Bimodal association of a *bis*-1,2,3-dithiazolyl radical

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The *N*-ethyl pyrazine-bridged *bis*-1,2,3-dithiazolyl radical 2 (R_1 = Et) associates at room temperature as a C–C bonded σ-dimer which, on heating, converts to a laterally S–S σ-bonded structure.

The potential applications of heterocyclic thiazyl radicals in the design of functional electronic[1] and magnetic materials[2] are driving the exploration for new stable radical systems.[3] In recent years we have characterized a number of *N*-alkylated pyridine-bridged *bis*-1,2,3-dithiazolyls **1**.[4,5] These resonance stabilized radicals enjoy low on-site Coulomb potentials, and as such serve as building blocks for single component molecular conductors. However, while the presence of the beltline substituents R_1 and R_2 helps suppress cofacial dimerization, their buffering action also militates against the close intermolecular interactions necessary for high bandwidth, a critical requirement for good conductivity. In search of higher bandwidth materials we have developed a preparative route to the related *N*-alkylated pyrazine-bridged *bis*-1,2,3-dithiazolyls **2**. The ethyl derivative **2** (R_1 = Et) described herein displays a rare form of polymorphism, crystallizing as two very different dimers, the C–C σ-bonded structure α-[**2**]$_2$ and the laterally S–S σ-bonded variant β-[**2**]$_2$ (Chart 1).

The general synthetic sequence to **2** (Scheme 1) starts from 2,6-diaminopyrazine **3**, which is conveniently prepared by reduction of the corresponding diazide[6] with iron in aqueous acetic acid. Conversion of **3** to the 3,5-*bis*-thiocyanate **4**, and reduction of the latter with tributylphosphine generates the phosphinimine-dithiol **5**, which undergoes double cyclocondensation with thionyl chloride to afford the protonated chloride [**2**][Cl] (R_1 = H). Treatment of this black, insoluble chloride salt with gallium trichloride in MeCN produces a deep blue solution of the corresponding gallate, which can be deprotonated with Proton Sponge to yield the zwitterion **6**. Subsequent alkylation of **6** with triethyloxonium tetrafluoroborate provides the desired *N*-ethylated salt [**2**][BF_4] (R_1 = Et), which crystallizes from acetonitrile as deep red flakes, λ_{max} (MeCN) 623 nm, log ε = 4.5.†

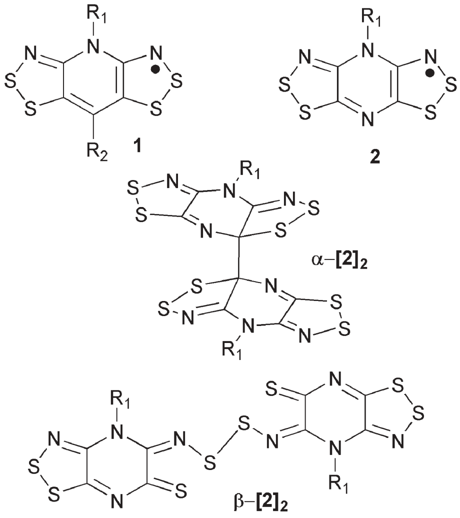
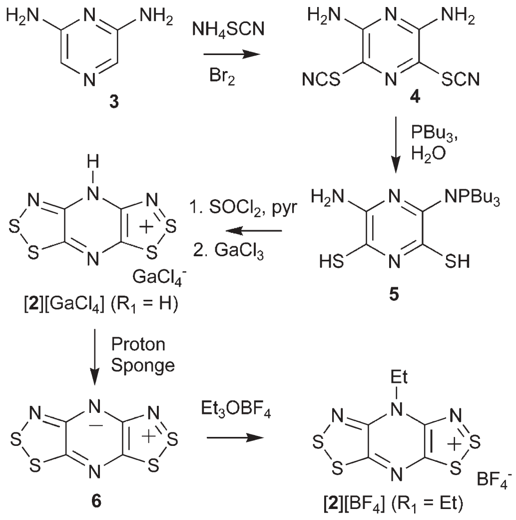


Chart 1



Scheme 1

Cyclic voltammetry on solutions of [**2**][BF_4] (R_1 = Et) in MeCN (Pt electrodes, Bu_4NPF_6 supporting electrolyte) reveals a reversible 0/+1 wave with $E_{½} = -0.029$ V, a value 50–100 mV more cathodic than that found for derivatives of **1**, and well within the reduction range of decamethylferrocene (DMFc).[7] Accordingly chemical reduction of [**2**][BF_4] (R_1 = Et) with DMFc in degassed MeCN leads to precipitation of the radical dimer α-[**2**]$_2$ (R_1 = Et) as a brown crystalline solid. While the dimer is diamagnetic (by EPR) in the solid state, it dissolves in CH_2Cl_2 to afford fuchsia colored solutions that display a strong and persistent EPR signal with g = 2.0087. The spectrum (Fig. 1) has been simulated in terms of the expected radical **2** (R_1 = Et); assignment of the experimental hyperfine splitting (hfs) constants was confirmed by comparison with computed hfs values and spin density data obtained from a B3LYP/6-31G** calculation.

