to 1,2,4,6-thiatriazinyl radicals which would allow for modification of the exocyclic substituents (Scheme 1). Various methods have been attempted to prepare both symmetric and asymmetrically substituted thiatriazines.⁵ Amidines have been reported to react with $S_3N_3Cl_3$ to form 1-chloro-1,2,4,6-thiatriazines.^{5e,f} In this work, we first converted amidines into *N*-imidoylamidines and found that these, when passivated as hydrochlorides, afford 1-chloro-1,2,4,6-thiatriazines by direct reaction with sulfur dichloride in high yield.^{5b,6} An established literature procedure was used to prepare the *para*-substituted benzamidine hydrochlorides,⁷ but the free bases **1a–e** have not previously been reported. Full characterization of these useful intermediates is provided in the Experimental Section, and the crystal structure of **1a** is presented in Figure S1 (Supporting Information).

Aryl *N*-imidoylamidines. In contrast to amidine chemistry, aryl *N*-imidoylamidines have received less attention, although

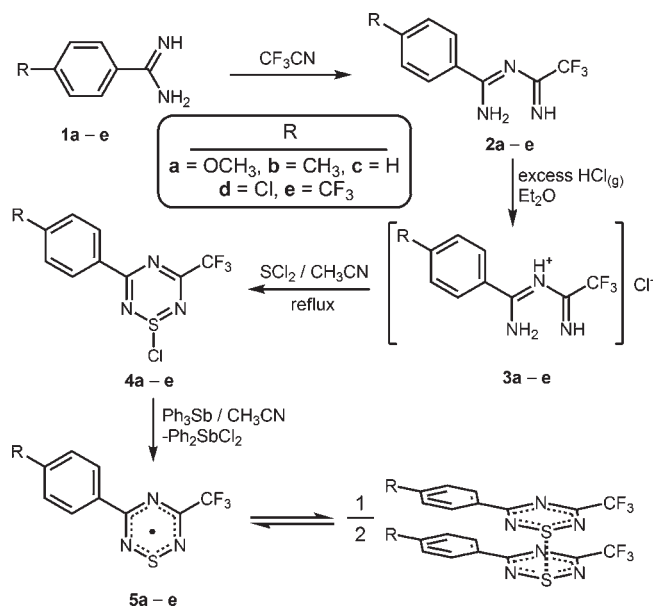
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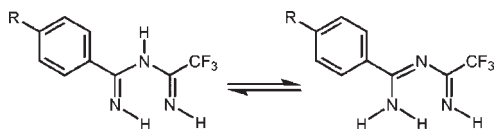
Chart 1. The 3-Trifluoromethyl-5-aryl-1 λ^3 -1,2,4,6-thiatriazinyls



Scheme 1. Synthetic Route to the 3-Trifluoromethyl-5-aryl-1,2,4,6-thiatriazines



several preparative routes have been reported.⁸ In this work, it was found that direct reaction of trifluoroacetonitrile with the free-base amidines gave the desired imidoamidines in high yields in accordance with the report by Schaeffer.⁹ The colorless sublimed products were found to be pure by ¹H and ¹³C NMR spectroscopy, MS, and elemental analysis. The expected signals for hydrogen atoms attached to carbon were observed in ¹H NMR spectra recorded in CDCl₃ (Table S1, Supporting Information). Three separate NH peaks are also observed (Figure S2, Supporting Information), indicating nonequivalency of the hydrogen atom environments. The signals resonating around 11 and 6.7 ppm are noticeably broadened compared to the one near 9 ppm, indicating a higher rate of exchange between the former.



These results are consistent with either of the above tautomers, i.e., either with hydrogen attached to three different N atoms as on the left or, as on the right, with one imino and two amino hydrogen atoms in which the latter are nonequivalent due to strong intramolecular hydrogen bonding. The solid-state structure (Figure 1) shows the dominance of the imino-amino tautomer but also shows H-bonding of H1B to the backbone

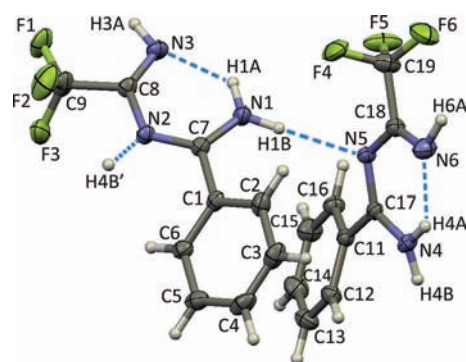


Figure 1. Thermal ellipsoid (30%) plot showing the two independent hydrogen-bonded molecules of **2c** as found in the crystal at $-100(2)^\circ\text{C}$ along with an additional H4B' atom to indicate how the chain propagates in the lattice. The H1B–N5 and H4B'–N2 bonds can be viewed as incipient tautomerism leading to the diimine isomer. Only the principal components of the disordered CF₃ groups are shown for clarity (Figures S3 and S4, Supporting Information, are plots of **2a** and **2e**).

nitrogen atom N5, which, if exchange occurred, would interconvert it to the diimine. In the ¹³C NMR spectra, seven distinct carbon peaks (Table S2) were observed, which are attributable to the seven different types of carbon atoms in **2a–e**.

X-ray structures of imidoamidines are rare. In fact, no structures of unsubstituted imidoamidines have been reported in the Cambridge Crystal Structure Database (CSD, version 5.31, updated Nov. 2009), and only one structure of an imidoamidinium salt is known (with [Se₂Cl₁₀]²⁻ as the counterion).¹⁰ However, crystal structures of imidoamidinate anions coordinated to various metals are known,¹¹ and the structure of the related parent biguanide has been reported.¹² Colorless crystalline plates of **2a**, **2c**, and **2e** were grown by sublimation in a three-zone tube furnace under a dynamic vacuum, and their structures were determined at low temperatures by X-ray diffraction. All three crystal structures contain two crystallographically independent molecules which display very similar inter- and intramolecular hydrogen bonding,¹³ as shown by dashed lines in Figure 1 for compound **2c** as a representative example. The atom numbering scheme is the same for all three structures to facilitate comparison; the H-bonding data for **2a**, **2c**, and **2e** are discussed in the Supporting Information (Table S3).

The average bond lengths and angles determined from all six crystallographically independent molecules of **2a**, **2c**, and **2e** are shown in Figure 2. This clearly shows that C8–N3 is short, characteristic of an imine, while C7–N1 and C7–N2 are identical within esd and of intermediate length, characteristic of a highly delocalized amidine. Aryl/CF₃ substitution therefore leads to a rather unsymmetrical imidoamidine geometry, approximating an imino-substituted amidine.

Conversion to N-Imidoamidine Hydrochlorides. Direct reaction between **2c** and sulfur dichloride to form **4c** resulted in low yields of the product as an intractable oil that proved hard to purify. However, pacifying the reactive nitrogen base with HCl increased the yield of **4c** significantly and afforded a low-melting solid. Therefore, all of the imidoamidines were converted with HCl(g) in dry diethyl ether to the corresponding hydrochloride salts **3a–e**, which precipitated as white, insoluble solids that were characterized by infrared spectroscopy. Each adduct has a unique fingerprint region but similar broad bands in the 3300 cm⁻¹ range characteristic for NH stretches involved in hydrogen bonding.

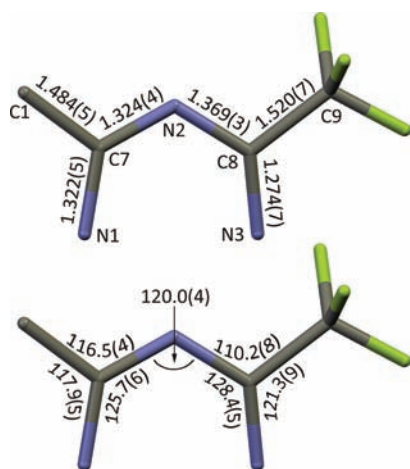


Figure 2. Average bond lengths (Å, top) and angles (deg, bottom) from crystal structures of the six independent imidoylamidine molecules found in **2a**, **2c**, and **2e**. Errors are standard deviations.

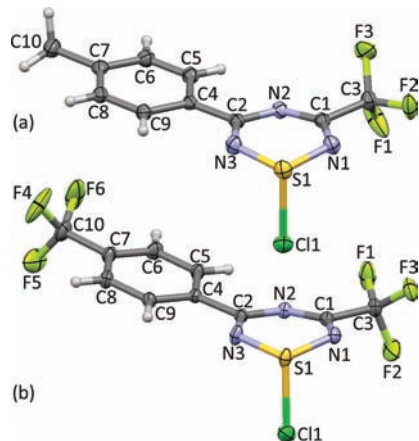


Figure 3. Thermal ellipsoid (30%) plots with atom numbering schemes showing the molecular structures of (a) **4b** and (b) **4e** as they are found within the crystal lattices at $-100(2)$ °C. Only the principal components of the disordered CF₃ groups are shown.

1-Chloro-3-trifluoromethyl-1,2,4,6-thiatriazines. An excess of SCl₂ was used to ensure the completion of the reaction of the imidoylamidine hydrochloride salts **3a–e** to the 1-chloro-thiatriazines **4a–e**. Crude yields were typically high (>80%), and these materials were used without further purification in the synthesis of the radicals. ¹H NMR spectra (Table S4, Supporting Information) confirmed ring formation through the absence of NH signals, and only the phenyl and *para*-substituted hydrogen atoms appear in the spectra between 7.0 and 8.6 ppm. The signals of H₁, *meta* to the thiatriazine core, are weakly affected by heterocycle formation, shifting only ~0.10 ppm downfield compared to the imidoylamidines. However, the signals of H₂, *ortho* to the heterocyclic core, are shifted downfield by ~0.60 ppm. This is diagnostic for the formation of a thiazyl ring; for example, the chemical shifts of the *ortho* hydrogen atoms in comparably substituted 1,5-dithia-2,4,6,8-tetrazocine heterocycles are very similar to those of **4a–e**.¹⁴ ¹³C NMR was not obtained due to instability of the compounds to hydrolysis. However, extremely moisture-sensitive X-ray-quality crystals could be grown for **4b**

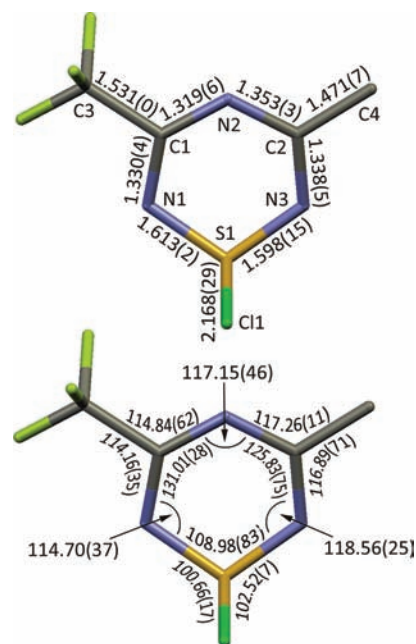
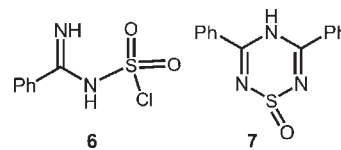


