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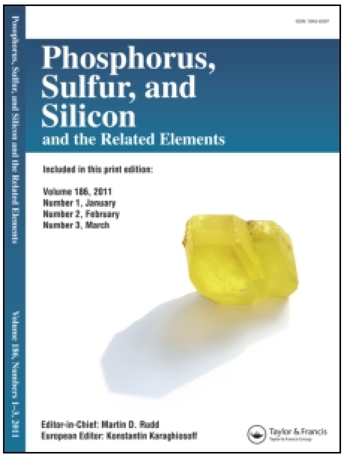

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# EPR STUDIES OF THE BISTABILITY IN $CF_3CNSSN$

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# EPR STUDIES OF THE BISTABILITY IN $CF_3CNSSN$

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*Condensation of $CF_3C(=NH)NH_2$ with $SCl_2$ yielded the dithiadiazolylium salt, $[CF_3CNSSN]Cl$ which could be reduced to $[CF_3CNSSN]_2$ with Zn/Cu couple in $SO_2$. $[CF_3CNSSN]_2$ is a diamagnetic dimer in the solid state but melts at 308 K to give a paramagnetic liquid. On cooling the radical enters a metastable state before immediately resolidifying below 295 K. The thermal hysteresis was probed by EPR spectroscopy. Metastable samples spontaneously solidified after an induction period, typically between ca. 5 and 30 min, consistent with the variable time necessary to form a seed crystal from which crystallization can occur.*

*Keywords:* Bistability; dithiadiazolyl; metastable

For some time we have been interested in the use of thiazyl radicals as novel magnetic materials, e.g., the dithiadiazolyl radical $p$-$O_2NC_6F_4CNSSN$ orders as a ferromagnet at 1.3 K[1] and $p$-$NCC_6F_4CNSSN$ orders as a canted antiferromagnet below 36 K.[2] More recently we and others have observed bistability in a number of dithiazolyl radicals; the benzo-derivative BDTA was found[3] to form a spin-paired diamagnetic structure on sublimation. More recent studies have shown that BDTA solidifies to form a metastable paramagnetic phase on cooling from the liquid state.[4] This phase orders as an antiferromagnet at 11 K. Other dithiazolyl radicals have been shown by Oakley to undergo solid-state transitions between diamagnetic (or antiferromagnetic) and paramagnetic phases.[5] Perhaps the most striking behavior

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is that of trithiatriazapentalenyl, $C_2S_3N_3$, which exhibits bistability between 230 K and 320 K.[6] This type of behavior provides the opportunity to use these derivatives in room temperature data storage devices. Phase switching of this type requires the crossing of two free energy surfaces with a small activation energy barrier to interconversion, e.g., minor perturbation of molecular coordinates in order to transform between solid state structures.[5,6]

We were interested in preparing new materials which exhibit narrower regions of bistability around room temperature and recently reported the magnetic behavior of $CF_3CNSSN$ (**1**).[7] The structure of **1** in the solid state is a spin-paired dimer[8] but converts to a paramagnetic liquid on melting. The detailed structure of **1** in the liquid phase is hard to probe but the large increase in volume coupled with its paramagnetism indicate uncoupling of the spin-paired dimers. We speculated that electrostatic association of radicals may be favored with the energy barrier to breaking down the $\pi^*$-$\pi^*$ dimerization and electrostatic interactions providing an activation barrier to interconversion. Here we report a novel synthesis of **1** and probe its stability in the metastable state.

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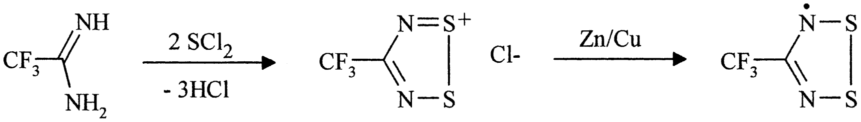
## RESULTS AND DISCUSSION

The synthesis of $CF_3CNSSN$ was first reported by Mews and coworkers in 1985 from the reaction of $CF_3CN$ with $(NSCl)_3$, followed by reduction of the resultant salt, $[CF_3CNSSN]Cl$ with Zn.[8] It also has been prepared by the rearrangement of the isomeric radical $CF_3CNSNS$.[9] We sought a more direct route to this material (Scheme 1) and found that condensation of trifluoroacetamide, $CF_3C(=NH)\cdot NH_2$, with $SCl_2$ yielded the salt $[CF_3CNSSN]Cl$ in good yield (45%). Subsequent reduction with Zn/Cu couple in $SO_2$ yielded the desired radical which was readily purified by vacuum sublimation ($10^{-2}$ Torr, 35–20°C).



