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Preparation and Solid-State Characterization of the Novel Mixed Biradical $^{\bullet}$NSNSC–CNSSN$^{\bullet}$

T. Stanley Cameron,[†] Martin T. Lemaire,[‡] Jack Passmore,*[,§] Jeremy M. Rawson,[||] Konstantin V. Shuvaev,[§] and Laurence K. Thompson[‡]

Department of Chemistry, Dalhousie University, Halifax, B4H 4J3 Canada,
Memorial University of Newfoundland, St. John's, A1B 3X7 Canada, Department of Chemistry,
University of New Brunswick, Fredericton, E3B 6E2 Canada, and Department of Chemistry,
The University of Cambridge, Lensfield Road, Cambridge, CB2 1EW U.K.

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Reduction of the radical-cation [$^{\bullet}$NSSNC–CNSNS][AsF$_6$] with ferrocene affords the novel biradical $^{\bullet}$NSNSC–CNSSN$^{\bullet}$ containing both 1,2,3,5- and 1,3,2,4-isomeric dithiadiazolyl rings. Biradicals form centrosymmetric dimers with π^*–π^* interactions between different isomeric rings. Biradical $^{\bullet}$NSNSC–CNSSN$^{\bullet}$ is diamagnetic in the solid state ($C = 0.00035$, TIP $= 6.5 \times 10^{-5}$ emu/Oe·mol); however, an increase in paramagnetism was observed upon grinding ($C = 0.003$, TIP $= 4.2 \times 10^{-4}$ emu/Oe·mol).

There has been considerable interest in the synthesis, geometrical and electronic structures, and wide range of novel physical properties of heterocyclic thiazyl 7π radicals.[1–6] For instance, **1a** is diamagnetic in the solid, but melts at 11 °C to a green paramagnetic liquid under a blue gas, with a dramatic increase in volume (ca. 22%). Melting and freezing is accompanied by thermal hysteresis in magnetic properties.[1] **1b** exhibits optical[2b] and magnetic[2c,d] bistability around room temperature with a large hysteresis loop. The radical-cation **2** orders below 7.0 K ($A^- = GaCl_4^-$)[3a] and 44 K ($A^- = FeCl_4^-$)[3b] as a ferromagnet and ferrimagnet, respectively. A number of derivatives of the most synthetically available and investigated 1,2,3,5-dithiadiazolyl radicals **3** show metallic conductivities upon doping, despite the fact that undoped radicals have a relatively large Hubbard energy (U) for electron transfer (U = IE − EA).[4] The β-phase of **4** (X = CN) is a weak ferromagnet at 36 K,[5a] whereas **4** (X = NO$_2$) is a ferromagnet below 1.3 K.[5b]

In contrast, few derivatives of the isomeric 1,3,2,4-dithiadiazolyl, **5**, have been reported,[6,7] with only one single-crystal X-ray-structure determination,[7b] and information on their magnetic and conducting properties is scant. This heterocycle can be prepared from the very general cycloaddition of SNS$^+$ (SNSAsF$_6$) to a nitrile giving **5**$^+$ quantitatively, which upon reduction leads to **5**.[6a] However, there is a tendency for **5** to rearrange to the more thermodynamically stable isomer **3** in solution,[6b,d] which in part accounts for the paucity of examples of **5**. Once isolated in the solid state, **5** is more stable, but upon heating, rearrangement has been observed.[6c,7b]

Cyanogen (CN)$_2$ and SNS$^+$ give **6**$^{2+}$ quantitatively.[8] Biradical **8** represents one of the eight possible compounds formally obtainable from **6**$^{2+}$ by reduction, isomerization, and reoxidation (see Scheme 1 in ref 8b). Of these, the three

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* To whom correspondence should be addressed. E-mail: passmore@unb.ca. Tel.: 1-506-453-4821. Fax: 1-506-453-4981.

[†] Dalhousie University.

[‡] Memorial University of Newfoundland.

[§] University of New Brunswick.

[||] The University of Cambridge.

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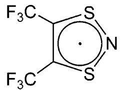
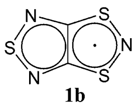


1a



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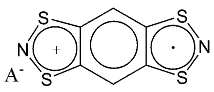

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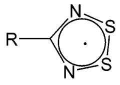

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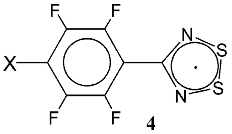

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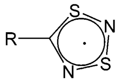
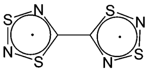


5

neutral biradicals **6**−**8** are possible. Oakley et al. reported the synthesis of the isomeric symmetric biradical **7**,[9] which gives a conducting material upon reaction with iodine. Recently, we reported the preparation and isolation of the symmetric biradical **6**,[6c] which undergoes a dramatic increase in paramagnetism upon mechanical grinding. Biradicals **6**−**8** and the isolobal $^{\bullet+}$SSSNC−CNSSS$^{\bullet+}$ [10] do not adopt classical Lewis structures in which the Lewis octet rule is obeyed, e.g., **9**, but like O_2, they have a thermodynamic preference for structures containing two unpaired electrons.