Figure 4. Average bond lengths (Å, top) and angles (deg, bottom) with standard deviations from crystal structures of the 1-chlorothiazines **4b** and **4e**.

and **4e** from acetonitrile solutions at -35 °C, and the crystal structures were determined at low temperatures. These structures confirm the formation of the six-membered ring with an almost perpendicular S–Cl bond, as shown in Figure 3. The C₂N₃ atoms are coplanar (maximum deviation 0.047(1) Å), with the sulfur atoms tipped slightly out of the plane (0.288(2) Å, **4b**; 0.323(2) Å, **4e**). The interatomic distances in **4b** and **4e** are quite comparable. Averaged bond lengths and angles from the two structures are presented in Figure 4. The phenyl rings in both structures have average C–C bond lengths of 1.389(10) Å and are essentially coplanar with the heterocyclic core. The packing of **4e** shows regular stacks aligned with the crystallographic *c* axis without any significant short contacts, but **4b** has typical S–(δ⁺)–N(δ[−]) short contacts between pairs of rings (Figure S5, Supporting Information).^{1d}



The sensitivity of **4** to moisture is highlighted by the hydrolysis of **4c** from adventitious H₂O in CH₃CN to give **6** as colorless blocks suitable for X-ray analysis (Figures S6–S8, Supporting Information). The hydrolysis product **6** surprisingly retains the S–Cl bond (unlike {PhCN}₂{NH}S=O, **7**),¹⁵ but a CF₃CH=NH moiety is eliminated while the sulfur is converted to oxidation state VI.

5-Aryl-3-trifluoromethyl-1,2,4,6-thiatriazinyls. Several reducing agents have been used previously to effect the reductive elimination of the chloride ion from 1-chloro-1,2,4,6-thiatriazines. In early work, sodium verdazyl was often used.⁵ Here, we employed triphenylantimony because of its general utility in the

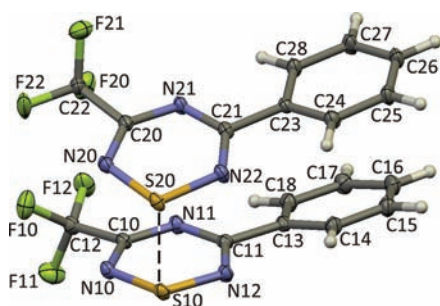
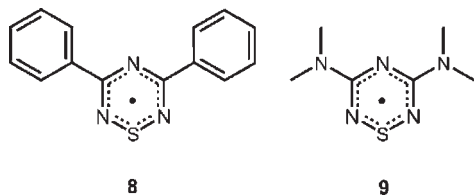


Figure 5. Thermal ellipsoid (30%) plot and atom numbering scheme showing the solid-state face-to-face and head-to-head dimerization of **5c**, which comprises the asymmetric unit in the lattice at $-100(2)$ °C. The dashed line indicates the close contact between sulfur atoms, for which the $S10 \cdots S20$ distance is $2.625(1)$ Å. The structure of **5a** (Figure S9, Supporting Information) is very similar, with an $S10 \cdots S20$ distance of $2.6370(3)$ Å.

reduction of thiazyl halides.^{5e,f} A half-molar ratio of solid triphenylantimony was added by a solids-addition bulb to acetonitrile solutions of **4a–e** after careful removal of oxygen via freeze–thaw–degassing. Reduction to the radical was immediate in all cases, as the solution turned from a clear dark red to a dark purple (almost black) solution with the precipitation of some solid. Precipitated crude products were purified by sublimation in a three zone tube furnace and produced X-ray-quality plates of the radicals **5a–e**. Diffraction data were obtained at -100 ± 2 °C and the structures solved and refined at this temperature. However, in the case of **5b**, persistent high R factors were encountered, and hence the structure was redetermined at RT with better results. Formation of a superlattice is suspected at the lower temperature. In each case, the solid-state structures display the same face-to-face and head-to-head (presumably diamagnetic) dimers obtained previously for bis(3,5-diphenyl-1,2,4,6-thiaziazinyl) (**8**),^{5e} despite the presence of the bulky CF_3 groups. For both **5a** and **5c**, one kind of crystallographically independent dimer is observed in their crystal lattices (Figure 5). For **5b** and **5d**, two sets of wedge-shaped dimers are found stacked back-to-front in the lattice (Figure 6).



The shortest contact between C_2N_3S rings is always through the sulfur atoms, with an average distance of $2.643(21)$ Å. This is longer than a normal disulfide linkage but within range of other known thiaziazinyls such as **8**,^{5e} whose shortest contact is $2.666(3)$ Å, and 3,5-bis(dimethylamino)-1,2,4,6-thiaziazinyl (**9**), whose shortest contact is again through the sulfur atoms at $2.5412(8)$ Å.¹⁶ Average bond lengths and angles were calculated for the entire series **5a–e**, and the results are presented in Figure 7. The average S–N bond length over both bonds ($SX0-NX0$ and $SX0-NX2$, $X = 1-4$) is $1.633(10)$ Å, which is shorter than the S–N single bond in $S_4N_4H_4$ (1.665 Å) and longer than the N–S bond in S_4N_4 (1.616 Å). The average C–N bond length in the ring is $1.332(16)$ Å, longer than an average C=N double bond ($\sim 1.270(15)$ Å)¹⁷ and shorter than

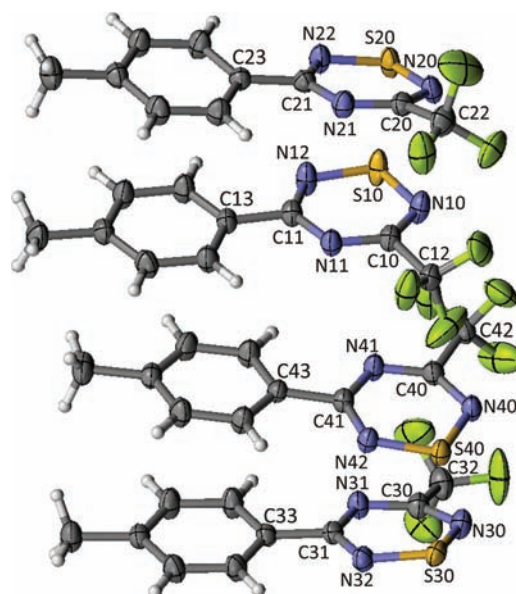


Figure 6. Thermal ellipsoid (30%) plot with atom numbering scheme showing the molecular structure of **5b** found within the crystal lattice at $23(2)$ °C. Four crystallographically independent molecules form two distinct dimers. The $S10 \cdots S20$ distance is $2.684(1)$ Å, and the $S30 \cdots S40$ distance is $2.6515(8)$ Å. A very similar arrangement is found in the lattice for **5d** (Figure S10, Supporting Information) with $S10 \cdots S20$ and $S30 \cdots S40$ distances of $2.659(1)$ Å and $2.635(1)$ Å, respectively.

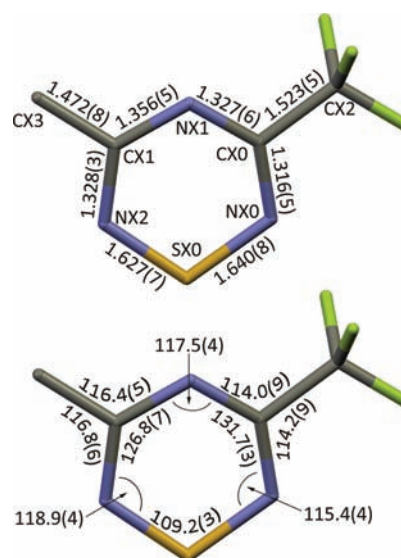


Figure 7. Average bond lengths (Å, top) and angles (deg, bottom) with standard deviations in 1,2,4,6-thiaziazinyls determined from five crystal structures. A common numbering scheme was used among crystallographically independent monomers ($X = 1-4$). The average intradimer short $S \cdots S$ contact distance is $2.643(21)$ Å.

an average C–N single bond ($1.472(5)$ Å). A typical heterocyclic C–S bond length is approximately $1.352(5)$ Å.¹⁷ The asymmetric substitution pattern seen in **5a–e** allows for a comparison of the bond lengths and angles with the symmetric diphenyl and dimethylamino analogues **8** and **9**. The C–N bond lengths are very similar, as are the S–N bond lengths with only the S–N bond closest to the CF_3 group averaging slightly longer than in **8**.

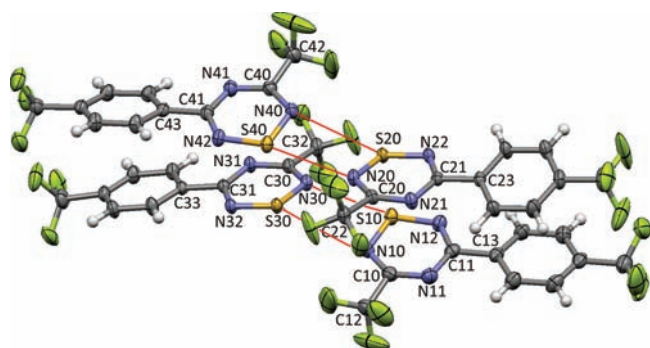


Figure 8. Thermal ellipsoid (30%) plot with atom numbering scheme showing the molecular structure of **5e** found within the crystal lattice at $-100(2)$ °C. Four crystallographically independent molecules form into two distinct dimers with intradimer $S10\cdots S20$ and $S30\cdots S40$ distances of $2.6237(9)$ Å and $2.6255(8)$ Å, respectively. These dimers associate into a single tetrameric set through $S(\delta^+)-N(\delta^-)$ interactions (shown in red). The $S20\cdots N30$ and $S30\cdots N20$ distances are $3.169(2)$ Å and $3.199(2)$ Å, while the $S40\cdots N20$ and $S10\cdots N30$ distances are $3.082(2)$ Å and $3.034(2)$ Å, respectively. The two dimers are out of register with each other.

The bond angles within the heterocyclic core are significantly less symmetrical with asymmetric substitution on the ring. Thus, the internal angles at the carbon of attachment of the CF_3 group are noticeably larger than in **8**.^{5e} Correspondingly, the average internal angles at sulfur are noticeably smaller than those in **8**.

