

Synthesis and Properties of Tetrathiadiazafulvalenes [RCNS₂C=CS₂NCR] (R = H, Me, Ph)

Richard T. Oakley,^{*1a} John F. Richardson,^{1b} and Rupert E. v. H. Spence^{1a}

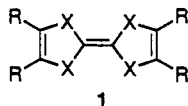
Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

Received December 10, 1993[®]

Reduction of 5-(methylthio)-1,4,2-dithiazolium (3, R = H, Me, Ph) salts with zinc powder yields the corresponding diazahexathioorthoaxalate derivatives (RCNS₂)(MeS)CC(SMe)(S₂NCR) (4, R = H, Me, Ph). Thermolysis of these materials in the presence of catalytic quantities of iodine affords the tetrathiadiazafulvalenes [RCNS₂C=CS₂NCR] (2, R = H, Me, Ph) in good yield. Separation of the *cis* and *trans* isomers can be achieved with relative ease for the R = Me and Ph derivatives, but co-crystallization occurs for the two isomers of the R = H compound. Tetrathiadiazafulvalenes are poorer electron donors than TTF; cyclic voltammetry nonetheless reveals two reversible oxidation processes. The ESR spectrum of the radical cation *trans*-2^{•+} (R = Ph) consists of a quintet with $a_N = 0.08$ mT, $g = 2.0071$.

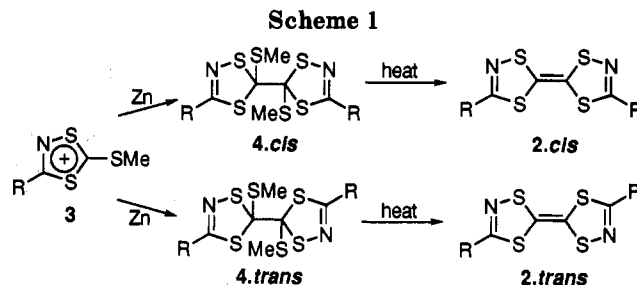
Introduction

The tetrathiafulvalene (TTF) framework 1 (X = S) represents an important building block in the design of organic conductors.² Derivatization of 1 has usually been achieved by altering the substituents R and by replacement of the sulfur atoms by selenium. However, and in the



hope of discovering new electronic properties for the fulvalenes, more dramatic structural changes have been examined, such as the replacement of one or more of the chalcogens with a non-Group 16 atom. For example, Mathey³ has recently prepared the tetraphosphafulvalenes (X = PR), while Metzger⁴ and others⁵ have described the dithiadiazafulvalenes (X = NR and S). This approach to derivatization is interesting but faces significant challenges. Firstly, the compounds are air-sensitive, making them difficult to handle. Secondly, introduction of additional substituents to the fulvalene framework may prohibit the formation of important intermolecular contacts in subsequent charge-transfer complexes.²

It occurred to us that as an alternative to chalcogen substitution, derivatization of tetrathiafulvalene 1 could also be achieved by replacement of one CR group in each of the two rings with a nitrogen atom to yield the tetrathiadiazafulvalenes 2.⁶ These compounds would be of interest because although expected to be poorer electron donors (due to the higher electronegativity of nitrogen



relative to carbon), they are sterically less encumbered than the parent tetrathiafulvalenes. Furthermore, the tetrathiadiazafulvalenes 2 can exist in *cis* and *trans* configurations, perhaps leading to subtle changes in chemistry.

We report here the synthesis and characterization details for the first tetrathiadiazafulvalenes 2 where R = H (2.H), Me (2.Me), or Ph (2.Ph). The high yield synthetic route, Scheme 1, utilizes the recently reported^{7,8} and readily prepared 2-(alkylthio)-1,4,2-dithiazolium salts 3 and is a development of a classic procedure^{9,10} for the preparation of tetrathiafulvalenes 1 (X = S) from 2-(alkylthio)-1,3-dithiolium salts. We include spectroscopic and physical characterization details (including crystallographic for *trans*-4.Ph) of the intermediate diazahexathioorthoaxalates 4 (R = H, Me, Ph) and their isomers. Furthermore, we report the isomer separation procedures for the tetrathiadiazafulvalenes 2, their electrochemical behavior, and the ESR spectra of their radical cations. Details of the crystal structure of the prototypical compound 2.H are also described.

Aside from the preparation of compounds 2, the reduction of the 1,4,2-dithiazolium cation 3 is of interest when compared to the chemistry of the isomeric 1,2,3- and 1,3,2-dithiazolium salts. Rather than form C-C bonded dimers, these latter compounds afford stable radicals upon reduction.^{11,12} Here we discuss the stabilities

[®] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) (a) University of Guelph. (b) University of Louisville.

(2) See, for a recent review: Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. In *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory*; Prentice-Hall: NJ, 1992.

(3) Maignot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 950; 1992, 31, 1031.

(4) Metzger, J.; Larive, H.; Dennilauler, R.; Barelle, R.; Gaurat, C. *Bull. Soc. Chim. Fr.* 1964, 11, 2857.

(5) Bssaibis, M.; Robert, A.; Lemaguerès, P.; Ouahab, L.; Carlier, R.; Tallec, A. *J. Chem. Soc., Chem. Commun.* 1993, 601.

(6) Oakley, R. T.; Richardson, J. F.; Spence, R. E. v. H. *J. Chem. Soc., Chem. Commun.* 1993, 1226.

(7) Greig, D. J.; McPherson, M.; Paton, R. M.; Crosby, J. *J. Chem. Soc., Chem. Commun.* 1985, 696.

(8) Wai, K.-F.; Sammes, M. P. *J. Chem. Soc., Perkin Trans. 1* 1992, 2065; 1990, 808.