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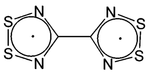

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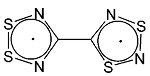

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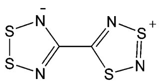


9

We report the synthesis and characterization of the previously unknown mixed biradical **8**, prepared according to Scheme 1.[11] It was necessary to undertake the final reduction step to generate biradical **8** in the dark to minimize rearrangement of **8** to the thermodynamically preferred **7** in solution.

The kinetic product **8** can be isolated because of its low solubility in SO_2, with an IR spectrum containing no bands due to **7**. The EPR spectra of **8** generated in situ or via dissolution of **8** in SO_2, in which it is slightly soluble, yielded

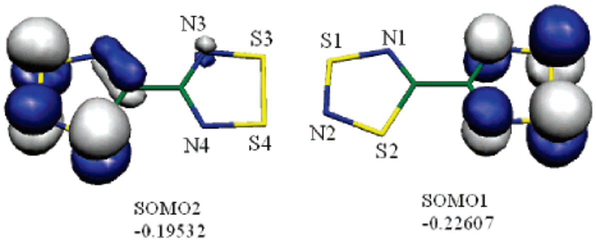
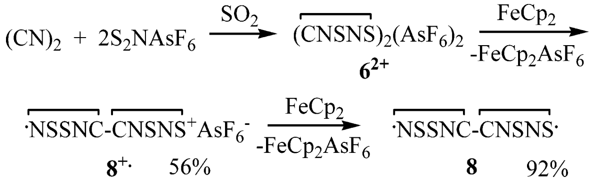


Figure 1. Calculated SOMOs[16] of **8** visualized using MOLEKEL 4.3.[17] ΔE = E (SOMO2) − E(SOMO1) = 81 kJ/mol.

Scheme 1



$$(CN)_2 + 2S_2NAsF_6 \xrightarrow{SO_2} (\overline{CNSNS})_2(AsF_6)_2 \xrightarrow[-FeCp_2AsF_6]{FeCp_2}$$

6^{2+}

$$\cdot\overline{NSSNC}\text{-}\overline{CNSNS}^{+}AsF_6^{-} \xrightarrow[-FeCp_2AsF_6]{FeCp_2} \cdot\overline{NSSNC}\text{-}\overline{CNSNS}\cdot$$

8$^{+\cdot}$ 56% **8** 92%

the anticipated mixture of triplet (g = 2.00413, a_N = 10.26 G) and quintet (g = 2.00884, a_N = 4.71 G) signals; the intensity ratio of 1:4 increased with time, indicating that rearrangement occurred in solution.

The unpaired electrons reside in two SOMOs almost completely localized in each of the rings. As seen in Figure 1, **8** should be considered as a pseudo-disjoint biradical, as there is no nodal plane along the long axis of the molecule (cf. rigorously disjoint SOMOs of **7** shown in the caption on p 333 in ref 9b; they are localized exclusively on NSSN subunits).

Vacuum-gradient sublimation of a gray powder of **8** at 110 °C/10^{-3} Torr afforded[12] **8** as royal-blue needlelike crystals.[13] The bond distances in the −CNSSN and −CNSNS rings in **8** are similar to those in **7**[9] and $C_6H_4(CNSNS)_2$.[7b] To our knowledge, **8** is only the second example of a structurally characterized 1,3,2,4-dithidiazolyl radical in the solid state. The X-ray crystal structure reveals that molecules of **8** form $\pi^*-\pi^*$ dimers of an almost unprecedented mode, with two molecules displaced about an inversion center such that there are $\pi^*-\pi^*$ interactions between different isomeric rings (Figure 2). Similar behavior is reflected in [PhCNSSN]-[S_3N_2]Cl, which comprises a $\pi^*-\pi^*$ dimer between PhCNSSN and $S_3N_2^{+\bullet}$ radicals.[14]

