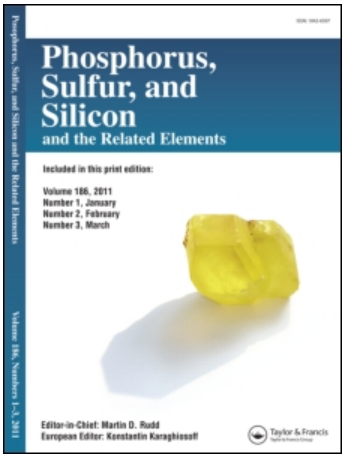

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Recent Developments in the Synthesis and Characterization of the Neutral Diradical Bis(1,3,2,4-dithiadiazolyl)

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RECENT DEVELOPMENTS IN THE SYNTHESIS AND CHARACTERIZATION OF THE NEUTRAL DIRADICAL BIS(1,3,2,4-DITHIADIAZOLYL) ($\overline{\text{SNSNC}}$-$\overline{\text{CNSNS}}$)$^{\bullet\bullet}$

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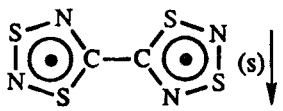
Abstract It has been shown[1] that SNS^+ undergoes cycloaddition with various nitriles to give 6π 1,3,2,4-dithiadiazolium salts that give 7π 1,3,2,4- dithiadiazolyl radicals on reduction. $SNSAsF_6$ reacts with cyanogen (NC-CN) to produce ($\overline{\text{SNSNC}}$-$\overline{\text{CNSNS}}$)$(AsF_6)_2$,[2] which on reduction forms the neutral species ($\overline{\text{SNSNC}}$-$\overline{\text{CNSNS}}$)$^{\bullet\bullet}$ (1). The X-ray single crystal structures of the related $^{\bullet+}\overline{\text{SSSNC}}$-$\overline{\text{CNSSS}}^{+\bullet}$,[3] and ($\overline{\text{SNSNC}}$-$\overline{\text{CNSNS}}$)$^{2+}$,[2] show the two rings of each dication to be coplanar. To date, we do not have a crystal structure of the title compound, but spectroscopic and computational evidence indicates that the two rings of the neutral ($\overline{\text{SNSNC}}$-$\overline{\text{CNSNS}}$)$^{\bullet\bullet}$ are also coplanar.

PREPARATION

$(\overline{\text{CNSNS}})_2(AsF_6)_2$ is prepared from $SNSAsF_6$ and cyanogen, according to Equation (1).[2] On reduction with a mixture of $SbPh_3$ and NBu_4Cl in SO_2, the neutral species (1) (black powder) is formed according to Equation (2). The soluble byproducts are washed from the insoluble product by filtration through a sintered glass frit in the reaction vessel.

$$2\ S_2NAsF_6\ (s) + NC\text{-}CN\ (g) \xrightarrow[50\ ^\circ C,\ 5\ days]{SO_2} \overline{(CNSNS)}_2^{2+}(AsF_6^-)_2\ (s) \quad \text{colourless crystals} \qquad (1)$$

$$\overline{(CNSNS)}_2^{2+}(AsF_6^-)_2\ (s) + 2\ NBu_4Cl\ (s) + SbPh_3\ (s) \xrightarrow[RT,\ stir\ 24\ h]{SO_2} \qquad (2)$$



(s)↓ + 2 NBu_4AsF_6 (s) + $SbPh_3Cl_2$ (s)

insoluble black fine powder

CHARACTERIZATION

Elemental analysis (Beller Mikroanalytisches Laboratorium, Göttingen, Germany) is consistent with the proposed formula $C_2N_4S_4$: calc (obs) C 11.53 (11.53); H 0.0 (< 0.1); N 26.90 (26.14); S 61.57 (59.08). The 3.25% 'missing mass' may be attributed to the presence of small amounts of reduction byproducts, which are observed in the vibrational spectra, and would account for the low observed amounts of nitrogen and sulfur. The infrared and FT-Raman spectra of (**1**) compare well with the related $(^{\bullet+}\overline{SSSNC}\text{-}\overline{CNSSS}^{+\bullet})$[3] and $(\overline{SNSNC}\text{-}\overline{CNSNS})^{2+}$,[2] indicating a similar structure in which the two rings of the compound are coplanar in a 'trans' orientation as depicted in Equation (2). Geometry optimization[4] at the UHF/MNDO level resulted in a structure with bond lengths and angles similar to those for $(\overline{SNSNC}\text{-}\overline{CNSNS})^{2+}$. The C-C bond length optimised to 1.46 Å, corresponding to an sp^2-sp^2 hybridized C-C single bond. The molecular ion (208 m.u.) is the most intense peak in the mass spectrum (E.I., 27 eV) of (**1**). A reasonable fragmentation pattern was constructed from the other peaks in the spectrum, which appeared to be free of peaks due to any reduction byproducts. An ESR spectrum of (**1**) in tetrahydrofuran at 20 °C showed a 1:1:1 triplet (g = 2.0043, $a(^{14}N)$ = 11.35 G). Three preparations of (**1**) have resulted in a magnetic moment (Gouy method) of 2.82 μ_B (average) at 20 °C, while many other preparations of (**1**) have given results averaging 1μ_B

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