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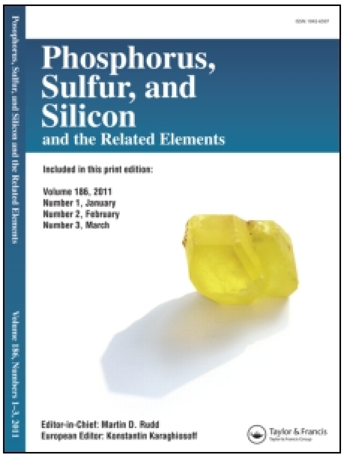

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Preparation, Structure and Chemistry of a Novel, Disjoint Diradical, 4,4'-Bis(1,2,3,5-Dithiadiazolyl)

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PREPARATION, STRUCTURE AND CHEMISTRY OF A NOVEL, DISJOINT DIRADICAL, 4,4′-BIS(1,2,3,5-DITHIADIAZOLYL)

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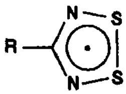
Abstract The reaction of oxamidrazone with SCl_2 affords 4,4′-bis(1,2,3,5-dithiadiazolium) dichloride, which can be reduced to the corresponding bis(1,2,3,5-dithiadiazolyl) diradical; the electronic structure of the diradical is discussed, and the solid state structure, charge transfer chemistry and transport properties of the dimer $[S_2N_2CCN_2S_2]_2$ are described.

INTRODUCTION

Derivatives of the 1,2,3,5-dithiadiazolyl neutral radical **1** have emerged as potential building blocks for molecular-based conductors.[1,2] To this end, several bi- and trifunctional radicals have been investigated. In all cases to date the molecular species consist of two or three heterocyclic rings bridged by an inert spacer, such as in the 1,4-phenylene-bridged diradical **2**. Herein we report on the title compound **3**, in which the spacer component has been removed to afford a directly linked ("back-to-back") diradical.



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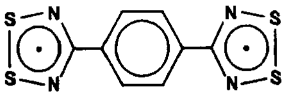

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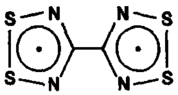

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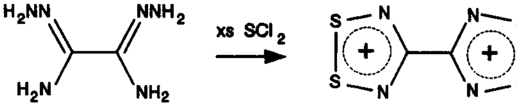
RESULTS

Our initial attempts to use an oxamidine/SCl_2 condensation approach to this diradical were unsuccessful, but we have found that oxamidrazone reacts with excess SCl_2 in acetonitrile to afford the dication **4** (as its dichloride) in 15% yield (equation 1). The dication can be reduced with triphenylantimony to afford the dimer of **3** as a black solid. We have been able to purify **3** (as its dimer) by fractional vacuum sublimation at 140°C/10^{-2} Torr to give lustrous blue-black needles of the dimer, m.pt. 275-80°C (50% yield based on the crude dication **4**).[3]



4

(1)

Compound **3** is a rare example of a disjoint diradical, i.e., the two unpaired electrons are located in non-interacting orbitals. The ESR spectrum, which consists of a simple 5-line pattern with a_N = 5.0 G, and cyclic voltammetric measurements, which show a single reduction wave for the two cationic centres in **4**, confirm that exchange interactions between the two radical centres are minimal.

The crystal structure of the dimer of **3**, space group $P2_1/c$, a = 6.7623(17) , b = 11.5180(8), c = 8.3834(14) Å, β = 110.20(2)°, consists of slipped stacks of centrosymmetric dimers running parallel to x. The dimers are packed in a herring-bone fashion in the yz plane. In the solid state the dimer is diamagnetic, with a residual spin density of 0.01%. The material exhibits a conductivity of 10^{-8} S cm^{-1} along the needle axis. Oxidation of radical with iodine affords a charge transfer salt of composition $[S_2N_2CCN_2S_2][I]$. The room temperature conductivity of this doped material is over 500 S cm^{-1} at room temperature.

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