(9) Moses, P. R.; Chambers, J. Q. *J. Am. Chem. Soc.* 1974, 96, 945.

(10) Fanghanel, E.; van Hinh, L.; Schukat, G. *Z. Chem.* 1976, 16, 317.

and modes of association of the different dithiazolyl radical isomers in light of the results of MNDO calculations on their electronic structures.

Results

In 1985 Paton and Crosby⁷ discovered that electrophilic alkylation of 3-aryl-1,4,2-dithiazole-5-thiones with dimethyl sulfate and subsequent treatment of the reaction mixture with tetrafluoroboric acid etherate gave the first examples of 1,4,2-dithiazolium salt **3**. There have since been several other reports^{13,14} dealing with the synthesis of these heterocycles, and Sammes⁵ was recently able to isolate the parent 3,5-diproto species by an elegant synthesis. Investigations into the chemistry of these cations have generally been restricted to their reactions with nucleophiles and it is found that initial attack occurs exclusively at the C5 ring position. For example, reaction with hydride anion leads to 5-H-1,4,2-dithiazole rings.¹³

As an alternative to reduction with hydride, we have examined the reaction of the 5-(methylthio)-1,4,2-dithiazolium tetrafluoroborate salts **3** (R = H,⁸ Me,⁸ Ph⁷) with zinc powder in acetonitrile. The reactions could be followed by TLC and were found to give a single product after 1.5 h. The product, the dimeric diazahexathioorthoaxalate **4**, resulted from the reduction of the 1,4,2-dithiazolium cation and coupling of two rings through the C5 position. After filtration through silica (using benzene eluent) and concentration, the diazahexathioorthoaxalates were isolated in good (H, 75%) to quantitative (Me, Ph) yield.¹⁵

This coupling of the 1,4,2-dithiazoles **3** is directly analogous to the reduction chemistry of the 2-(alkylthio)-1,3-dithiolium cations mentioned previously.^{9,10} However, the 1,3-dithiolium salts give only a single hexathioorthoaxalate while the 1,4,2-dithiazolium salts yield 1:1 isomeric mixtures of the *cis* and *trans* diazahexathioorthoaxalates **4**. The presence of two isomers in the reduction reaction product was readily observed by NMR spectroscopy. All three derivatives showed two signals for C3 ring carbons in their ¹³C NMR spectra (**4.H**, 146.3, 146.1; **4.Me**, 157, 156.7; **4.Ph**, 158.2, 157.9) while two pairs of signals were observed for **4.H** (SCH₃, 1.92 and 1.93; CH, 6.77 and 6.81) and **4.Me** (SCH₃, 1.69 and 1.70; CCH₃, 2.08 and 2.10) by ¹H NMR. In the case of **4.Ph**, the isomers

could also be identified using TLC (silica, 50% CH₂Cl₂/hexane), with the faster moving species being the *trans*-**4.Ph** isomer (see below). ¹³C NMR spectroscopy of the isomerically mixed reaction product showed only single resonances for the methylthio and C3 carbon centers and no signal was observed for the C5 bridging atoms. The diazahexathioorthoaxalates **4** were characterized by elemental analysis or mass spectroscopy. It is noteworthy that only compound **4.H** showed a parent ion in the mass spectrum; the Me and Ph derivatives gave the (M - SMe)⁺ and (M - S₂Me₂)⁺ ions, respectively, as their highest mass signals.

The separation of the *cis* and *trans* isomers for compounds **4** has met with only limited success. The diazahexathioorthoaxalate **4.Ph** was initially isolated as an oil that slowly crystallized over 1–2 weeks. Crystallization of this solid from hot ethanol and then from CH₂Cl₂/hexane led to the isolation of isomerically pure (by TLC) transparent crystals which, by single-crystal X-ray analysis, were determined to be the *trans* isomer (*vide infra*). In a similar fashion, recrystallization of compound **4.H** from a variety of solvents (including methanol, hexane, toluene, and benzene) led to the preferential crystallization of one isomer [δ (SMe) 1.93, (CH) 6.77] as determined by ¹H NMR spectroscopy. However, this process was limited only to the enrichment of one isomer over the other and not to the isolation of a single isomer. Compound **4.Me** is an oil at room temperature and no attempt was made to separate the isomers.

Thermolysis of Diazahexathioorthoaxalates 4. When dilute solutions of the colorless or yellow diazahexathioorthoaxalates **4** (R = H, Me, Ph) in redistilled methylene chloride were heated to 100 °C (in a sealed vessel), they were found to be stable for 1–2-h periods. However, when the same solutions were heated in the presence of small amounts of iodine, they slowly turned an orange-red color. This color is the result of Me₂S₂ elimination from the oxalate and the formation of the red-orange tetrathiadiazafulvalenes **2**. The thermolysis process is analogous to that observed for the formation of tetrathiafulvalenes **1** (X = S) from hexathioorthoaxalates.^{9,10,16,17}

In our initial communication iodine was not used to effect elimination of dimethyl disulfide.⁶ We reported that the elimination could be achieved solely by heating the oxalates **4** at 140 °C in tetrachloroethane. However, we have since found that the thermolysis is difficult to reproduce consistently under these conditions and that in fact it is highly dependent on the amounts of impurities present in the commercial grade solvent.¹⁸ In this regard we note that previous studies on the hexathioorthoaxalate conversion to tetrathiafulvalenes **1** (X = S) have found the choice of thermolysis solvent to be very important.^{2,16} Perhaps this too has been more a reflection of the need for (unknown) impurities than the special properties associated with a particular solvent. We have found that conversion of **4.H** to **2.H** occurs at room temperature in very dilute solutions of commercial grade deuteriochloroform. Furthermore, Smith¹⁶ found that addition

