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

Clinton D. Bryan,[a] A. Wallace Cordes,[a] Robert C. Haddon,[b] Robin G. Hicks,[c] Richard T. Oakley,[c] Thomas T. M. Palstra[b] and Alexander J. Perel[b]

[a] Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA
[b] AT&T Bell Laboratories, 600 Mountain Ave., Murray Hill, New Jersey, 07974, USA
[c] Guelph–Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

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 conductors[1] 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 bifunctional[6] 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 carbon[8] and mercury[9] 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 solution[11] and the solid state.[12] Our initial attempts to apply an oxamidine/SCl$_2$ condensation approach to the 1,2,3,5-isomer **4** were unsuccessful, but we have now discovered that oxamidrazone[13] 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$_2$S$_2$]$^+$), 104 (5%, M^{2+}), 78 (45%, S$_2$N$^+$), 64 (100%, S$_2^+$), 46 (80%, NS$^+$). The ESR signal of **4** (in CH$_2$Cl$_2$, 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
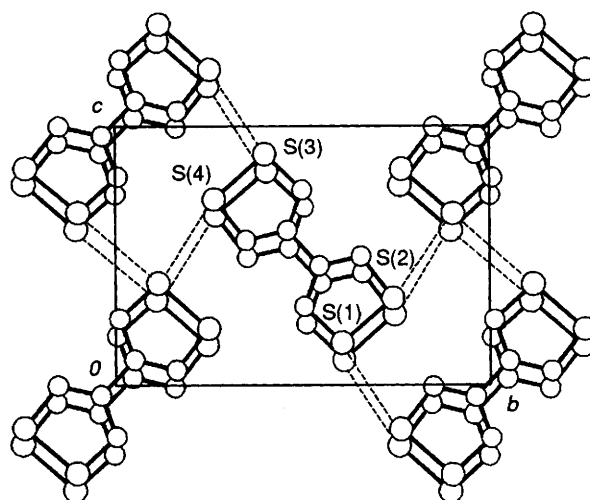

Fig. 1 Packing of $[S_2N_2CCN_2S_2]_2$ dimers viewed down the x axis. Selected intramolecular distances and angles (mean values) are S–S, 2.088(2); S–N, 1.630(5); N–C, 1.331(7); C–C, 1.488(7) Å; N–S–S, 94.4(2); S–N–C, 114.1(4); N–C–N, 123.1(5)°. Close lateral S$\cdots$S interactions are indicated with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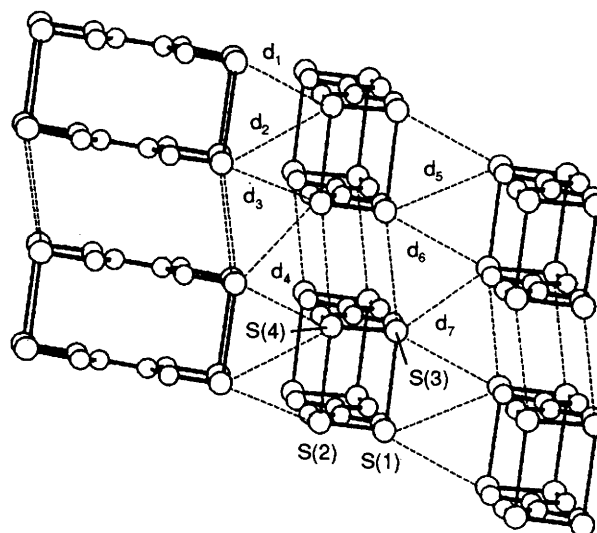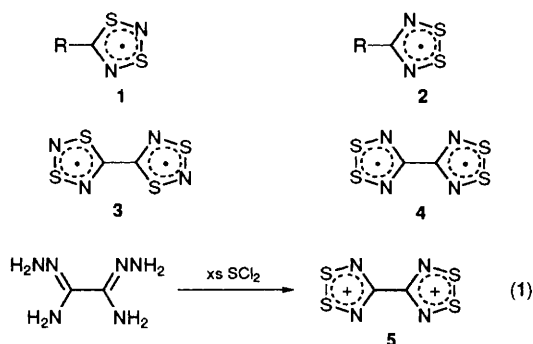