The two ring planes within the dimer are linked by one S···S and two $S^{\sigma+}\cdots N^{\sigma-}$ contacts [NBO charges: S(3), 0.46; N(2), −0.87; S(4), 0.46; S(1), 0.84; N(3), −0.61; S(2), 0.63; N(4), −0.65; N(1), −0.58; C(2), 0.33; C(1), 0.00] in the

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(11) In a typical experiment, $[(CNSNS)_2][AsF_6]_2$ (2.33 g, 0.00398 mol) and Cp_2Fe (0.74 g, 0.00398 mol) were placed in separate bulbs of a two-bulb vessel, and SO_2 (ca. 15 mL) was condensed into each bulb. The Cp_2Fe solution was added in five aliquots over 3 days while exposed to light to afford a gray-black precipitate of crude [NSSNC−CNSNS][AsF_6], [**8**$^+$][AsF_6^-], which was washed with SO_2 (3 × 10 mL) and collected in a drybox. This intermediate was further extracted with degassed MeCN (10 mL) to separate it from impurities of **6**, which is insoluble in acetonitrile. Finally, the black solid was washed with a small quantity of SO_2 to yield pure [**8**$^+$][AsF_6^-] (0.910 g, 56%) as a black-violet powder (full characterization will be published elsewhere). Pure [**8**$^+$][AsF_6^-] (0.72 g, 0.0018 mol) was stirred with an additional mole equivalent of Cp_2Fe (0.37 g, 0.0020 mol) in SO_2 in the dark for 2 days. The resultant insoluble gray precipitate of **8** was washed with SO_2 until the washings turned almost colorless. Yield 0.350 g (92%). Elemental analysis, found/calculated (%): C, 11.52/11.53; N, 25.81/26.90; S, 58.52/61.57. IR (cm^{-1}): 1500 w, 1343 vw, 1318 w, 1296 sh, 1076 s, 1047 w, 875 mw, 838 vw, 808 s, 769 s, 738 s, 696 vs, 675 vw, 665 vw, 648 vw, 544 w, 520 mw, 501 mw, 420 sh. Mass spectrum (20 eV, EI): 208 (100%, M^+), 162 (19%, $[M - NS]^+$), 144 (18%, $[M - S_2]^+$), 130 (80%, $[M - NS_2]^+$), 116 (3%, $[M - N_2S_2]^+$), 104 (1%, M_2^+), 78 (52%, S_2N^+), 64 (4%, S_2^+), 46 (7%, NS^+).

(12) An oven of length 76 cm, temperature gradient 110, 80, 50 °C, was used. **8** sublimed into the 80 °C zone, and a small amount of **7** (X-ray and IR spectroscopy) sublimed into the 50 °C zone.

(13) Crystal data for **8**: $C_2N_4S_4$, M = 208.29, crystal dimensions 0.06 × 0.17 × 0.37 mm, royal-blue needle, monoclinic, space group $P2_1/n$ (No. 14), a = 6.717(4) Å, b = 11.701(2) Å, c = 8.269(3) Å, β = 106.69(3)°, V = 622.6(4) Å^3, T = 203 K, Z = 4, 2052 reflections collected, 1822 unique [R_{int} = 0.059 (1σ)]. R1 = 0.053, wR2 = 0.183 refined on F^2. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation [μ(Mo Kα) = 14.32 cm^{-1}]. The structure was solved by direct methods (SHELX97: Sheldrick, G. M., University of Göttingen, Göttingen, Germany, 1997), and all atoms were refined anisotropically.

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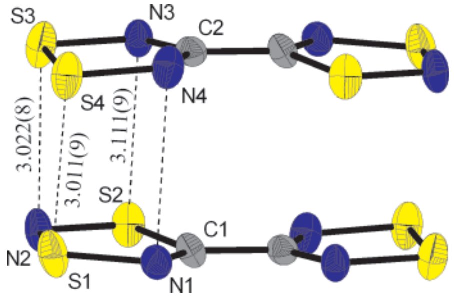

Figure 2. X-ray structure of $\mathbf{8}_2$. Selected bond distances (Å): S(1)−N(2), 1.649(6); S(2)−N(2), 1.648(6); S(1)−N(1), 1.668(5); N(1)−C(1), 1.286(9); S(2)−C(1), 1.718(7); S(3)−N(3), 1.634(5); S(4)−N(4), 1.638(6); N(3)−C(2), 1.341(8); S(3)−S(4), 2.098(3); N(4)−C(2), 1.338(8); C(1)−C(2), 1.491(9). Dihedral angle between least-squares planes, 5.42°.