(11) (a) Wolmershäuser, G.; Kraft, G. *Chem. Ber.* **1990**, *123*, 881. (b) Awere, E. G.; Burford, N.; Haddon, R. C.; Parsons, S.; Passmore, J.; Waszczak, J. V.; White, P. S. *Inorg. Chem.* **1990**, *29*, 4821. (c) Awere, E. G.; Burford, N.; Mailer, C.; Passmore, J.; Schriver, M. J.; White, P. S.; Banister, A. J.; Oberhammer, H.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1987**, 66. (d) Wolmershäuser, G.; Schnauber, M.; Wilhelm, T. *J. Chem. Soc., Chem. Commun.* **1984**, 573. (e) Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O., Jr.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594. MacLean, G. K.; Passmore, J.; Roa, M. N. S.; Schriver, M. J.; White, P. S.; Bethell, D.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1405. MacLean, G. K.; Passmore, J.; Schriver, M. J.; White, P. S.; Bethell, D.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* **1983**, 807.

(12) (a) Harrison, S. R.; Pilkington, R. S.; Sutcliffe, L. S. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 669. (b) Mayer, R.; Domschke, G.; Bleisch, S.; Fabian, J.; Bartl, A.; Stasko, A. *Collect. Czech. Chem. Commun.* **1984**, *49*, 684. (c) Mayer, R. *Phosphorus Sulphur* **1985**, *23*, 277.

(13) Chan, F. S. Y.; Sammes, M. P.; Harlow, R. L. *J. Chem. Soc., Perkin Trans. 1* **1988**, 899.

(14) Yonemoto, K.; Shibuya, I.; Tsuchiya, T.; Yasumoto, M.; Taguchi, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2933. Xie, S.; Fan, S.; Wang, X.; Sammes, M. P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2465. Shibuya, I.; Yonemoto, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2017. Chan, F. S. Y.; Sammes, M. P. *J. Chem. Soc., Chem. Commun.* **1985**, 1641.

(15) Compound **4.H** was found to be very susceptible to decomposition until pure and the workup procedures described in the Experimental Section should be followed closely when repeating this work.

(16) Lindsay, C. M.; Smith, K.; Brown, C. A.; Betterton-Cruz, K. *Tetrahedron Lett.* **1984**, *25*, 995.

(17) Kini, A. M.; Tytko, S. F.; Hunt, J. E.; Williams, J. M. *Tetrahedron Lett.* **1987**, *28*, 4153.

(18) The best results were obtained from older bottles of tetrachloroethane. The use of fresh or redistilled solvent invariably led to a drastic decrease in the yield of compound **2**.

of small amounts of toluene-4-sulfonic acid to various solvent systems greatly increased the elimination rate of dimethyl disulfide from benzohexathioorthoalates.¹⁹ The iodine doping procedure is consistently reproducible and the only method suitable for the preparation of the prototetrathiadiazafulvalene **2.H** in good yield.

The thermolysis proceeded cleanly when performed at high dilution, and it could be readily followed by TLC. The tetrathiadiazafulvalenes **2** were isolated as isomeric mixtures in good yield (**2.H**, 80%; **2.Me**, 67%; **2.Ph**, 88%) after chromatography on silica (to remove iodide complexes) and washing the residues with hexane (to abstract Me₂S₂). The compounds are air-stable red or orange crystalline solids which have been characterized by both elemental analysis and mass spectrometry.

Tetrathiadiazafulvalene Isomer Separation and Characterization. Recrystallization of the aryltetrathiadiazafulvalene **2.Ph** from CH₂Cl₂ led to the preferential precipitation of isomerically pure red needles of the *trans* isomer. The *trans* conformation was determined by single-crystal X-ray analysis which we have reported previously.⁶ The ready crystallization of *trans*-**2.Ph** eventually allowed for its complete removal, permitting the isolation of isomerically pure samples of the corresponding *cis* derivative, *cis*-**2.Ph**. The *cis* and *trans* isomers are distinguished by dramatically different melting points (*trans*, 212–14 °C; *cis*, 152–155 °C), their TLC *R_f* values (*trans*, 0.58; *cis*, 0.53; silica, 50% CH₂Cl₂/hexane), and small differences in their IR spectra. These later differences, consisting primarily of single bands for *trans*-**2.Ph** (931; 791 cm⁻¹) being split into two bands for *cis*-**2.Ph** (938, 932; 799, 790 cm⁻¹), are likely a consequence of the point group symmetry change (*trans*, *D*_{2h}; *cis*, *C*_{2v}). No significant difference between the two isomers was observable by ¹H NMR spectroscopy at 200 MHz.

Isomerically pure *trans* tetrathiadiazafulvalene **2.Me** can be isolated preferentially by two recrystallizations from toluene starting from the mixed isomers. It is an orange powder with a melting point (146–48 °C) significantly different from the *cis*-**2.Me** isomer (114 °C). Specimens of this latter compound were isolated by column chromatography (silica) starting from a *cis*-**2.Me**-enriched sample of the mixed isomers. The conformation of the isomers was assigned on the basis of a single-crystal X-ray analysis of *cis*-**2.Me**⁶ and they are readily distinguished by ¹H NMR (*trans*, δ 1.58; *cis*, δ 1.60) and small differences in their IR spectra.

The presence of *cis* and *trans* isomers for the prototypal tetrathiadiazafulvalene **2.H** was confirmed by the observation of two signals (δ 6.89 and 6.86) in the ¹H NMR spectrum of the thermolysis product. However, although it was possible to achieve a slight enrichment of one isomer (¹H NMR, δ 6.86) through recrystallization, we were unable to isolate isomerically pure samples of compounds *cis*-**2.H** and *trans*-**2.H** due to their co-crystallization (*vide infra*) from most solvents. The analyses discussed below were therefore obtained on isomerically mixed **2.H**.