**SCHEME 1** Synthesis of **1**.

X-band EPR studies on pure **1** clearly revealed the bistability between 295 and 308 K evident in the magnetic measurements[7] and showed that there were no marked differences in the width of the hysteresis loop as a function of heating/cooling rate (Figure 1a). In order

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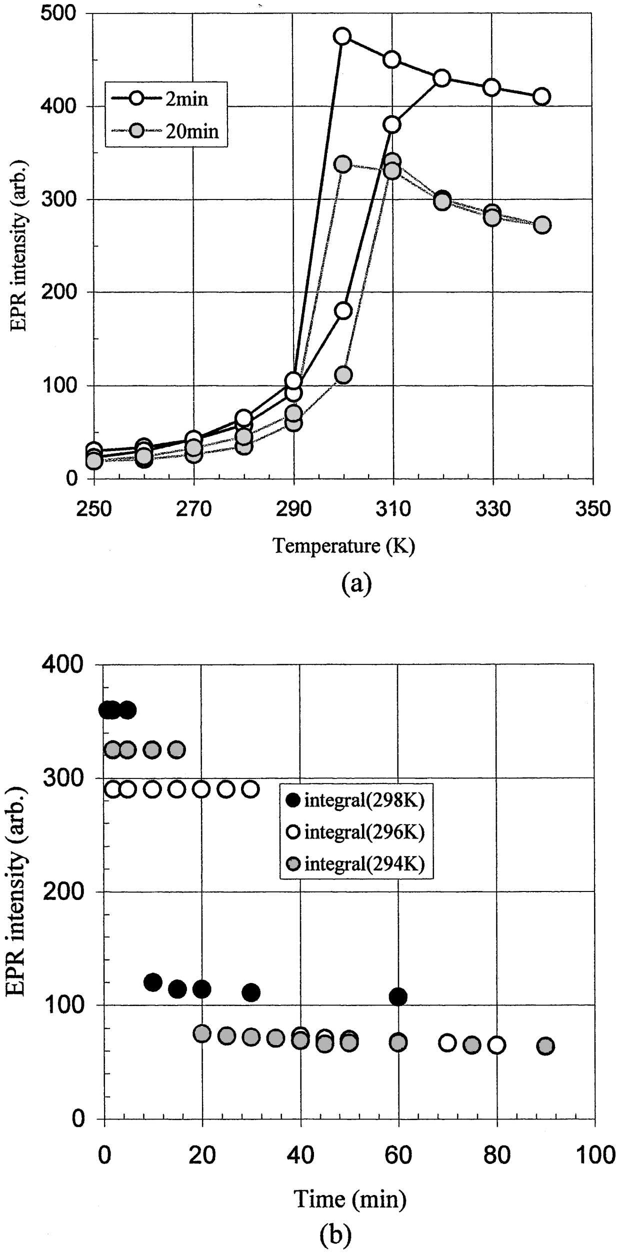

**FIGURE 1** (a) Intensity of the EPR spectrum of **1** with dwell times of 2 min and 20 min between measurements. (b) Intensity of the EPR spectrum of **1** as a function of time at fixed temperatures in the metastable region.

to probe the stability of the metastable state the sample was heated into the liquid phase, cooled into the metastable region and the EPR signal measured as a function of time at fixed temperatures [294(2), 296(2), and 298(2) K]. In all cases an abrupt decrease in EPR intensity was observed [5 min at 298 K, 30 min at 296 K, and 15 min at 294 K] (Figure 1b). The abrupt decrease in EPR signal is indicative of a complete and rapid transformation from the metastable liquid phase to the solid state. No clear time/temperature correlation appeared evident, consistent with the variable time to form a nucleation site for the crystallization process.

## CONCLUSION

The current studies show that the super-cooled liquid state of $CF_3CNSSN$ is not indefinitely stable. Stabilization of this state might be achieved through the generation of a liquid crystal phase between the solid and liquid phases. Approaches to this end are underway.

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## EXPERIMENTAL

Radical **1** is extremely air-sensitive and its low melting point made handling difficult. For EPR studies we found that sublimation directly into a quartz EPR tube joined with a quartz-glass graded seal minimized sample degradation.

### Preparation of [$CF_3$CNSSN]Cl

Trifluoroacetamide (2.0 g, 17.85 mmol) was stirred in $CH_2Cl_2$ (50 ml) and $SCl_2$ (2.8 ml, 35.3 mmol) was added slowly. The mixture was refluxed at ca. 43°C for 14 h under $N_2$ until no HCl evolution could be detected. The orange precipitate was filtered, washed (2 × 10 ml of $CH_2Cl_2$), and dried in vacuo. Yield 1.7 g, 45%. +EI-MS 172.9 ($M^+$).

### Preparation of [$CF_3$CNSSN]

[$CF_3$CNSSN]Cl (1.00 g, 4.8 mmol) and Zn/Cu couple (0.16 g, 2.45 mmol) were stirred in $SO_2$ in one limb of a three-limbed reaction vessel for 18 h. The resultant deep red solution was filtered into the middle-limb and the $SO_2$ removed to yield a dark solid which was then vacuum transferred into the third limb ($10^{-2}$ Torr, −196°C). It was then sublimed to yield **1** as a metallic green-black crystalline product. Recovered yield

0.32 g, 39%. +EI-MS 172.9 ($M^+$); Found C: 13.5%, H: 0.0%, N: 15.3%; Calc. for **1**. C: 13.9%, H: 0.0%, N: 16.2%.

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