In all five structures, the many independent C_2N_3S rings are almost planar (deviations in the range of $0.003-0.054$ Å). The mean planes of each set of dimers are tipped toward each other such that the shortest contacts are always $S\cdots S$, and the planes intersect with angles between normals in the range of $5-17^\circ$. Three distinct packing modes are found in the solid state among these five thiatriazinyl structures. In **5a** and **5c**, there is a simple $2 + 2$ mode, wherein two dimeric units (Figure 5) are centrosymmetrically associated through sideways $S(\delta^+)\cdots N(\delta^-)$ short contacts. However, the pairs of dimers are essentially coplanar in the case of **5a** (Figure S11, Supporting Information), while in **5c** they are almost exactly out of register (Figure S12, Supporting Information). These tetrameric units are isolated from other such units in the crystal lattice. Sideways $S\cdots N$ contacts range from $2.941(1)$ to $3.341(1)$ Å. In **5b** and **5d**, there are four independent molecules that form two sets of typical dimers. However, the two sets of dimers are each associated with each other through $S(\delta^+)\cdots N(\delta^-)$ short contacts (Figures S13 and S14, Supporting Information). Interestingly, in each structure, one such tetrameric unit is closer to the coplanarity that is observed in **5a**, while a second is out of register as in **5c**. The variation in sideways $S\cdots N$ contacts observed in these two structures is larger, from $3.025(2)$ to $3.551(2)$ Å. The final example is **5e** (Figure 8), for which four independent thiatriazinyls form *one* tetramer in the asymmetric unit. The sideways $S(\delta^+)\cdots N(\delta^-)$ interactions for this structure range from $3.034(2)$ to $3.199(2)$ Å, and the association is out of register as in **5c**. This structure is particularly interesting because there is a further interaction between neighboring rings, leading to a partial overlap of two adjacent tetramers (Figures S15 and S16, Supporting Information). The shortest atomic contacts are $S40\cdots C41'$ at $3.447(2)$ Å. This structure contains the most extensive set of interactions between thiatriazinyls ever

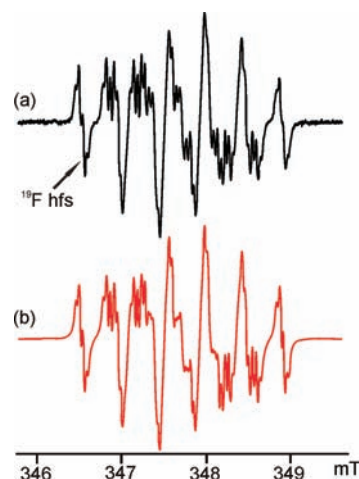


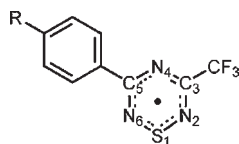
Figure 9. (a) Experimental and (b) simulated EPR spectra of **5d** in CH_2Cl_2 at 18 °C, modulation amplitude 0.01 mT, modulation frequency 100 kHz. Simulations were performed with WinSim (version 0.98 , 2002)¹⁹ software using a 100% Lorentzian line shape.

reported, but, although eight radicals are thereby associated, the interactions do not extend throughout the lattice.

EPR Spectroscopy. The 1,2,4,6-thiatriazinyls are members of a larger class of unsaturated C,N,S compounds for which stable neutral free radicals can be generated.^{1a} In this work, the trifluoromethyl thiatriazinyls **5a–e** were generated by dissolving high purity sublimed crystals in dichloromethane inside vacuum sealed EPR tubes. In all cases, well-defined EPR spectra with high signal-to-noise ratios were obtained, displaying complex splitting patterns due to coupling to the three nonequivalent nitrogen nuclei in the thiatriazinyl ring along with three equivalent fluorine atoms of the directly attached CF_3 groups, which cause each subpeak to split into small quartets. Excellent agreement was obtained between the experimental and simulated EPR spectra for all five compounds (Figure 9 shows a typical example; see also Figures S17–S20, Supporting Information). However, the assignment of the hyperfine splitting (hfs) to the three nitrogen atoms required input from quantum calculations. The electronic structures of **5a–e** were determined from UB3LYP/6-31G(d) hybrid-DFT calculations (using Gaussian 98)¹⁸ for the monomeric radicals in the gas phase. Full geometry optimization was undertaken for each structure, and frequency calculations confirmed the geometries to be minima. The experimental and calculated hfs constants are compiled in Table 1.

The unpaired electron occupies a π -SOMO which is delocalized over the heterocyclic core, a representation of which is shown in Figure 10 using **5b** as a typical example. The largest coefficient is on sulfur, but there is considerable unpaired electron density on each of the three nitrogen atoms and to a lesser extent on the carbon atoms in the ring. There are small coefficients on the fluorine atoms of the directly bound CF_3 group, as well as on the phenyl carbon atoms. There is, however, no experimental evidence for hyperfine coupling to the aryl ring hydrogen atoms, and hfs from ^{19}F is likely to result mostly from spin polarization.

In each case, there are three distinct a_N values, except for **5a**, where two of the values are nearly identical. (Such accidental degeneracy of symmetry-nonequivalent nitrogen atoms has been reported for 3,5-bis(4-methoxyphenyl)-1,2,4,6-thiatriazinyl, for which all three nitrogen atoms appear to have identical hfs of 0.3927 mT.)²⁰ The trends in the hfs with the remote *para* R

Table 1. Experimental and Calculated^a EPR Spectroscopic Data for 5a–e

compd	a_{N2}		a_{N4}		a_{N6}		$a_{C3,S(avg)}$		a_{S1}	$a_{F(avg)}$	
	expt (mT)	calc (mT)	expt (mT)	calc (mT)	expt (mT)	calc (mT)	expt (mT)	calc (mT)	calc ^b (mT)	expt ^c (mT)	calc (mT)
5a	0.310	0.297	0.435	0.409	0.436	0.460	0.705	-0.518	0.555	0.032	-0.063
5b	0.320	0.309	0.444	0.418	0.429	0.443	0.545	-0.531	0.555	0.036	-0.068
5c	0.325	0.313	0.445	0.422	0.425	0.437	0.675	-0.536	0.555	0.039	-0.069
5d	0.324	0.313	0.446	0.422	0.419	0.433	0.572	-0.534	0.558	0.040	-0.068
5e	0.332	0.319	0.454	0.428	0.404	0.423	0.666	-0.542	0.558	0.044	-0.070

^a From UB3LYP calculations, multiplied by a scaling factor of 0.81. ^b Sulfur hfs was not observable due to the very small natural abundance of this isotope.

^c hfs is to the three fluorine atoms in the directly bound CF₃ group.

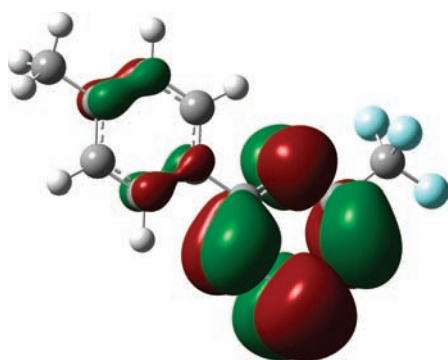


Figure 10. Kohn–Sham isosurface of the π -SOMO of 5b from a UB3LYP/6-31G(d) calculation.

substituents on the phenyl ring are quite convincing. As controls, we can cite the powerfully π -electron donating NMe₂ groups directly bound in 3,5-bis(dimethylamino)-1,2,4,6-thiatriazinyl (**9**),²⁰ in which $a_{N2} = a_{N6}$ is twice as large as a_{N4} . Conversely, with two powerfully electron withdrawing CF₃ and CCl₃ groups directly attached in 3,5-bis(trifluoromethyl)-1,2,4,6-thiatriazinyl²⁴ and 3,5-bis(trichloromethyl)-1,2,4,6-thiatriazinyl,^{5d,20b} a_{N4} is found to be larger by about 40% than a_{N2} and a_{N6} . The hyperfine splitting constants of 5a–e are intermediate between these extremes, as expected. Nevertheless, as the remote *para* substituents become more electron donating (from e to a), the a_{N6} value increases due to greater spin density on the N=S=N region of the ring. The spin density on the remaining nitrogen atoms decreases correspondingly, such that the sums of a_N values are found to be 1.190(5) for all five exemplars (standard deviation). Moreover, the variation in a_N values smoothly follows Hammett $\sigma(p)$ coefficients (Figure S21, Supporting Information). Thus, EPR spectroscopy proves to be a very sensitive probe of the unpaired spin density on thiatriazinyl rings. The directly bound CF₃ group causes further splitting of the EPR signals into quartets, implying rotational averaging of the three fluorine nuclei, but the a_F values are small. Similar a_F values have been reported for 3,5-bis(trifluoromethyl)-1,2,4,6-thiatriazinyl.²⁰

Voltammetry. The study of redox active heterocycles requires handling of low concentrations of free radicals in solution which

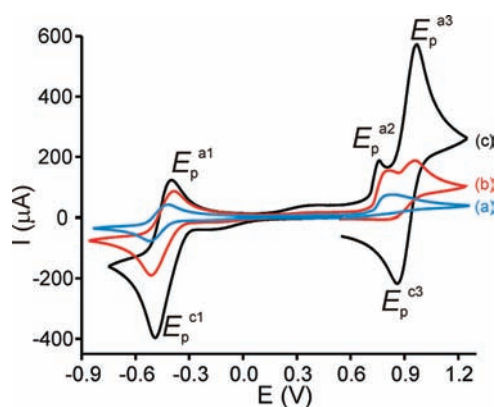


Figure 11. Overlapping CVs of the redox couples of 5e in CH₃CN solution (0.1 M [ⁿBu₄N][PF₆]) at (a) dilute concentration (blue), (b) moderate concentration (red), and (c) high concentration (black).

are highly susceptible to decomposition from oxygen or hydrolysis by adventitious moisture. An all-glass electrochemical cell sealed under vacuum conditions which has been described previously was used in this work to avoid interference.²¹ Cyclic voltammetric studies were performed in both CH₂Cl₂ and CH₃CN solutions at temperatures of 20 ± 2 °C and scan rates of $\nu = 0.1$ –10 V s⁻¹. The voltammetric results at full concentration are summarized in Table 2.

The 1,2,4,6-thiatriazinyls are very soluble in dichloromethane and moderately soluble in acetonitrile. In all cases, the electrochemical response changed with analyte concentration, with the appearance of a new redox couple at more positive potentials as the solution became more concentrated (Figure 11). This change correlated with the color of the solution (from pale yellow to deep brown) as more analyte was added. From the current response of the CV data, the active concentrations from voltammetry taken when the solutions were pale yellow are estimated to be 10–20 times lower than the nominal concentration values listed in Table 2. At very low concentrations (evidenced by a pale yellow color in solution), the peaks associated with a reduction of neutral material ($E_p^{c1/a1}$) have a large return wave over a range of scan rates, while that for oxidation (E_p^{a2}) shows no return wave at scan rates up to 10 V s⁻¹.