Crystal Structure of Tetrathiadiazafulvalene 2.H. We were anxious to determine the crystal structure of compound **2.H**, the parent derivative of the tetrathiadiazafulvalenes. Crystallization of *cis/trans* mixtures of the compound from acetonitrile affords long red needles which, when redissolved, were shown to contain an

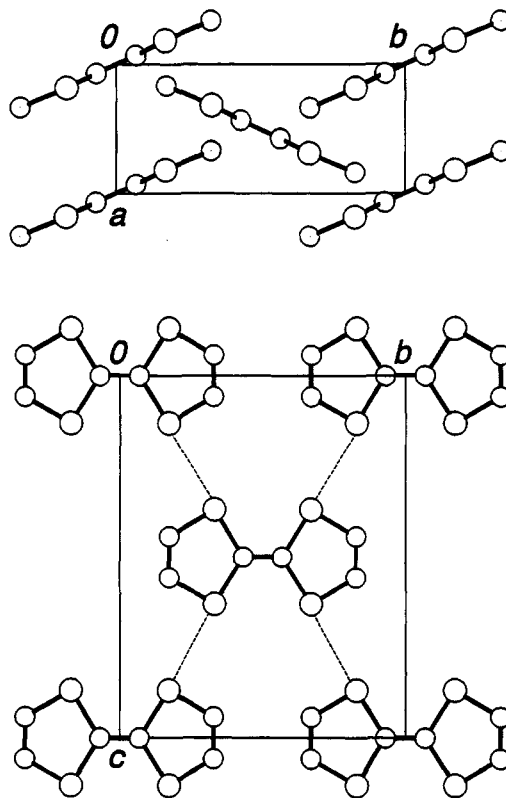


Figure 1. Packing diagrams for **2.H**, showing intermolecular S---S contacts.

approximately 1:1 ratio of the isomers by ¹H NMR. The crystals belong to the space group *Pnmm*, which requires that molecules lie on two intersecting mirror planes. This symmetry results in the two isomers co-crystallizing with near equal probability, leading to complete disorder of the 3-C and 4-N positions. Indeed, in the event that isomerically pure material were available, disorder (by reflection across a single mirror plane) would still be apparent. The structure was therefore solved with the assumption of complete statistical disordering of the CH and N positions. The molecular structure is consequently an average of the two isomers and bond lengths and angles are of no structural significance. However, a discussion of the crystal structure packing remains valid. In that regard, the molecular packing of compound **2.H** (Figure 1) is very similar to that observed for tetrathiafulvalene²⁰ (space group *P2₁/c*), with the molecules forming slipped stacks. There are close, lateral intermolecular S---S contacts of about 3.56 Å. These distances are between those observed for the sulfur atoms in bis(ethylenedithio)-tetrathiafulvalene (1, R = SCH₂; 3.69 Å)²¹ and TTF (3.4 Å).²⁰

Cyclic Voltammetry. In order to explore the potential of the tetrathiadiazafulvalenes as electron-donor compounds, we obtained the cyclic voltammograms of *trans*-**2.Ph**, *trans*-**2.Me**, and **2.H**. Two reversible oxidation waves, corresponding to the formation of a radical cation and a closed shell dicationic species, were observed. The half-wave potentials (*vs* saturated calomel electrode) occur at

(19) Kini and Williams found (alkylthio)-substituted hexathioalates to decompose in the presence of toluene-4-sulfonic acid (ref 17).

(20) Cooper, W. F.; Edmonds, J. W.; Wudl, F.; Coppens, P. *Crystal. Struct. Commun.* 1974, 3, 23. Cooper, W. F.; Kenny, N. C.; Edmonds, J. W.; Nagel, A.; Wudl, F.; Coppens, P. *J. Chem. Soc., Chem. Commun.* 1971, 889.

(21) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* 1986, 59, 301.

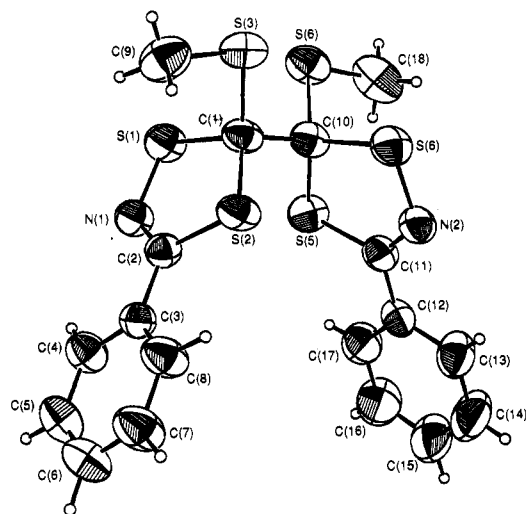


Figure 2. ORTEP drawing of *trans*-4.Ph.

0.63 (H), 0.59 (Me), and 0.65 V (Ph) for the $2/2^{++}$ process and at 1.00 (H), 0.95 (Me), and 1.01 V (Ph) for the $2^{+}/2^{2+}$ step, with the slight differences between the three compounds reflecting the expected inductive effects of the substituents. The cyclic voltammogram of the isomerically mixed **2.H** shows no indication of differing half-wave potentials for the *cis* and *trans* isomers. Similarly, cyclic voltammetric study of *cis*-**2.Me** gave identical half-wave potentials, within experimental error, to those of *trans*-**2.Me**.

