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Preparation and Solid State Characterization of 4,4'-Bis(1,2,3,5-dithiadiazolyl)

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The reaction of oxamidrazone with sulfur dichloride affords 4,4'-bis(1,2,3,5-dithiadiazolium) dichloride, which can be reduced with triphenylantimony to the corresponding bis(1,2,3,5-dithiadiazolyl) diradical; the solid state structure and transport properties of the dimer $[S_2N_2CCN_2S_2]_2$ are reported.

The concept of using neutral π -radicals as building blocks in the design of molecular conductors¹ has catalysed the study of heterocyclic thiazyl radicals, in particular derivatives of the two isomeric dithiadiazolyls **1** and **2**.^{2,3} Recently we have shown that both monofunctional^{4,5} and bifunctional⁶ 1,2,3,5-radicals can be doped with iodine to form conductive charge transfer salts. As part of the development of these new materials a wide variety of monofunctional derivatives of both isomers have been prepared, as well as several polyfunctional derivatives in which two or more heterocyclic rings are linked by a bridging benzene ring.⁷ Bifunctional materials with rings linked through carbon⁸ and mercury⁹ bridges have also been characterized.

As key structural units the back-to-back radicals **3** and **4** have been synthetic targets for some time. The 1,3,2,4-isomer **3** has been isolated as a black powder,¹⁰ but its structure remains elusive. This may be related to the known tendency of 1,3,2,4-dithiadiazolyls to isomerize to the 1,2,3,5-derivatives both in solution¹¹ and the solid state.¹² Our initial attempts to apply an oxamidrazone/ SCl_2 condensation approach to the 1,2,3,5-isomer **4** were unsuccessful, but we have now discovered that oxamidrazone¹³ reacts with (excess) SCl_2 in acetonitrile to afford the dication **5** (as its hydrochloride) in 15% yield [eqn. (1)]. The crude dication can be reduced with triphenylantimony to afford the dimer of diradical **4** as a black solid. We have been able to purify **4** by fractional vacuum sublimation at 140 °C/10⁻² Torr in a gradient tube furnace to give lustrous blue-black needles of the dimer, mp 275–80 °C (50% yield based on the crude dication **5**).[†] Mass spectrum (70 eV, EI): 208 (84%, M^+), 162 (97%, $[M - NS]^+$), 144 (11%, $[M - S_2]^+$), 130 (31%, $[M - NS_2]^+$), 116 (14%, $[M - N_2S_2]^+$), 104 (5%, M^{2+}), 78 (45%, S_2N^+), 64 (100%, S_2^+), 46 (80%, NS^+). The ESR signal of **4** (in CH_2Cl_2 , 273 K) consists of a quintet, with $g = 2.0110$ and $a_N = 0.50$ mT; there is an indication above 273 K of the onset of exchange coupling between the two rings, but this is less extensive than was observed in the 1,4-phenylene-bridged bis(1,2,3,5-dithiadiazolyl).^{7b}

The crystal structure of **4** has been determined by X-ray diffraction.[‡] It consists of stacks of centrosymmetric dimers packed in a herring-bone fashion. Fig. 1 illustrates the packing in the yz plane, while Fig. 2 shows the stacking of dimers parallel to x . The internal features of the heterocyclic rings are

normal; the S–S, S–N and S–C bonds are all similar to those found in other dithiadiazolyl dimers.¹⁴ The C–C distance suggests little double bond character; at 1.488 Å the separation is only slightly shorter than that expected (1.516 Å)¹⁵ for an sp^2 – sp^2 single bond. The mean intradimer S–S distance (3.078 Å) and interdimer $S \cdots S$ contact along the stack

Fig. 1 Packing of $[S_2N_2CCN_2S_2]_2$ dimers viewed down the x axis. Selected intramolecular distances and angles (mean values) are S–S, 2.088(2); S–N, 1.630(5); N–C, 1.331(7); C–C, 1.488(7) Å; N–S–S, 94.4(2); S–N–C, 114.1(4); N–C–N, 123.1(5)°. Close lateral $S \cdots S$ interactions are indicated with dashed lines.

Fig. 2 Stacked dimers running parallel to x . Intradimer distances are S(1)–S(3), 3.131(2); S(2)–S(4), 3.025(2) Å. Interdimer distances (dashed lines) a long stack are S(1)–S(3), 3.711(2); S(2)–S(4), 3.811(2) Å. Lateral $S \cdots S$ contacts (dashed lines) between stacks are d_1 , 3.336(2); d_2 , 3.965(2); d_3 , 3.368(2); d_4 , 3.669(2); d_5 , 3.821(3); d_6 , 3.662(2); d_7 , 3.570(3) Å.

(3.761 Å) are also similar to those seen in related dimers. In the monoclinic phase of $[\text{HCN}_2\text{S}_2]_2$, for example, these distances (average values) are 3.11 and 3.76 Å.¹⁴

Perhaps the most striking feature of the structure is the number and shortness of the lateral interdimer S...S contacts. Many of these interactions, all of which (d_1 – d_7) are defined in Figs. 1 and 2, are well within the standard van der Waals separation for two sulfurs;¹⁶ collectively they generate a very densely packed structure. Extended Hückel band calculations confirm a high degree of dispersion in both the valence and conduction bands.

In the solid state the dimer is diamagnetic, with a residual spin density at room temperature of 0.01% on a per molecule basis. The measured diamagnetism is -90 ppm emu mol⁻¹ and the θ -value is -0.5 K. The material exhibits a conductivity of 10^{-8} S cm⁻¹ along the needle axis. This value will likely be enhanced by iodine doping, as found for other systems.^{4,5,6}

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Footnotes

† A satisfactory elemental (C,N) analysis has been obtained. IR/cm⁻¹ 1294(m), 1264(m), 1244(s), 1090(br), 1012(m), 820(w), 804(s), 793(s), 784(s), 559(m), 507(m), 495(m), 421(m).

‡ Crystal data for 4: $\text{S}_4\text{N}_4\text{C}_2$, $M = 208.29$, monoclinic, $P2_1/c$, $a = 6.7623(17)$, $b = 11.5180(8)$, $c = 8.3834(14)$ Å, $\beta = 110.20(2)^\circ$, $V = 612.8(2)$ Å³, $Z = 4$, $D_c = 2.26$ g cm⁻³, $\mu = 1.40$ mm⁻¹. Data were collected with an Enraf-Nonius CAD-4 automated diffractometer, with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using θ – 2θ scans to a $2\theta_{\text{max}} = 50^\circ$. The structure was solved by direct methods and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. 91 Parameters were refined using 1071 unique observed reflections [$I > 3\sigma(I)$] to give $R = 0.037$ and $R_w = 0.070$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Information for Authors, Issue No. 1.

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