Table 2. Voltammetry Data for Compounds 5a–e in CH₃CN and CH₂Cl₂ at Full Concentration^a

compd	conc. (mM)	E_p^{c1} (V)	E_p^{a1} (V)	E_m (V) ^b	E_p^{a2} (V) ^c	E_p^{c3} (V)	E_p^{a3} (V)	E_n (V) ^d	E_{cell} (V) ^e
CH ₃ CN solns with 0.1 M [ⁿ Bu ₄ N][PF ₆] supporting electrolyte									
5a ^f	7.3	−0.64	−0.51	−0.58	0.59	0.62	0.76	0.69	1.27
5b	6.3	−0.60	−0.51	−0.56	0.67	0.71	0.81	0.76	1.32
5c ^g	10.0	−0.60	−0.48	−0.54	0.73	0.74	0.89	0.82	1.36
5d ^h	11.0	−0.55	−0.45	−0.50	0.74	0.78	0.90	0.84	1.34
5e ⁱ	6.7	−0.51	−0.42	−0.47	0.84	0.85	0.96	0.91	1.38
CH ₂ Cl ₂ solns with 0.4 M [ⁿ Bu ₄ N][PF ₆] supporting electrolyte									
5a ^j	10.0	−0.66	−0.55	−0.61	0.66	0.66	0.78	0.72	1.33
5b	8.7	−0.66	−0.54	−0.60	0.71	0.74	0.86	0.80	1.40
5c ^k	11.0	−0.64	−0.52	−0.58	0.76	0.78	0.92	0.85	1.43
5d ^l	9.0	−0.63	−0.47	−0.55	0.81	0.79	0.98	0.89	1.44
5e ^m	6.7	−0.55	−0.44	−0.50	0.91	0.87	1.01	0.94	1.44

^a Reported vs Fc^{0/+} on a Pt working electrode, $\nu = 0.2 \text{ V s}^{-1}$, $T = 20 \pm 2 \text{ }^\circ\text{C}$. ^b $E_m = [E_p^{a1} + E_p^{c1}]/2 \approx E^{0/}$. ^c Irreversible wave observed. ^d $E_n = [E_p^{a3} + E_p^{c3}]/2 \approx E^{0/}$. ^e $E_{cell} = E_n - E_m$. ^f IRR oxidation wave at 1.75 V. ^g IRR reduction wave at −1.87 V. ^h IRR reduction wave at −1.80 V. ⁱ IRR reduction wave at −2.07 V. ^j IRR oxidation wave at 1.84 V. ^k IRR reduction wave at −1.78 V. ^l IRR reduction wave at −1.76 V. ^m IRR reduction wave at −1.65 V.

Table 3. Voltammetry Data for Compounds 5a–e in CH₃CN and CH₂Cl₂ at Low Concentration^a

compd	E_p^{c1} (V)	E_p^{a1} (V)	E_m (V) ^b	E_p^{a2} (V) ^c	E_{cell} (V) ^d
CH ₃ CN solns with 0.1 M [ⁿ Bu ₄ N][PF ₆] supporting electrolyte					
5a	−0.60	−0.54	−0.57	0.59	1.13
5b	−0.59	−0.52	−0.56	0.67	1.19
5c	−0.57	−0.50	−0.54	0.73	1.23
5d	−0.53	−0.46	−0.50	0.74	1.20
5e	−0.51	−0.41	−0.46	0.84	1.25
CH ₂ Cl ₂ solns with 0.4 M [ⁿ Bu ₄ N][PF ₆] supporting electrolyte					
5a	−0.54	−0.47	−0.51	0.66	1.13
5b	−0.53	−0.47	−0.50	0.71	1.18
5c	−0.50	−0.45	−0.48	0.76	1.21
5d	−0.49	−0.42	−0.46	0.81	1.23
5e	−0.45	−0.38	−0.42	0.91	1.29

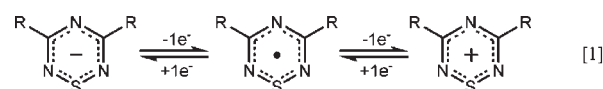
^a Reported vs Fc^{0/+} on a Pt working electrode, $\nu = 0.2 \text{ V s}^{-1}$, $T = 20 \pm 2 \text{ }^\circ\text{C}$. ^b $E_m = [E_p^{a1} + E_p^{c1}]/2 \approx E^{0/}$. ^c Irreversible wave observed. ^d $E_{cell} = E_p^{a2} - E_p^{a1}$.

As the concentration increased (evidenced by development of a brown color), a second oxidation process ($E_p^{a3/c3}$) appeared at a more positive potential, and in the limit, this process displayed return waves of comparable peak current height ($I_p^{c3}/I_p^{a3} = 0.95$ (5a), 0.96 (5b), 0.89 (5c), 0.93 (5d), 0.93 (5e)) under all of the conditions used in this study. Figure 11 shows overlapping traces at three different concentrations of 5e. At the highest concentration, process E_p^{a2} is just a residual shoulder on the reversible wave at more anodic potential. Much the same thing occurred for all five compounds in both solvents. In each case, there was only a single potential associated with reduction of neutral material at all concentrations studied.

When the solutions are at the full indicated concentration (Table 2), the potential range for the “reduction” process is from −0.58 to −0.47 V vs Fc^{0/+} in CH₃CN and −0.61 to −0.50 V vs Fc^{0/+} in CH₂Cl₂ and has an overall change of 0.11 V in both solvents. The potential range for the “oxidation” process is from

0.69 to 0.91 V vs Fc^{0/+} in CH₃CN and 0.72 to 0.94 V vs Fc^{0/+} in CH₂Cl₂ and has an overall change of 0.22 V. The average E_{cell} values ($E_{cell} = E_n - E_m$) are $1.33 \pm 0.04 \text{ V}$ in CH₃CN and $1.41 \pm 0.05 \text{ V}$ in CH₂Cl₂, with a small but notable increase (0.11 V in both solvents) as the substituent R moves from electron donating to electron withdrawing. Values for 5d are slightly lower than expected in both solvents, although the individual E_m and E_n values for 5d still follow the expected trend.

At lower concentrations (Table 3), the potential range for the “reduction” process is from −0.57 to −0.46 V vs Fc^{0/+} in CH₃CN (change of 0.11 V) and −0.51 to −0.42 V vs Fc^{0/+} in CH₂Cl₂ (change of 0.09 V). The potential range for the irreversible “oxidation” process is from 0.59 to 0.84 V vs Fc^{0/+} in CH₃CN and 0.66 to 0.91 V vs Fc^{0/+} in CH₂Cl₂ for an overall change of 0.25 V in both solvents. Average E_{cell} values (where $E_{cell} = E_p^{a2} - E_p^{a1}$) are $1.20 \pm 0.05 \text{ V}$ in CH₃CN and $1.21 \pm 0.06 \text{ V}$ in CH₂Cl₂, which are essentially identical for both solvents. This contrasts with the small but notable change in E_{cell} values ($\sim 100 \text{ mV}$) at higher concentrations between the two solvents. For a monomeric neutral thiatriazinyl radical, the redox process is assumed to involve removal from or addition to the π -SOMO and can be represented as



Since the same redox orbital is involved in the electrochemical oxidation and reduction reactions, one expects the substituents R to influence both redox processes by the same amount, so long as the influence is purely inductive. Exactly this has been observed in electrochemical investigations of more than 20 1,2,3,5-dithiadiazolyls.³ However, unlike the dithiadiazolyls, the redox orbital of the thiatriazinyls (the SOMO, Figure 10) does not have a node at the substituent-bearing carbon atoms. It is to be expected, therefore, that resonance effects can have a significant influence. These are expected to affect the oxidation and reduction processes differently.

Another factor that cannot be discounted is the effect of dimer formation on the redox processes since thiatriazinyls form strong

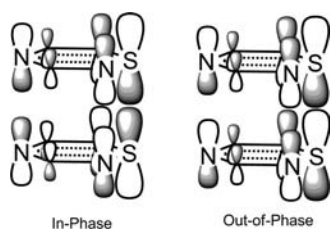
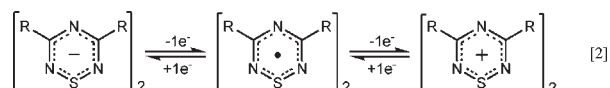


Figure 12. The in-phase and out-of-phase combinations of the $3b_1$ SOMO of model 3,5-dihydro-1,2,4,6-thiatriazinyls.

dimers ($d(\text{S}\cdots\text{S}) = 2.643(21) \text{ \AA}$) compared to 1,2,3,5-dithiadiazolyls (mean $d(\text{S}\cdots\text{S}) = 3.03\text{--}3.16 \text{ \AA}$).^{3c,22} In a dimeric thia-triazine, the redox process can be represented as



The formation of thia-triazinyl dimers has been convincingly interpreted as the result of diffuse side-on overlap of the $3b_1$ π orbital of the individual thia-triazinyl rings (Figure 12) in a face-to-face dimeric arrangement similar to that found in the solid state for dithionite salts.^{5e,23} This overlap represents the only net “bonding” interaction between the rings; that it is centered on a single sulfur atom which has the largest share of the unpaired spin density leads to relatively strong bonding. The dimer is a diamagnetic species, and hence oxidation occurs from a different orbital (the in-phase combination) than reduction (the out-of-phase combination). It is therefore to be expected that the substituents influence these distinct orbitals by different amounts.

Digital Modeling of CVs of the 1,2,4,6-Thiatriazinyls. In order to further probe the effect of monomer–dimer equilibrium on the voltammetry, we turned to digital modeling of the voltammograms at both low and high concentrations using DigiElch software.²⁴ Starting with lower concentrations of the radical in solution ($\sim 1/10$ the values listed in Table 2), we established a plausible model for the monomer undergoing both a chemically irreversible oxidation and a reversible reduction. The resultant CV is shown as the blue trace in Figure 13. In this case, the model assumes that following a one-electron oxidation of the thia-triazinyl radical (abbreviated as $[\text{TTA}]^\bullet$ in Scheme 2) there is a chemically irreversible first-order decay step ($K_{\text{eq}4} = 10^6$, $k_{f4} = 5 \text{ s}^{-1}$). No chemical step is associated with the one-electron reduction. Then, at higher concentrations, the model which fit most closely to the experimental CVs follows the “ladder” scheme shown in Scheme 2.²⁵ The favorable formation of the dimer $[\text{TTA}_2]$ at higher concentrations ($K_{\text{eq}1} = 400\text{--}800$, $k_{f1} = 1 \text{ M}^{-1} \text{ s}^{-1}$) and the unfavorable formation of the dication dimer $[\text{TTA}_2]^{2+}$ ($K_{\text{eq}2} < 1$, $k_{f2} = 0.01 \text{ M}^{-1} \text{ s}^{-1}$) results in very satisfactory simulations (they are a good visual match to experimental data, see black trace in Figure 13) when the oxidation of the $[\text{TTA}_2]$ dimer is a two-electron process. Assuming a one-electron oxidation for this step does not result in a good match. The formation of the monoanionic dimer $[\text{TTA}_2]^\bullet$ from $[\text{TTA}]^\bullet + [\text{TTA}]^-$ was also favored ($K_{\text{eq}3} = 271$, $k_{f3} < 10 \text{ M}^{-1} \text{ s}^{-1}$).