Both half-wave potentials of the tetrathiadiazafulvalenes are greater than those observed for tetrathiafulvalene (1, R = H: 0.30 and 0.66 V)²² and its derivatives (e.g., R = SMe: 0.47, 0.71 V).⁹ Given the greater electronegativity of nitrogen (3.04)²³ compared to carbon (2.55), this trend is not unexpected. The higher oxidation potentials of the diazafulvalenes limit their ability to be involved in charge-transfer (CT) complexes similar to those observed for the tetrathiafulvalenes. For example, **2.H** does not react with TCNQ. The disadvantages associated with its lower donor capacity may, however, be offset by the more exposed periphery of the nitrogen-containing system, which should allow it to form closer intermolecular contacts in its CT complexes. We have found that the diazafulvalenes form conducting complexes with iodine, and these will be the subject of a future report.

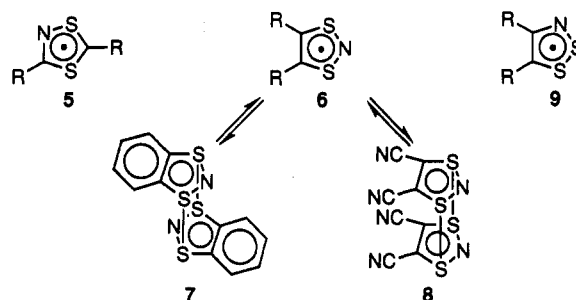
Electronic Structures and Modes of Association of Dithiazolyls. To define the molecular conformation of *trans*-4.Ph, we performed a single-crystal X-ray analysis. A view of the structure is shown in Figure 2 along with selected bond lengths and angles. The dimeric compound has a *cis*-orientation for the two MeS-groups, a feature which presumably favors a ready release of dimethyl-disulfide during the thermolysis step. The bond lengths within the molecule are typical of covalent values, the central bridging C-C bond is 1.564 Å in length.

The formation of the dimeric diazahexathioorthoxalates **4** can be viewed as resulting from the reduction of the 1,4,2-dithiazolium salts **3** and subsequent coupling of the putative dithiazolyl radicals **5**. The coupling occurs at the C5 carbon of the rings and is irreversible. This

Table 1. MNDO (RHF) Spin Densities for Dithiadiazolyl Isomers $H_2C_2S_2N$

	1,4,2 (5)		1,3,2 (6)		1,2,3 (9)
S1	0.191	S1	0.237	S1	0.150
N2	0.011	N2	0.460	N3	0.195
C3	0.016	S3	0.237	S2	0.221
S4	0.163	C4	0.034	C4	0.004
C5	0.619	C5	0.034	C5	0.431

irreversible coupling is in contrast to the very weak coupling observed for 1,3,2-dithiazolyl radicals **6**.¹¹ These radicals, obtained by reduction of their 1,3,2-dithiazolium salts, are stable species in solution and the gas phase that dimerize in the solid state through long intermolecular sulfur-sulfur contacts.¹¹ This alternative mode of dimerization has been established by X-ray crystallographic study of the benzo [S---S, 3.175(1) Å] **7**^{11b} and the 4,5-dicyano [S---S, 3.142 (2) Å] **8**^{11a} 1,3,2-dithiazolyl systems.



In order to explain the differing modes of dimerization for the 1,3,2- and 1,4,2-dithiazolyl radicals, we have performed MNDO calculations on a series of model radicals (R = H) representative of the two isomers. In addition, we have also examined the 1,2,3-dithiazolyl radical **9** (R = H). A wide variety of benzo derivatives of this species have been characterized by ESR spectroscopy, but no structural data on dimers have yet been reported.¹²

The results, summarized in terms of the ROHF singly occupied molecular orbitals (SOMOs) and spin densities (Table 1), confirm that spin density in both the 1,2,3 and 1,3,2 isomers is heavily localized on sulfur and nitrogen. This is in agreement with observed hyperfine coupling constants to nitrogen in the ESR spectra of these compounds.^{11,12} By contrast, the putative 1,4,2 system has a very high calculated spin density at C5. That strong C-C bond formation (at C5) follows upon reduction of 1,4,2-dithiazolium salts is not, therefore, surprising. The results also reveal an interesting question regarding the 1,2,3-dithiazolyl radicals. Significant spin density exists at the C5 carbon position of these rings, an observation that suggests C-C dimerization as the ultimate fate of these systems.

Electron Spin Resonance Spectra. Solutions of the radicals *trans*-**2.Ph**^{•+}, *trans*-**2.Me**^{•+}, and **2.H**^{•+} were conveniently generated by the addition of bromine to CH_2-Cl_2 solutions of the parent heterocycles.²⁴ ESR spectra were recorded after degassing the samples with several freeze-pump-thaw cycles. All three derivatives (R = Ph, Me, H) exhibit similar spectra, with $g = 2.0071$ (cf. 2.0081

(22) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(23) Porterfield, W. W. *Inorganic Chemistry*; Addison-Wesley: Don Mills, Canada, 1984.

(24) In our earlier communication the radical cations were generated electrochemically for ESR work, and triplet signals ($a_N = 1.56$ mT) were observed. These rather anomalous signals could arise from trace impurities or side reactions, as they are not observed during a bulk oxidation experiment.

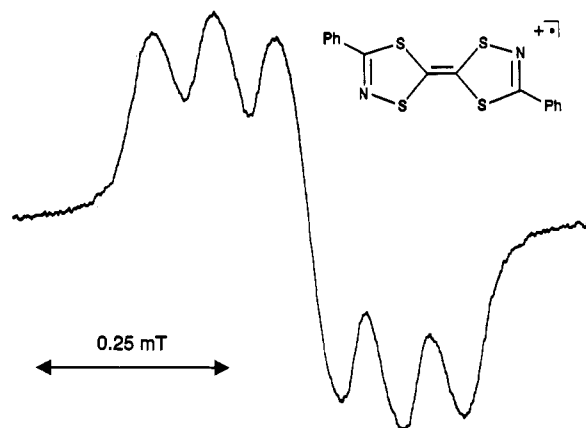


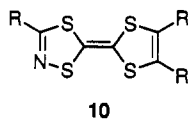
Figure 3. ESR spectrum of $2^{+\bullet}$ (R = Ph) in CH_2Cl_2 .