Fig. 2 Stacked dimers running parallel to x. Intradimer distances are S(1)–S(3), 3.131(2); S(2)–S(4), 3.025(2) Å. Interdimer distances (dashed lines) a long stack are S(1)$\cdots$S(3), 3.711(2); S(2)$\cdots$S(4), 3.811(2) Å. Lateral S$\cdots$S contacts (dashed lines) between stacks are d$_1$, 3.336(2); 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 $[HCN_2S_2]_2$, 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]

We thank the Natural Sciences and Engineering Research Council of Canada, the National Science Foundation (EPSCOR program) and the State of Arkansas for financial support. One of us (C. D. B.) acknowledges a DOE/ASTA Traineeship.

Received, 7th March 1994; Com. 4/01346H

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**: $S_4N_4C_2$, $M = 208.29$, monoclinic, $P2_1/c$, $a = 6.7623(17)$, $b = 11.5180(8)$, $c = 8.3834(14)$ Å, $\beta = 110.20(2)°$, $V = 612.8(2)$ Å^3, $Z = 4$, $D_c = 2.26$ g cm^{-3}, $\mu = 1.40$ mm^{-1}. Data were collected with an Enraf–Nonius CAD-4 automated diffractometer, with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using $\theta-2\theta$ scans to a $2\theta_{max} = 50°$. 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.

References

1 R. C. Haddon, *Nature*, 1975, **256**, 394.
2 A. J. Banister and J. M. Rawson, in *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, ed. R. Steudel, 1992, p. 323.
3 A. W. Cordes, R. C. Haddon and R. T. Oakley, in *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, ed. R. Steudel, 1992, p. 295.
4 C. D. Bryan, A. W. Cordes, R. C. Haddon, S. H. Glarum, R. G. Hicks, D. K. Kennepohl, C. D. MacKinnon, R. T. Oakley, T. T. M. Palstra, A. S. Perel, L. F. Schneemeyer, S. R. Scott and J. V. Waszczak, *J. Am. Chem. Soc.*, 1994, **116**, 1205.
5 C. D. Bryan, A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, A. S. Perel and S. R. Scott, *Chem. Mater.*, 1994, **6**, 508.
6 C. D. Bryan, A. W. Cordes, R. M. Fleming, N. A. George, S. H. Glarum, R. C. Haddon, R. T. Oakley, T. T. M. Palstra, A. S. Perel, L. F. Schneemeyer and J. V. Waszczak, *Nature*, 1993, **365**, 821.
7 (*a*) A. J. Banister, I. Lavender, J. M. Rawson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1992, 859; (*b*) A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. A. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582; (*c*) M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, G. W. Trucks, R. R. Tycko, J. V. Waszczak, W. W. Warren, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 3559; (*d*) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc.*, 1992, **114**, 1729; (*e*) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc.*, 1992, **114**, 5000.
8 A. J. Banister, J. M. Rawson, W. Clegg and S. L. Birkby, *J. Chem. Soc., Dalton Trans.*, 1991, 1099.
9 A. J. Banister, I. Lavender, S. E. Lawrence, J. M. Rawson and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1994, 29.
10 S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1991, 369; S. Parsons, J. Passmore and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1499.
11 N. Burford, J. Passmore and M. J. Schriver, *J. Chem. Soc., Chem. Commun.*, 1986, 140.
12 C. Aherne, A. J. Banister, A. W. Luke, J. M. Rawson and R. J. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1992, 1277.
13 P. M. Hergenrother, *J. Macromol. Sci.*, 1973, **A7**, 573.
14 A. W. Cordes, C. D. Bryan, W. M. Davis, R. H. deLaat, S. H. Glarum, J. D. Goddard, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, S. R. Scott and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1993, **115**, 7232.
15 R. McWeeny, *Coulson's Valence*, 3rd edition, 1979.
16 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.