The value for $K_{\text{eq}1}$ of 400–800 is in reasonable agreement with previously derived equilibrium constants for the association of diphenyl thia-triazinyls and selenatriazinyls from Oakley et al. from EPR experiments ($K_{\text{eq}} = 33$ for sulfur and $K_{\text{eq}} = 2000$ for selenium).⁶ Similar investigations into the monomer–dimer equilibrium for 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl ($K_{\text{eq}} \cong 0.05$ at RT)

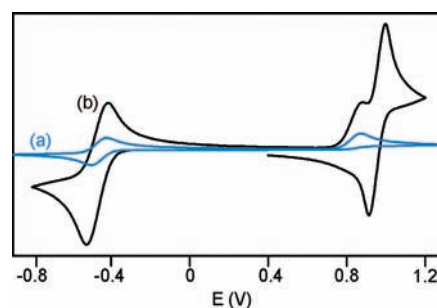
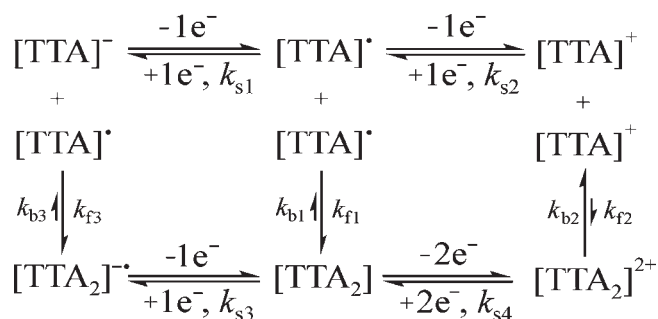


Figure 13. Calculated CVs for both (a) monomeric (blue line) and (b) dimeric (black line) solutions of **5e** resulting from the input of kinetic parameters listed in the text and following the “ladder” scheme shown in Scheme 2. These CVs follow the specific case of $\nu = 0.2 \text{ V s}^{-1}$, $K_{\text{eq}1} = 400$, $k_{f1} = 1 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}2} = 0.0766$, $k_{f2} = 0.01 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}3} = 271$, $k_{f3} = 1 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}4} = 10^6$, $k_{f4} = 5 \text{ s}^{-1}$ (first-order decay of $[\text{TTA}]^+$), $k_{s1} = k_{s2} = k_{s3} = k_{s4} = 0.03 \text{ cm s}^{-1}$, conc. dimer = 0.01 mol L^{-1} , conc. monomer = 0.001 mol L^{-1} . The potential was first swept in the cathodic direction starting from 0.4 V.

Scheme 2. Proposed “Ladder” Scheme Interrelating the Voltammetric Behavior of Thiatriazinyls at Lower and Higher Concentrations



have been undertaken using absorption spectroscopy.^{2e} The self-consistent fit of these data to the “ladder” scheme is thus satisfying and chemically reasonable in view of the large association constants expected for thia-triazinyls. That the dication favors monomers fits well with removal of the very electrons involved in the association. The only surprise is the apparent “decomposition” of the monomeric cation under inert conditions where these 6π Hückel species are expected to be thermally stable.⁵ⁱ We propose that the irreversibility of this electrode process may involve electron self-exchange.²⁶ Thus, a rapid pseudo-first-order cascade reaction:



could remove the cation from the electrode surface when the dominant species in solution is $[\text{TTA}]^\bullet$. On the other hand, when $[\text{TTA}_2]$ is the dominant species, the driving force for the self-exchange reaction weakens, and this reaction may become sluggish. While we believe that this mechanism is a plausible proposal, detailed testing in which actual voltammograms are fit to theory will be required to obtain precise values for the kinetic parameters. Such an undertaking is beyond the scope of the current project.

Correlation of Redox Potentials with Gas Phase Calculations. Previous studies have shown that quantum calculations, when used judiciously, can provide corroboration of electrochemical results.³ Fully geometry optimized calculations at the (U)B3LYP/6-31G(d) level of theory were performed for the

Table 4. Calculated and Experimental Redox Potentials of 5a–e for the Monomeric Radical

compd	–1/0 process			0/+1 process		
	E_m (V)		calc (eV)	E_p^{a1} (V)		calc (eV)
	CH ₃ CN	CH ₂ Cl ₂		CH ₃ CN	CH ₂ Cl ₂	
5a	–1.89	–0.57	–0.51	7.29	0.59	0.66
5b	–1.94	–0.56	–0.50	7.50	0.67	0.71
5c	–1.99	–0.54	–0.48	7.65	0.73	0.76
5d	–2.16	–0.50	–0.46	7.72	0.74	0.81
5e	–2.25	–0.46	–0.42	7.90	0.84	0.91
Δ	0.36	0.11	0.09	0.61	0.25	0.25

monomeric cation, anion, and neutral thiazine derivatives. No attempt was made to model the weakly bound dimeric molecules. The energies of these optimized molecules were then used to define the theoretical redox reactions:

$$0/+1 \text{ process} : E_{\text{cation}} - E_{\text{radical}} = E_{\text{oxidation}} \quad (4)$$

$$-1/0 \text{ process} : E_{\text{anion}} - E_{\text{radical}} = E_{\text{reduction}} \quad (5)$$

Table 4 lists the calculated and experimental redox potentials for 5a–e from the experimental CV data at low concentrations taken from Table 3, and correlation curves are presented in Figure 14. The results are graphed by process type, and each graph includes results for both solvents.

Excellent correlation is obtained between the calculated gas phase and experimental solution phase oxidation and reduction potentials of the monomeric radicals 5a–e, which is particularly noteworthy for the 0/+1 process, which uses peak potentials from an irreversible process in both solvents.^{3b} The reliability of the electrochemical data for this series obtained from CV is confirmed by this correlation. The solution oxidation and reduction potentials also correlate well with Hammett σ_p substituent constants (Figures S22 and S23, Supporting Information).²⁷

CONCLUSIONS

This paper reports a comprehensive investigation of a complete series of unsymmetrical aryl/trifluoromethyl-substituted thiazinyls. The synthetic work has elaborated new and versatile imidoamidine reagents and demonstrated their ability to form the ring compounds through direct condensation with sulfur halides. Conversion to the neutral thiazinyls was successful for all five exemplars. All of the synthetic results are supported by thorough structural studies that provide extremely reliable mean parameters from high-quality, low-temperature diffraction data. The complex EPR spectral data are shown to fit to well-defined substituent trends even though the variation in hfs values is small. Finally, complex voltammetric behavior involving the first reliably detected monomer–dimer equilibria in the history of the electrochemistry of thiazyl rings has been modeled using sophisticated digital software to provide an interpretation that is consistent with the predicted chemical nature of the various redox products. Further work on thiazinyls including detailed fitting of monomer–dimer equilibria to voltammetric data is in progress in our laboratory and will be reported at a future time.

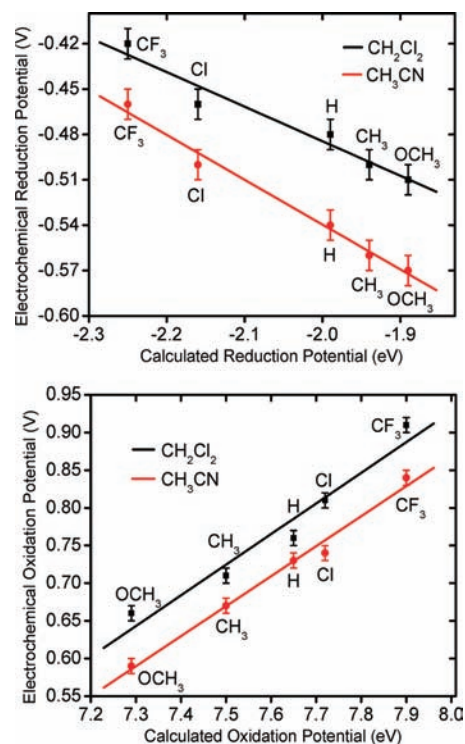


Figure 14. Plot of the calculated vs experimental monomer reduction potentials (top) and oxidation potentials (bottom) of 5a–e as measured by cyclic voltammetry in CH₂Cl₂ (black line, $R = 0.975$, top; $R = 0.975$, bottom), and (b) CH₃CN (red line, $R = 0.993$, top; $R = 0.994$, bottom) solution. Error bars express an estimated error in measured potential of ± 0.01 V.

EXPERIMENTAL SECTION

General Procedures. Trifluoroacetonitrile (PCR Inc.) was obtained commercially and used as received. SCl₂ (Aldrich) was distilled from PCl₃ with CaCl₂ moisture protection. Triphenylantimony (Aldrich) and HCl(g) (Praxair) were obtained commercially and used as received. The substituted aryl amidine hydrochlorides were prepared according to the literature method.⁷ Unless otherwise indicated, all procedures were performed under an atmosphere of purified N₂ using a drybox, Schlenkware, and vacuum-line techniques. Solvents used were reagent-grade or better. Acetonitrile (HPLC grade) was double-distilled from P₂O₅ and CaH₂. Dichloromethane was distilled from CaH₂. *n*-Heptane was dried by distillation over LiAlH₄ and toluene over sodium. Anhydrous diethyl ether was dried by distillation from sodium wire.

Spectroscopic Methods. Infrared spectra were obtained as KBr plates and were recorded on a Bomem MB102 Fourier transform spectrometer. Melting points were determined on an electrothermal melting point apparatus (capillaries) and are uncorrected. EPR spectra (X band) were recorded on a Bruker EMX-113/12 spectrometer as solutions in dichloromethane in 4 mm Pyrex glass tubes sealed under vacuum conditions. NMR spectra were acquired at 250.13 (¹H) and 62.90 (¹³C) MHz on a Bruker/Tecmag AC250 spectrometer using CDCl₃ as the solvent and thus a reference. Mass spectra were recorded by the Mass Spectrometry Center, University of Alberta, Edmonton. Microanalyses were performed by M–H–W Laboratories in Phoenix, Arizona.