Table 2. MNDO (RHF) Spin Densities for Radical Cations $1^{+\bullet}$ and $\text{trans-}2^{+\bullet}$ (R = H)

$1^{+\bullet}$		$\text{trans-}2^{+\bullet}$	
C(=C)	0.130	C(=C)	0.144
S	0.144	S(C)	0.125
C(H)	0.041	S(N)	0.181
		C(H)	0.025
		N	0.024

for $\text{TTF}^{+\bullet}$).²⁵ In the case of R = Me and H, the signal consists of a broadened (by hyperfine coupling to hydrogen) singlet, but for R = Ph the absence of close-range hyperfine coupling to H affords better resolution. The spectrum now appears as a broad quintet with $a_N = 0.08$ mT (Figure 3). The small hyperfine coupling to nitrogen is consistent with the calculated (MNDO) spin distributions obtained, which show a depletion in spin density at the periphery (NCH region) of the molecule relative to that observed in the equivalent positions of $\text{TTF}^{+\bullet}$ (Table 2).²⁵ Correspondingly, spin densities at the sulfur atoms are increased.

Tetrathiamonoazafulvalene. In an attempt to draw together the chemistry of fulvalene 1 and diazafulvalene 2, we examined two routes to the mixed heterocyclic fulvalene 10. The first route involved the zinc reduction



of equimolar mixtures of 3-phenyl-5-(methylthio)-1,4,2-dithiazolium tetrafluoroborate and 3,4,5-tris(methylthio)-1,3-dithiolium tetrafluoroborate. Somewhat surprisingly, this gave only diazahexathioorthooxalate 4 and standard hexathioorthooxalate; no cross-coupled species were observed. An alternative route to the cross-coupled species involved addition of the 2-(butylthio)-1,3-benzodithiolate anion to 3-phenyl-1,4,2-dithiazole-5-thione²⁶ and subsequent treatment with methyl iodide.²⁷ Unfortunately the thione did not react with the anion, nor, in separate experiments, did it react with methylolithium.

(25) See, for example: Bock, H.; Roth, B.; Schumaker, R. *Phosphorus Sulphur* 1984, 21, 79 and references therein.

(26) Greig, D. J.; McPherson, M.; Paton, R. M.; Crosby, J. *J. Chem. Soc., Perkin Trans. 1* 1985, 1205.

(27) Brown, C. A.; Miller, R. D.; Lindsay, C. M.; Smith, K. *Tetrahedron Lett.* 1984, 24, 991.

Summary and Conclusions

Tetrathiadiazafulvalenes (*cis* and *trans*) represent a new variation on the tetrathiafulvalene framework. They behave as weak charge-transfer donors but form stable radical cations on oxidation. We have demonstrated that they are readily synthesized in high yield and that the configurational isomers can be separated when the substituents are groups other than a proton. The charge-transfer chemistry of these compounds is presently under investigation.

Experimental Section

General Procedures and Starting Materials. Thioacetamide, perchloromethyl mercaptan (Aldrich), zinc powder, chloroform, hexane, toluene (Fisher), and tetrabutylammonium hexafluorophosphate [TBAP] (Fluka) were obtained commercially and used without further purification. Acetonitrile (HPLC grade) and methylene chloride (Fisher) were distilled from P_2O_5 under a nitrogen atmosphere. The 5-(methylthio)-1,4,2-dithiazolium salts were prepared by alkylation of their respective 1,4,2-dithiazole-5-thiones with dimethyl sulfate (Kodak) and treatment with etheral tetrafluoroboric acid (Alfa)⁷ and were recrystallized (R = H, Ph from CH_3CN /ether; R = Me from CH_2Cl_2) before reduction. The 3-phenyl and 3-methyl substituted thiones were prepared from their respective thioamides (Aldrich) and Cl_3CSCl (see below). The 3-proto thione was prepared by the Sammes⁸ procedure from sodium piperidinedithiocarboxylate²⁸ in four steps using hydroxylamine-*O*-sulfonic acid (Aldrich), formic acetic anhydride, 70% perchloric acid (Fisher), and hydrogen sulfide (Matheson). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200-MHz NMR spectrometer; chemical shift values are internally referenced to TMS or the residual proton signals of the solvents (δ , CHCl_3 , 7.24; δ , $\text{C}_6\text{D}_6\text{H}$, 7.15). Infrared spectra (Nujol mulls, CsI optics) were recorded on a Nicolet 20SX/C FTIR spectrometer at 2 cm^{-1} resolution. X-band ESR spectra were recorded on a Varian E-109 spectrometer with DPPH as field marker; samples of the radical cations were prepared by addition of bromine to CH_2Cl_2 solutions of compounds 2. Visible spectra were obtained on CHCl_3 solutions using a HP 8452A diode array spectrometer. Cyclic voltammetry was performed on a PAR 273A electrochemical system (EG&G Instruments) using a two-compartment cell with Pt working, counter, and quasi-reference electrodes. Electrolyte solutions contained 2–5 mg of the tetrathiadiazafulvalene in 20 mL of 0.1 M TBAP in acetonitrile. Potentials were scanned from –0.5 to +1 V with respect to the quasi-reference electrode. Ferrocene was used as an internal reference (0.307 V vs SCE) and the half-wave potentials are reported with reference to SCE. Mass spectra (70 eV, EI) were obtained on a Kratos MS890 spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Signals were not observed for the bridging C-5 carbon atoms of compounds 4 and 2 (R = H, Me, Ph) in their ^{13}C NMR spectra.