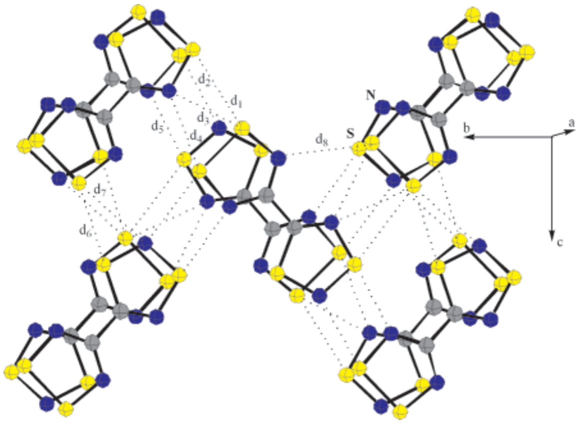

Figure 3. Unit cell of **8** with lateral S$\cdots$S and S$\cdots$N contacts illustrated as follows (Å): d1, 3.447(3); d2, 3.406(18); d3, 3.157(9); d4, 3.208(7); d5, 3.218(18); d6, 4.014(35); d7, 4.332(30); d8, 3.331(8).

range 3.011(9)−3.111(9) Å (cf. the sums of the van der Waals radii of 3.60 and 3.26 Å for S$\cdots$S and S$\cdots$N,[15] respectively) that maximize electrostatic attractions between the biradicals.

The crystal packing of **8** comprises a layerlike herringbone motif in the *bc* plane (Figure 3) with numerous lateral S$\cdots$S and $S^{\sigma+}\cdots N^{\sigma-}$ contacts, close to the sum of van der Waals radii.[15] The molecules form a slipped π-stacked structure along the crystallographic *a* axis, with an interdimer S$\cdots$S distance of 3.732 Å (cf 3.761 Å in **7**[8a]). The slippage of dimers in **8** along the central C−C bond is ~3° (cf 18° in **7**[8a]).

Magnetic measurements on a powder bulk sample of **8**[18] indicated that it is essentially diamagnetic in the solid state; the room-temperature susceptibility corresponds to just 5% of unpaired spins. The magnetic behavior in the range 2−300 K can be adequately described with a small number of Curie centers and a temperature-independent paramagnetic term ($C = 0.00035$, TIP $= 6.5 \times 10^{-5}$ emu/Oe·mol). However, as for **6**,[6c] the paramagnetism of **8** increased upon grinding[19] ($C = 0.003$, TIP $= 4.2 \times 10^{-4}$ emu/Oe·mol). The magnetic data for a pristine sample and a representative sample subjected to mechanical grinding are presented in Figure 4.

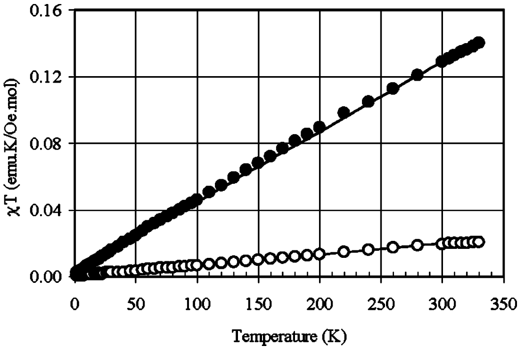

Figure 4. Temperature dependence of χT for a sample of **8** before (○) and after (●) grinding. Values of χT are quoted per radical center (i.e., per half molecule of **8**). The solid lines correspond to fits to a Curie-paramagnet with a temperature-independent paramagnetic (TIP) term ($\chi = C/T +$ TIP). Values are given in the text.

The origin of a relatively high TIP term in the ground sample of **8** is not clear at the present time. It might possibly arise from mixing of nonthermally populated excited paramagnetic states of the dimer $\mathbf{8}_2$ into the singlet ground state.[20] Further studies on the electronic and physical properties of **8** and related systems are in progress.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048306K

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(16) Hybrid functional method MPW1PW91 (Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664) with the 6-31G* basis set as implemented in the Gaussian 98W suite of programs (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.) was employed. SOMOs were those obtained from the calculation of an open-shell triplet.

(17) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3*; Swiss Center for Scientic Computing: Manno, Switzerland, 2000−2002.

(18) The presence of an impurity of rearranged **7** was ruled out on the basis of "clean" IR spectra in the ranges where the strongest peaks of **7** occur (ref 8). The X-ray powder diffraction pattern of the unground bulk **8** was consistent with the single-crystal data with small additional features that could be attributed to Pyrex glass.

(19) The X-ray powder diffraction of the ground sample showed that it was the same as the unground sample, but there was a decrease in particle size indicated by a broadening of the peaks and a decrease of the diffraction intensities at high angle.

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