Electrochemical Methods and Procedures. Crystals of high purity 5a–e were collected, weighed, and loaded into individual break-seal tubes and attached to the electrochemical cell by fusing the glass along with a known mass of ferrocene in a separate break-seal.²⁵ The electrodes are all platinum and were sealed into the glass and cleaned in

between experiments using concentrated HNO₃. Cyclic voltammograms (CVs) were obtained at temperatures of 21 ± 2 °C in CH₃CN and CH₂Cl₂ solutions containing 0.1 and 0.4 M [¹⁴Bu₄N][PF₆], respectively, as the supporting electrolyte. The electrolyte was loaded into the cell and dried under vacuum conditions in an oil bath set at 80 °C overnight prior to transfer of the solvent. Both CH₂Cl₂ and CH₃CN were distilled and stored over molecular sieves prior to use. The solvents were freeze–thaw–degassed at least five times prior to their transfer into the cell over a vacuum line. For CVs, all measurements were recorded at room temperature (22 ± 2 °C), and the scan rates were varied between 0.1 and 10 V s^{−1}.

In a typical experiment, the electrolyte solution is scanned to obtain a background current and determine the effective electrochemical window. Next, the seal to the analyte is broken, and a small amount is dissolved until a signal with satisfactory S/N is obtained. The concentration of the analyte is incrementally increased while obtaining CV traces. Finally, all of the analyte is thoroughly mixed with the electrolyte solution to establish a known “full” concentration. After all CV data are satisfactorily recorded, the seal to the reference is broken, and a sufficient quantity of ferrocene is added to the cell to obtain an accurate reference for the voltage scale.

X-Ray Crystallography. Crystals were selected and mounted in Paratone on the ends of thin glass capillaries and cooled on the goniometer head to −100 °C with the Bruker low-temperature accessory attached to the APPEX-II diffractometer. Mo Kα radiation (λ = 0.71073 Å) was used throughout. Multiscan absorption corrections were applied to all of the data sets, and refinement was conducted with full-matrix least-squares on F² using SHELXTL 6.14.²⁸ In the case of **5b**, data sets collected at −100 °C solve and refine but are stuck at R₁ = 0.14 due to a suspected superlattice formation. Therefore, another crystal was selected, covered in epoxy cement, and glued to the end of a glass fiber. Diffraction data collected at 23 °C refined to a low R factor and provided a fully acceptable structure. Details of the refinements and disorder models for typical rotational disorder of CF₃ groups are provided in the electronic crystallographic information file. Crystal data and refinement parameters are also summarized in Table S. Structures of **2c** and **3c** were determined at room temperature and at −100 °C.

Computational Details. DFT calculations undertaken for this study employed geometry optimization at the (U)B3LYP/6-31G(d) level. Harmonic vibrational frequencies were calculated for all optimized geometries to confirm that they are stationary points. Calculations of energies and EPR hyperfine splitting (hfs) constants used the same level of theory. All calculations were performed using the Gaussian 98 suite of programs.¹⁸

Synthesis of Amidines 1a–e. C₆H₄C(NH)NH₂, **1c**. Benzamidine hydrochloride hydrate (26.3 g, 0.173 mol) and KOH (32.4 g, 0.576 mol) were added to 175 mL of distilled water. CH₂Cl₂ (2 × 200 mL) was used to extract the product. The solvent was rotary evaporated, leaving a pale yellow oil which solidified overnight in the freezer. The solid was sublimed at 80 °C under vacuum conditions to give 12.79 g (61.9% yield) of pure white **1c**. ¹H NMR (CDCl₃): δ 5.28 (s, 3H, NH), 7.42–7.62 (m, 5H, phenyl).

CH₃OC₆H₄C(NH)NH₂, **1a**. 4-Methoxybenzonitrile (15.08 g, 0.1133 mol) was added to Et₂O · LiN(SiMe₃)₂ (27.26 g, 0.1129 mol) in 200 mL of distilled diethyl ether and stirred for 20 h with a drying tube attached. A 1:1 mixture of ethanol and concentrated HCl (30 mL) was added slowly through a dropping funnel, leaving a white precipitate. The solid was recovered by filtration and dried in the air. It was then redissolved in distilled water and treated with excess NaOH solution, affording a pale purple solid. This was sublimed at 91 °C under vacuum conditions to give 3.72 g (22.2% yield) of pure **1a**. Plate-shaped X-ray-quality crystals were collected on a coldfinger following vacuum sublimation. ¹H NMR (CDCl₃): δ 3.85 (s, 3H, CH₃), 4.99 (s, 3H, NH), 6.93 (d, 2H, J_{H–H} = 9.0 Hz, C_{Ar}H), 7.57 (d, 2H, J_{H–H} = 8.4 Hz, C_{Ar}H).

CF₃C₆H₄C(NH)NH₂, **1b**. *p*-Tolunitrile (6.356 g, 0.05425 mol) was added to Et₂O · LiN(SiMe₃)₂ (12.47 g, 0.05165 mol) in 200 mL of distilled diethyl ether and stirred for 22 h with a drying tube attached.

A 1:1 mixture of ethanol and concentrated HCl (30 mL) was added slowly through a dropping funnel to give a pink precipitate. The solid was recovered by filtration and dried in the air. It was then redissolved in distilled water and treated with excess KOH. CH₂Cl₂ (2 × 200 mL) was used to extract the product. The solvent was rotary evaporated, and the solution was dried using anhydrous sodium sulfate to give a yellow solid. The solid was sublimed at 70 °C under vacuum conditions to give 1.51 g (21.8% yield) of pure **1b**. ¹H NMR (CDCl₃): δ 2.40 (s, 3H, CH₃), 4.83 (s, 3H, NH), 7.23 (d, 2H, J_{H–H} = 8.1 Hz, C_{Ar}H), and 7.51 (d, 2H, J_{H–H} = 8.4 Hz, C_{Ar}H).

ClC₆H₄C(NH)NH₂, **1d**. Amidine **1d** was prepared by the same method reported for **1a** using 4-chlorobenzonitrile (7.69 g, 0.0559 mol) and Et₂O · LiN(SiMe₃)₂ (12.7 g, 0.0524 mol) in 200 mL of distilled diethyl ether. The pale pink-colored solid was sublimed at 91 °C under vacuum conditions to give 4.33 g (53.7% yield) of pure **1d**. ¹H NMR (CDCl₃): δ 3.88 (s, 3H, NH), 7.41 (d, 2H, J_{H–H} = 8.4 Hz, C_{Ar}H), and 7.75 (d, 2H, J_{H–H} = 8.7 Hz, C_{Ar}H).

CF₃C₆H₄C(NH)NH₂, **1e**. Amidine **1e** was prepared by the same method reported for **1a** using α,α,α-trifluoro-*p*-tolunitrile (8.94 g, 52.2 mmol) and Et₂O · LiN(SiMe₃)₂ (12.4 g, 51.5 mmol) in 200 mL of distilled diethyl ether. After the solid was collected by filtration and air-dried, it was sublimed at 85 °C under vacuum conditions to give 5.61 g (57.9% yield) of pure **1e**. ¹H NMR (CDCl₃): δ 4.90 (s, 3H, NH), 7.75 (d, 2H, J_{H–H} = 8.4 Hz, C_{Ar}H), 7.70 (d, 2H, J_{H–H} = 8.4 Hz, C_{Ar}H). ¹⁹F NMR (CDCl₃): δ −62.02 (CF₃).

Synthesis of Trifluoromethyl Imidoylamidines 2a–e. C₆H₅C₃N₃H₃F₃, **2c**. Trifluoroacetone (2.06 g, 21.7 mmol) was measured on a vacuum line by PVT methods and added to 2.53 g (21.1 mmol) of benzamidine **1c** in 20 mL of acetonitrile in a 300 × 25 mm heavy-wall Pyrex reactor fitted with a Rotaflow stopcock equipped with a small magnetic stirring bar at −196 °C. The mixture was warmed to RT, heated to 60 °C with stirring for 10 min, and then cooled to RT and evaporated, leaving a clear oil. Upon refrigeration, this solidified to leave 4.37 g of a white solid (20.3 mmol, 96% yield), mp 42–45 °C. ¹H NMR (δ, CDCl₃): 6.8 (s, NH), 7.38–7.54 (m, 3H, phenyl), 7.83–7.88 (m, 2H, C_{Ar}H), 9.1 (s, NH), 11.0 (s, NH). ¹³C NMR (δ, CDCl₃): 117.8 (q, 281 Hz), 127.4 (s), 129.0 (s), 132.2 (s), 135.2 (s), 163.5 (q, 33 Hz), 165.9 (s). Mass spectrum (*m/e*): 214 (PhC₂N₃H₂CF₃⁺, 100%), 169 (PhC₂N₂H₂F₂⁺, 4%), 146 (PhC₂N₃H₃⁺, 12%), 129 (PhC₂N₂⁺, 6%), 104 (PhCNH⁺, 48%). Analysis calculated (found): 50.24 (50.35)% C, 3.75 (4.01)% H, 19.53 (19.37)% N.

4-CH₃OC₆H₅C₂N₃H₃CF₃, **2a**. Imidoylamidine **2a** was prepared by the same method as **2c** using CF₃CN (1.09 g, 11.5 mmol) and **1a** (1.58 g, 10.5 mmol) in 10 mL of acetonitrile. A white solid remained, which was sublimed *in vacuo* at 46 °C to leave 1.43 g of pure white crystals (5.8 mmol, 56% yield), mp 41–45 °C. ¹H NMR (δ, CDCl₃): 3.9 (s, OCH₃), 6.7 (s, NH), 6.9 (d, 2H, C_{Ar}H), 7.9 (d, 2H, C_{Ar}H), 9.0 (s, NH), 11.0 (s, NH). ¹³C NMR (δ, CDCl₃): 55.7 (s), 114.3 (s), 117.9 (q, 281 Hz), 127.3 (s), 129.3 (s), 163.1 (s), 163.4 (q, 33 Hz), 165.3 (s). Mass spectrum (*m/e*): 244 (CH₃OPhC₂N₃H₂CF₃⁺, 42%), 199 (CH₃OPhC₂N₂H₂F₂⁺, 4%), 176 (CH₃OPhC₂N₃H₃⁺, 20%), 159 (CH₃OPhC₂N₂⁺, 13%), 134 (CH₃OPhCNH⁺, 100%). Analysis calculated (found): 48.98 (48.85)% C, 4.11 (4.22)% H, 17.14 (17.32)% N.