3-Methyl-1,4,2-dithiazole-5-thione. To a gently refluxing solution of thioacetamide (18.78 g, 250 mmol) in CHCl_3 (650 mL) was added, over 5–10 min, a solution of perchloromethyl mercaptan (23.25 g, 125 mmol; CHCl_3 , 30 mL). A vigorous reaction ensued. After 1 h at reflux, the orange/red reaction was cooled and the volatiles were removed *in vacuo*. The residues were passed thorough a silica column (20 \times 3 cm), eluting with CHCl_3 /hexane (1:4), to give the product as an orange oil. Crystallization from hexane yielded 1.87 g (12.5 mmol, 10%) of the desired product (mp 32 $^\circ\text{C}$; lit. mp 29–30 $^\circ\text{C}$). This reaction, although low in yield, represents a more direct and experimentally simpler route to the thione than the Sammes⁸ procedure.

Reduction of the 1,4,2-Dithiazolium Salts. To a solution of the dithiazolium tetrafluoroborate salts 3 (R = H, 3.21 g, 13.6 mmol; R = Me, 1.56 g, 6.21 mmol; R = Ph, 5.50 g, 17.6 mmol) in CH_3CN (H, Me 20 mL; Ph, 100 mL), under nitrogen, was added excess Zn dust (H, 68 mmol; Me, 30 mmol; Ph, 158 mmol).

(28) Uhlir, A.; Åkerström, S. *Acta Chem. Scand.* 1971, 25, 393.

The reaction solution become slightly yellow and TLC (silica, 50% hexane/CH₂Cl₂) indicated complete reaction after 1.5 h. The reaction mixture was added directly to a silica column (10 × 2 cm) and the diazhexathioorthoxalate 4 eluted with benzene. Details on individual reactions follow:

R = H. Removal of solvent under vacuum yielded a colorless isomerically mixed crystalline solid (1.523 g, 75%) that was washed with benzene/ether and recrystallized from hot toluene or ethanol: ¹H NMR (C₆D₆) δ 1.92, 1.93, 6.77, 6.81; ¹³C NMR (C₆D₆) δ 146.3, 146.1, 17.2. MS *m/e* (rel intensity) 300 (M⁺, 1), 206 (M - S₂Me₂⁺, 25), 194 (42), 167 (60), 150 (100). Anal. Calcd for C₆H₈N₂S₆: C, 23.98; H, 2.68; N, 9.32. Found: C, 24.18; H, 2.50; N, 9.36.

R = Me. Removal of solvent yielded a yellow isomerically mixed oil (1.02 g, 100%). It could not be further purified and was used directly in the subsequent thermolysis step: ¹H NMR (C₆D₆) δ 1.69, 1.7, 2.08, 2.1; ¹³C NMR (C₆D₆) δ 157, 156.7, 20, 17.3; MS *m/e* (rel intensity) 281 (M - SMe⁺, 2), 164 (100).

R = Ph. Removal of solvent yielded a viscous isomerically mixed oil (3.97 g, 100%) that crystallized slowly over several weeks: ¹H NMR (C₆D₆) δ 2.12, 6.97 (m), 7.6 (m); ¹³C NMR (CDCl₃) δ 158.2, 157.9, 132.3, 130.6, 128.6, 127.6, 17.5; MS *m/e* (rel intensity) 358 (M - S₂Me₂⁺, 8), 226 (67), 103 (100). Anal. Calcd for C₁₈H₁₆N₂S₆: C, 47.76; H, 3.56; N, 6.19. Found: C, 47.95; H, 3.72; N, 6.21. Recrystallization of the oil product from hot ethanol yielded a white solid which was enriched in the *trans* isomer. Subsequent crystallization from CH₂Cl₂/hexane at -30 °C gave colorless crystals (mp 134–136 °C) of *trans*-4.Ph, pure by TLC [*R_f* 0.35, silica, 50% CH₂Cl₂/hexane (cf. *cis*-4.Ph, *R_f* 0.32)].

Tetrathiadiazafulvalenes 2. A solution of the diazhexathioorthoxalate 4 (R = H, 602 mg, 2 mmol; R = Me, 810 mg, 2.47 mmol; R = Ph, 230 mg, 0.51 mmol) in CH₂Cl₂ (100 mL) with 5–10 mg of iodine was heated to 100 °C in a sealed vessel equipped with a Rotaflo tap. The reaction was followed by TLC (CH₂Cl₂/hexane, 1:1; silica) and found to be complete in 30–120 min. The rate of the reaction is proportional to the amount of iodine added. The solvent was removed *in vacuo*, and the red solid residue was chromatographed on a short silica column (2.5 × 10 cm; CH₂Cl₂/hexane) to remove iodides. The final red solid was washed with a little cold hexane to remove Me₂S₂. Details on individual products follow:

R = H: yield 328 mg, 80%; visible, λ_{max} = 390 nm, ε = 1300 L⁻¹ mol⁻¹ cm⁻¹; ¹H NMR (C₆D₆) δ 6.89 (s), 6.86 (s); ¹³C NMR (C₆D₆) δ 150.7, 150.4; MS *m/e* (rel intensity) 206 (M⁺, 87), 179 (M - HCN⁺, 78), 103 (73), 76 (100). Anal. Calcd for C₄H₂N₂S₄: C, 23.29; H, 0.98; N, 13.58. Found: C, 23.46; H, 0.88; N, 13.66. Cyclic voltammetry showed two reversible one-electron waves at 0.63 and 1.00 V.

R = Me: yield 289 mg, 67%; ¹H NMR (C₆D₆) δ 1.58 (s), 1.6 (s); MS *m/e* (rel intensity) 234 (M⁺, 20), 193 (M - MeCN⁺, 23), 152 (7), 117 (14), 88 (33), 76 (100). Anal. Calcd for C₆H₆N₂S₄: C, 30.77; H, 2.56; N, 11.97. Found: C, 30.91; H, 2.61; N, 11.88.

R = Ph: yield 160 mg, 88%; ¹H NMR (C₆D₆) δ 7.6 (m), 6.95 (m); MS *m/e* (rel intensity) 358 (M⁺, 10), 255 (M - PhCN⁺, 7), 152 (8), 103 (96), 76 (100). Anal. Calcd for C₁₆H₁₀N₂S₄: C, 53.63; H, 2.79; N, 7.82. Found: C, 53.85; H, 2.81; N, 7.59.

Tetrathiadiazafulvalene Isomer Separation. *trans*-2.Me. This isomer preferentially crystallizes from warm toluene on cooling and slow solvent evaporation. Two recrystallizations gave isomerically pure orange (λ_{max} = 372 nm, ε = 1800 L mol⁻¹ cm⁻¹) crystalline flakes. Isomeric purity was determined by ¹H NMR (δ 1.58): mp 146–148 °C; *R_f* 0.29 (silica, 50% CH₂Cl₂-hexane); IR 1598, 1429, 1141, 778, 738, 618, 545, 450 cm⁻¹. Cyclic voltammetry showed two reversible one-electron waves at 0.59 and 0.95 V.

***cis*-2.Me.** After maximum removal of *trans*-2.Me by the above procedure, the *cis*-enriched material was chromatographed on a silica column (40 × 4.5 cm; CH₂Cl₂/hexane 1:10). The tailing

band was collected, concentrated, and recrystallized from hexane. The resulting orange (λ_{max} = 365 nm, ε = 1600) crystalline blocks were found to be >99% isomerically pure by ¹H NMR (δ 1.6): mp 114 °C; *R_f* 0.26 (silica, 50% CH₂Cl₂-hexane); IR 1578, 1430, 1419, 1140, 783, 727, 605, 543, 494, 429 cm⁻¹.

***trans*-2.Ph.** This isomer preferentially crystallized as long, deep red (λ_{max} = 440 nm, ε = 4200), transparent needles when hot (100 °C) CH₂Cl₂ solutions of isomeric mixtures were allowed to cool. A second recrystallization was sometimes required. The isomeric purity was determined by TLC and IR: mp 212–214 °C; *R_f* 0.58 (silica, 50% CH₂Cl₂-hexane); IR 1523, 1489, 1447, 1246, 932, 791, 761, 680, 657, 584 cm⁻¹. Cyclic voltammetry showed two reversible one electron waves at 0.65 and 1.01 V.

***cis*-2.Ph.** The ready precipitation of the *trans* isomer allowed its complete removal through repeated crystallizations from CH₂Cl₂, CH₂Cl₂/hexane, and CH₃CN. *trans*-2.Ph has extremely low solubility in CH₃CN while *cis*-2.Ph has moderate solubility. The product, obtained by concentration of the final mother liquor, crystallized from hexane, by slow evaporation, as long, thin, orange-red (λ_{max} = 410 nm, ε = 3100 L mol⁻¹ cm⁻¹) needles: mp 152–55 °C; *R_f* 0.53 (silica, 50% CH₂Cl₂-hexane); IR 1522, 1488, 1445, 1249, 938, 932, 914, 799, 790, 754, 683, 657, 585.

Spin Density Calculations. MNDO spin distributions were obtained from MOPAC5 calculations (ROHF) performed on a 486/50 computer. The code was compiled with the NDP Fortran 4.0.2 compiler and run under DOS. The calculations were performed with H-substituents on carbon. Full geometry optimization was invoked within a constraint of ring planarity.

Crystal Structure Determination. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) and the ω-2θ scan technique. Data were corrected for Lp and absorption (ψ scans) and equivalent reflections were averaged. C₄H₂N₂S₄ (2.H), *M_r* = 206.33, *Pnmm* (No. 58), *a* = 3.925(2), *b* = 8.755(6), and *c* = 11.073(7) Å, *V* = 380.4 Å³, *Z* = 2, *d_x* = 1.80 g cm⁻³, *μ* = 11.2 cm⁻¹. A total of 792 reflections were scanned and reduced to a unique set of 418 reflections of which 305 were considered observed (*I* > 3σ(*I*)). The structure converged with 29 variables to *R* = 0.038 and *R_w* = 0.046. C₁₈H₁₆N₂S₆ (*trans*-4.Ph), *M_r* = 452.73, *P2₁/c* (No. 14), *a* = 10.914(8), *b* = 16.852(10), and *c* = 11.373(6) Å, β = 99.34(5)°, *V* = 2064.0 Å³, *Z* = 4, *d_x* = 1.46 g cm⁻³, *μ* = 6.43 cm⁻¹. A total of 3764 unique reflections were scanned with 2505 considered observed (*I* > 3σ(*I*)). The structure converged with 29 variables to *R* = 0.038 and *R_w* = 0.036. Both structures were solved using direct methods (MULTAN) and refined using the MolEn package (Enraf-Nonius).²⁹ H-atom positional parameters were refined but isotropic thermal parameters were set to 1.3 × *B_{eq}* of the bonded atom. The 2/*m* symmetry imposed on 2.H requires that the N and C-H units occupy two sites with 50% occupancy of each. This was accomplished by using a hybrid scattering factor (50% N, 50% CH) for the non-H position and an occupancy factor of 0.5 for the disordered H atom.³⁰

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (R.T.O.) and the Kentucky/NSF EPSCOR program (J.F.R.) for financial support. The help of Dr. Chandana Senaratne with the electrochemical experiments is gratefully acknowledged.

(29) MolEn, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.

(30) The authors have deposited atomic coordinates for structure 2.H and *trans*-4.Ph with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.