4-CH₃C₆H₅C₂N₃H₃CF₃, **2b**. Imidoylamidine **2b** was prepared by the same method as **2c** using CF₃CN (1.34 g, 14.1 mmol) and **1b** (1.96 g, 14.6 mmol) in 15 mL of acetonitrile. A pink solid remained, which was sublimed *in vacuo* at 48 °C to leave 2.48 g of white crystals (10.8 mmol, 77% yield), mp 54–57 °C. ¹H NMR (δ, CDCl₃): 2.4 (s, CH₃), 6.7 (s, NH), 7.3 (d, 2H, C_{Ar}H), 7.8 (d, 2H, C_{Ar}H), 9.1 (s, NH), 11.0 (s, NH). ¹³C NMR (δ, CDCl₃): 21.7 (s), 117.8 (q, 281 Hz), 127.6 (s), 129.7 (s), 132.4 (s), 142.8 (s), 163.6 (q, 33 Hz), 165.8 (s). Mass spectrum (*m/e*): 228 (CH₃PhC₂N₃H₂CF₃⁺, 100%), 183 (CH₃PhC₂N₂H₂F₂⁺, 2%), 160 (CH₃PhC₂N₃H₃⁺, 7%), 143 (CH₃PhC₂N₂⁺, 4%), 118 (CH₃PhCNH⁺, 30%). Analysis calculated (found): 52.40 (52.34)% C, 4.40 (4.60)% H, 18.33 (18.50)% N.

Table 5. Crystallographic Data and Refinement Parameters for Compounds 1–6

complex	1a	2a	2c	2e	4b	4e
empirical formula	C ₈ H ₁₀ N ₂ O	C ₁₀ H ₁₀ F ₃ N ₃ O	C ₉ H ₈ F ₃ N ₃	C ₁₀ H ₇ F ₆ N ₃	C ₁₀ H ₇ ClF ₃ N ₃ S	C ₁₀ H ₄ ClF ₆ N ₃ S
<i>M_r</i>	150.18	245.21	215.18	283.19	293.70	347.67
cryst size (mm ³)	0.25 × 0.15 × 0.12	0.45 × 0.37 × 0.20	0.401 × 0.208 × 0.116	0.652 × 0.429 × 0.310	0.31 × 0.16 × 0.16	0.17 × 0.14 × 0.14
cryst syst	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ ₁ ₂	<i>P</i> ₂ / <i>c</i>
<i>a</i> (Å)	5.005(10)	9.2967(19)	8.8135(17)	11.2481(8)	14.507(3)	14.5920(14)
<i>b</i> (Å)	10.15(2)	10.538(2)	16.356(3)	14.6690(10)	17.395(3)	11.8343(11)
<i>c</i> (Å)	15.54(3)	11.787(3)	14.069(3)	14.3328(10)	4.7852(8)	7.4331(7)
α (deg)	86.58(2)	93.783(2)	90.00	90.00	90.00	90.00
β (deg)	87.40(2)	105.567(2)	101.503(2)	93.7750(10)	90.00	94.7720(10)
γ (deg)	79.77(2)	97.335(2)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	775(3)	1097.2(4)	1987.3(7)	2359.8(3)	1207.6(3)	1279.1(2)
<i>Z</i>	4	4	8	8	4	4
<i>D_c</i> (Mg·m ⁻³)	1.287	1.484	1.438	1.594	1.615	1.805
μ (mm ⁻¹)	0.088	0.134	0.130	0.165	0.511	0.530
θ range	2.04–27.89	1.80–27.00	1.93–27.42	1.99–26.36	1.83–29.59	2.22–28.83
coll. reflns	8956	12270	28147	24664	12307	14808
obsd reflns	3580	4750	4532	4826	2987	3137
no. of params	219	333	345	404	192	217
<i>F</i> (000)	320	504	880	1136	592	688
<i>T</i> (K)	173(2)	173 (2)	173(2)	173(2)	173(2)	173(2)
R1, wR2 [<i>I</i> > σ (<i>I</i>)]	0.0410, 0.0959	0.0338, 0.0842	0.0370, 0.0859	0.0468, 0.1217	0.0379, 0.0965	0.0327, 0.0843
R1, wR2 [all data]	0.0695, 0.1053	0.0420, 0.0896	0.0496, 0.0934	0.0538, 0.1298	0.0550, 0.1026	0.0414, 0.0895
GOF	0.978	1.038	1.041	1.038	1.031	1.056

complex	5a	5b	5c	5d	5e	6
empirical formula	C ₁₀ H ₇ F ₃ N ₃ OS	C ₁₀ H ₇ F ₃ N ₃ S	C ₉ H ₅ F ₃ N ₃ S	C ₉ H ₄ ClF ₃ N ₃ S	C ₁₀ H ₄ F ₆ N ₃ S	C ₇ H ₇ ClN ₂ O ₂ S
<i>M_r</i>	274.25	258.25	244.22	278.66	312.22	218.66
Cryst size (mm ³)	0.476 × 0.192 × 0.118	0.185 × 0.171 × 0.153	0.287 × 0.215 × 0.086	0.29 × 0.22 × 0.14	0.311 × 0.155 × 0.06	0.13 × 0.12 × 0.12
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	tetragonal
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₄ ₂ ₂
<i>a</i> (Å)	7.1075(8)	11.5126(12)	9.136(4)	11.1851(15)	10.7943(6)	9.4879(9)
<i>b</i> (Å)	11.5130(13)	14.7539(15)	10.728(4)	14.799(2)	13.3162(8)	9.4879(9)
<i>c</i> (Å)	13.3832(15)	15.0498(15)	11.016(5)	14.806(2)	16.7910(10)	21.584(4)
α (deg)	88.0000(10)	111.2160(10)	84.652(4)	110.9450(10)	94.0420(10)	90.00
β (deg)	86.2810(10)	99.9130(10)	69.663(4)	103.210(2)	107.4760(10)	90.00
γ (deg)	80.4830(10)	107.6770(10)	68.715(3)	106.5720(10)	96.1190(10)	90.00
<i>V</i> (Å ³)	1077.5(2)	2153.0(4)	942.6(7)	2038.8(5)	2275.6(2)	1943.0(5)
<i>Z</i>	4	8	4	8	8	8
<i>D_c</i> (Mg·m ⁻³)	1.691	1.593	1.721	1.816	1.823	1.495
μ (mm ⁻¹)	0.333	0.321	0.362	0.600	0.358	0.576
θ range	1.79–27.42	1.96–26.59	1.97–27.45	1.61–28.49	1.90–28.73	2.34–26.86
coll. reflns	15562	23211	13575	22885	26627	21297
obsd reflns	4872	8841	4267	9467	10697	2076
no. of params	327	729	577	629	777	124
<i>F</i> (000)	556	1048	492	1112	1240	896
<i>T</i> (K)	173(2)	296(2)	173(2)	173(2)	173(2)	173(2)
R1, wR2 [<i>I</i> > σ (<i>I</i>)] ^{a,b}	0.0273, 0.0732	0.0379, 0.1035	0.0368, 0.0976	0.0426, 0.0893	0.0440, 0.1137	0.0421, 0.1102
R1, wR2 [all data] ^{a,b}	0.0302, 0.0757	0.0572, 0.1127	0.0444, 0.1036	0.0825, 0.1054	0.0689, 0.1256	0.0610, 0.1166
GOF ^c	1.032	1.026	1.047	1.022	1.036	0.984

^a wR2 = $[\sum\{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$; R1 = $\sum||F_o| - |F_c|| / \sum|F_o|$. ^b $F_o > 4\sigma(F_o)$. ^c GOF = $[\sum\{w(F_o^2 - F_c^2)^2\} / (n - p)]^{1/2}$, where *n* = number of reflections and *p* = number of refined parameters.

4-ClC₆H₅C₂N₃H₃CF₃, **2d**. Imidoylamidine **2c** was prepared by the same method as **2c** using trifluoroacetonitrile (2.07 g, 21.8 mmol) and **1d** (3.25 g, 21.0 mmol) in 20 mL of acetonitrile. A white solid remained

which was sublimed *in vacuo* at 49 °C to leave 4.72 g of pure white crystals (18.9 mmol, 90% yield), mp 45–48 °C. ¹H NMR (δ , CDCl₃): 6.7 (s, NH), 7.4 (d, 2H, C_{Ar}H), 7.8 (d, 2H, C_{Ar}H), 9.2 (s, NH), 11.0

(s, NH). ^{13}C NMR (δ , CDCl_3): 117.7 (q, 281 Hz), 128.8 (s), 129.3 (s), 133.6 (s), 138.6 (s), 163.3 (q, 34 Hz), 164.8 (s). Mass spectrum (m/e): 248 ($\text{CIPhC}_2\text{N}_3\text{H}_2\text{CF}_3^+$, 42%), 180 ($\text{CIPhC}_2\text{N}_3\text{H}_3^+$, 10%), 163 ($\text{CIPhC}_2\text{N}_2^+$, 13%), 138 (CIPhCNH^+ , 100%). Analysis calculated (found): 43.31 (43.50)% C, 2.83 (3.00)% H, 16.83 (17.06)% N.

$4\text{-CF}_3\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{H}_3\text{CF}_3$, **2e**. Imidoylamidine **2e** was prepared by the same method as **2c** using trifluoroacetonitrile (1.02 g, 10.7 mmol) and **1e** (1.98 g, 10.5 mmol) in 10 mL of acetonitrile. A white solid remained which was sublimed *in vacuo* at 60 °C to leave 2.52 g of white crystals (8.9 mmol, 85% yield), mp 80–83 °C. ^1H NMR (δ , CDCl_3): 6.8 (s, NH), 7.7 (d, 2H, C_{Ar}H), 8.0 (d, 2H, C_{Ar}H), 9.3 (s, NH), 11.1 (s, NH). ^{13}C NMR (δ , CDCl_3): 117.7 (q, 281 Hz), 123.9 (q, 273 Hz), 126.0 (q, 4 Hz), 127.9 (s), 133.9 (q, 33 Hz), 138.6 (s), 163.2 (q, 34 Hz), 164.7 (s). Mass spectrum (m/e): 282 ($\text{CF}_3\text{PhC}_2\text{N}_3\text{H}_2\text{CF}_3^+$, 100%), 237 ($\text{CF}_3\text{-PhC}_2\text{N}_2\text{H}_2\text{F}_2^+$, 5%), 214 ($\text{CF}_3\text{PhC}_2\text{N}_3\text{H}_3^+$, 13%), 197 ($\text{CF}_3\text{PhC}_2\text{N}_2^+$, 3%), 172 ($\text{CF}_3\text{PhCNH}^+$, 45%). Analysis calculated (found): 42.42 (42.32)% C, 2.49 (2.39)% H, 14.84 (14.88)% N.

Synthesis of Trifluoromethyl Imidoylamidine Hydrochlorides 3a–e. $\text{C}_6\text{H}_5\text{C}_3\text{N}_3\text{H}_3\text{F}_3 \cdot \text{HCl}$, **3c**. Anhydrous HCl was bubbled through a suspension of **2c** (2.04 g, 9.5 mmol) in diethyl ether. The white precipitate was filtered in the air and dried to leave 2.34 g of crude solid (9.3 mmol, 98% yield), mp (dec.) 174–175 °C. For FTIR data, see the Supporting Information.

$4\text{-CH}_3\text{OC}_6\text{H}_4\text{C}_3\text{N}_3\text{H}_3\text{F}_3 \cdot \text{HCl}$, **3a**. Imidoylamidine hydrochloride **3a** was prepared using the same method as **3c** from **2a** (1.01 g, 4.1 mmol), providing 1.09 g of a crude white solid (3.9 mmol, 94% yield), mp (dec.) 213–215 °C.

$4\text{-CH}_3\text{C}_6\text{H}_4\text{C}_3\text{N}_3\text{H}_3\text{F}_3 \cdot \text{HCl}$, **3b**. Imidoylamidine hydrochloride **3b** was prepared using the same method as **3c** from **2b** (1.59 g, 6.9 mmol), providing 1.50 g of solid **3b** (5.7 mmol, 82% yield), mp (dec.) 198–200 °C.

$4\text{-ClC}_6\text{H}_4\text{C}_3\text{N}_3\text{H}_3\text{F}_3 \cdot \text{HCl}$, **3d**. Imidoylamidine hydrochloride **3d** was prepared using the same method as **3c** from **2d** (2.40 g, 9.6 mmol), providing 2.65 g of a white solid (9.3 mmol, 97% yield), mp (dec.) > 244 °C.

$4\text{-CF}_3\text{C}_6\text{H}_4\text{C}_3\text{N}_3\text{H}_3\text{F}_3 \cdot \text{HCl}$, **3e**. Imidoylamidine hydrochloride **3e** was prepared using the same method as **3c** from **2e** (2.37 g, 8.4 mmol), providing 2.65 g of a white solid (8.3 mmol, 99% yield), mp (dec.) 181–183 °C.

Synthesis of 1-Chloro-5-aryl-3-trifluoromethyl-1,2,4,6-thiatriazines 4a–e. $\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{SClCF}_3$, **4c**. Freshly distilled SCl_2 (2.8 mL, 44.1 mmol) in 10 mL of acetonitrile was added dropwise to a suspension of imidoylamidine $\cdot \text{HCl}$, **3c** (2.24 g, 8.9 mmol), in 30 mL of acetonitrile. The yellow mixture was heated to reflux for 1.5 h, giving an orange-red color. After filtering to remove any solids, the solvent was removed *in vacuo* to leave an orange oil (2.23 g, 8.0 mmol, 90% yield). ^1H NMR (δ , CDCl_3): 7.52–7.58 (m, 2H, C_{Ar}H), 7.67–7.74 (m, H, C_{Ar}H), 8.45–8.48 (m, 2H, C_{Ar}H).

$4\text{-CH}_3\text{OC}_6\text{H}_5\text{C}_2\text{N}_3\text{SClCF}_3$, **4a**. Compound **4a** was prepared using the same method as **4c** using SCl_2 (1.6 mL, 25.1 mmol) in 10 mL of acetonitrile added dropwise to **3a** (1.45 g, 5.1 mmol) in 25 mL of acetonitrile. The solvent was removed *in vacuo*, leaving a dark orange oil. Recrystallization with hot toluene followed by hot acetonitrile left an orange oil (1.29 g, 81% yield). ^1H NMR (δ , CDCl_3): 3.94 (s, CH_3O), 7.02 (d, 2H, C_{Ar}H), 8.45 (d, 2H, C_{Ar}H).

$4\text{-CH}_3\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{SClCF}_3$, **4b**. Compound **4b** was prepared using the same method as **4c** using SCl_2 (1.8 mL, 28.3 mmol) in 10 mL of acetonitrile and **3b** (1.47 g, 5.5 mmol) in 25 mL of acetonitrile. The solvent was removed *in vacuo*, leaving an orange-red solid (1.77 g, 97% yield). ^1H NMR (δ , CDCl_3): 2.49 (s, CH_3), 7.35 (d, 2H, C_{Ar}H), 8.37 (d, 2H, C_{Ar}H).

$4\text{-ClC}_6\text{H}_5\text{C}_2\text{N}_3\text{SClCF}_3$, **4d**. Compound **4d** was prepared using the same method as **4c** using SCl_2 (2.2 mL, 34.6 mmol) in 10 mL of acetonitrile and **3d** (2.54 g, 8.9 mmol) in 40 mL of acetonitrile. The solvent was removed *in vacuo*, leaving a dark orange oil. This was

recrystallized with hot heptane to leave an orange solid (2.78 g, 99% yield). ^1H NMR (δ , CDCl_3): 7.53 (d, 2H, C_{Ar}H), 8.41 (d, 2H, C_{Ar}H).

$4\text{-CF}_3\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{SClCF}_3$, **4e**. Compound **4e** was prepared using the same method as **4c** using SCl_2 (2.2 mL, 34.6 mmol) in 10 mL of acetonitrile and **3e** (2.13 g, 6.7 mmol) in 40 mL of acetonitrile. The solvent was removed *in vacuo*, leaving a dark orange oil (2.50 g, 98% yield). ^1H NMR (δ , CDCl_3): 7.82 (d, 2H, C_{Ar}H), 8.59 (d, 2H, C_{Ar}H).

Synthesis of 3-Trifluoromethyl-5-aryl-1,2,4,6-thiatriazines 5a–e. $\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{SCF}_3$, **5c**. A pear-shaped solids addition funnel was loaded with triphenylantimony (1.42 g, 4.0 mmol) and attached to a side arm flask containing **4c** (2.23 g, 8.0 mmol) and 25 mL of acetonitrile. After degassing the solvent with three freeze–thaw cycles and warming to RT, while still under a vacuum, the Ph_3Sb was added with stirring. A fine dark purple precipitate formed, and the crystals were vacuum filtered under nitrogen to give 1.14 g of crude product (4.7 mmol, 59% yield), mp (dec.) 110–3 °C. Purification was achieved by vacuum sublimation in a three-zone tube furnace. Mass spectrum (m/e): 245 ($\text{PhC}_3\text{N}_3\text{SF}_3^+$, 43%), 149 (PhCN_2S^+ , 6%), 129 (PhC_2N_2^+ , 3%), 104 (PhCN^+ , 100%). Analysis calculated (found): 44.26 (44.12)% C, 2.06 (2.24)% H, 17.21 (17.13)% N.

$4\text{-CH}_3\text{OC}_6\text{H}_5\text{C}_2\text{N}_3\text{SCF}_3$, **5a**. Compound **5a** was prepared using the same method as **5c** from **4a** (1.25 g, 4.0 mmol) and Ph_3Sb (0.79 g, 2.2 mmol) in 20 mL of acetonitrile to give 0.41 g of dark purple solids (1.5 mmol, 37% yield), mp (dec.) 135–40 °C. Purification was achieved by vacuum sublimation in a three-zone tube furnace. Mass spectrum (m/e): 274 ($\text{CH}_3\text{OPhC}_3\text{N}_3\text{SF}_3^+$, 65%), 255 ($\text{CH}_3\text{OPhC}_3\text{N}_3\text{SF}_2^+$, 4%), 179 ($\text{CH}_3\text{OPhCN}_2\text{S}^+$, 3%), 117 ($\text{CH}_3\text{OPhCN}^+$, 100%). Analysis calculated (found): 43.80 (43.90)% C, 2.57 (2.71)% H, 15.32 (15.18)% N.

$4\text{-CH}_3\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{SCF}_3$, **5b**. Compound **5b** was prepared using the same method as **5c** from **4b** (1.05 g, 3.6 mmol) and Ph_3Sb (0.64 g, 1.8 mmol) in 15 mL of acetonitrile to give 0.46 g of dark purple solids (1.8 mmol, 50% yield), mp (dec.) 140–2 °C. Purification was achieved by vacuum sublimation in a three-zone tube furnace. Mass spectrum (m/e): 258 ($\text{CH}_3\text{PhC}_3\text{N}_3\text{SF}_3^+$, 100%), 239 ($\text{CH}_3\text{PhC}_3\text{N}_3\text{SF}_2^+$, 4%), 163 ($\text{CH}_3\text{PhCN}_2\text{S}^+$, 24%), 117 (CH_3PhCN^+ , 45%). Analysis calculated (found): 46.51 (46.67)% C, 2.73 (2.96)% H, 16.27 (16.41)% N.

$4\text{-ClC}_6\text{H}_5\text{C}_2\text{N}_3\text{SCF}_3$, **5d**. Compound **5d** was prepared using the same method as **5c** from **4d** (2.78 g, 8.9 mmol) and Ph_3Sb (1.71 g, 4.8 mmol) in 30 mL of acetonitrile to give 1.36 g of dark purple solids (4.9 mmol, 55% yield), mp (dec.) 131–4 °C. Purification was achieved by vacuum sublimation in a three-zone tube furnace. Mass spectrum (m/e): 278 ($\text{CIPhC}_3\text{N}_3\text{SF}_3^+$, 100%), 259 ($\text{CIPhC}_3\text{N}_3\text{SF}_2^+$, 5%), 183 ($\text{CIPhCN}_2\text{S}^+$, 18%), 137 (CIPhCN^+ , 47%). Analysis calculated (found): 38.79 (38.72)% C, 1.45 (1.41)% H, 15.08 (15.08)% N.

$4\text{-CF}_3\text{C}_6\text{H}_5\text{C}_2\text{N}_3\text{SCF}_3$, **5e**. Compound **5e** was prepared using the same method as **5c** from **4e** (2.32 g, 6.7 mmol) and Ph_3Sb (1.31 g, 3.7 mmol) in 25 mL of acetonitrile to give 0.45 g of a dark purple product (1.4 mmol, 20% yield), mp (dec.) 101–5 °C. Purification was achieved by vacuum sublimation in a three-zone tube furnace. Mass spectrum (m/e): 312 ($\text{CF}_3\text{PhC}_3\text{N}_3\text{SF}_3^+$, 100%), 197 ($\text{CH}_3\text{PhC}_2\text{N}_2^+$, 24%), 171 (CF_3PhCN^+ , 30%). Analysis calculated (found): 38.47 (38.52)% C, 1.29 (1.53)% H, 13.46 (13.34)% N.

Isolation of N-Chlorosulfonyl-N,N'-benzamidine, 6. Attempts to grow crystals of **4** by slow cooling (–30 °C) in anhydrous CH_3CN were successful only for **4b** and **4e**; in the case of **4c**, colorless crystals of a hydrolysis product (**6**) were obtained, which could be identified as N-chlorosulfonyl-N,N'-benzamidine by a single-crystal X-ray diffraction structure determination. Further characterization of this material was not undertaken.

■ ASSOCIATED CONTENT

Supporting Information. Supplemental crystal structure information, a representative NMR spectrum of imidoylamidine,

infrared spectral data, tables of hydrogen bonds, graphs showing correlation of hfs and solution redox potentials with Hammett parameters, additional EPR spectra, data from Gaussian calculations, and electronic crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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