Translucent amber blocks of α-[**2**]$_2$ suitable for X-ray work can be grown by vacuum sublimation at 10^{-4} Torr down a

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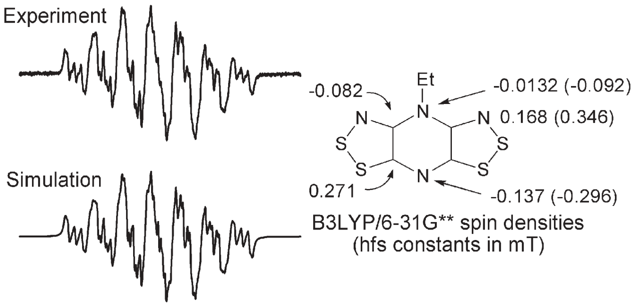

Fig. 1 Observed (CH_2Cl_2) and simulated EPR spectrum (SW = 3 mT) of **2** (R_1 = Et). Experimentally derived hfs constants are a_N = 0.313 (2N), 0.267 (1N), 0.073 mT, a_H = 0.025 (2H) mT. Computed (B3LYP/6-31G**) spin densities and hfs constants (in parentheses) are also shown.

temperature gradient from 100 °C to 50 °C. At the same time, however, thin, jet black blades of β-[**2**]$_2$ are also produced. The relative proportions of the two phases are sensitive to temperature. Thus, at more elevated temperatures, *i.e.*, a gradient from 110 °C to 60 °C, the β-phase is favored. Crystals of the two phases can be separated manually, and the β-phase can be generated almost exclusively by resublimation of a mixture of the two. Like the α-phase, crystals of β-[**2**]$_2$ dissolve in CH_2Cl_2 to afford fuchsia colored solutions which exhibit the characteristic EPR spectrum of **2**.

Crystals of α-[**2**]$_2$ (R_1 = Et) belong to the monoclinic space group $P2_1/n$, and consist of centrosymmetric pairs of radicals linked by a C3–C3′ σ-bond (Fig. 2).‡ At 1.607(4) Å, this bond is significantly longer than a standard sp^3–sp^3 C–C linkage (1.54 Å),[8] and comparable to those found in other strained systems in which a σ-bond forms at the expense of a π-system.[9] The concomitant rehybridization at C3 causes a severe distortion of the otherwise planar heterocycle into a butterfly-like conformation, and the internal bond lengths become localized into a pattern consistent with the valence bond formulation shown in Chart 1.

Inspection of the packing of the dimers in the unit cell (Fig. 3) indicates that the molecules are laced together by a web of intermolecular S···S′ (d1–d3) and S···N′ (d4, d5) contacts. These interactions play a role in stabilizing the dimers with respect to dissociation.

Crystals of β-[**2**]$_2$ (R_1 = Et) belong to the monoclinic space group $P2_1/c$, and consist of centrosymmetric dimers possessing a lateral S4–S4′ σ-bond (Fig. 4). The nearly coplanar association of radicals is accompanied by ring opening and formation of an exocyclic thione group, the sulfur atom of which (S3) develops a long range (2.817(4) Å) hypervalent interaction with S4. This mode of dimerization was recently observed for mixed *bis*-1,2,3-thiaselenazolyls,[10] but to date has never been seen for any 1,2,3-dithiazolyl radical. The dimers are tightly packed into intersecting slipped π-stacked arrays (Fig. 5), a motif that affords a series of close intermolecular S···S′ (d1) and S···N′ (d2, d3) contacts. Like the C–C bonded α-dimer, this S–S linked β-dimer is diamagnetic in the solid state (by EPR). It behaves as a semiconductor, with a room temperature conductivity $\sigma_{RT} \sim 10^{-7}$ S/cm.

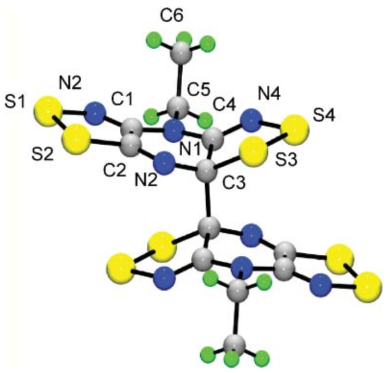

Fig. 2 The radical dimer α-[**2**]$_2$ (R_1 = Et), with atom numbering. Selected distances: C3–C3′, 1.607(4); N2–C1, 1.289(3); N4–C4, 1.276(3) Å.

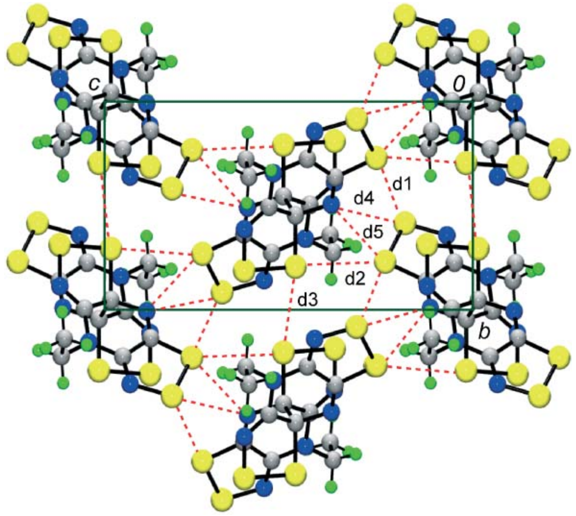

Fig. 3 Packing of α-[**2**]$_2$ (R_1 = Et), with interdimer contacts: d1 = 3.432(1), d2 = 3.534(1), d3 = 3.317(1), d4 = 3.140(2), d5 = 2.959(2) Å.

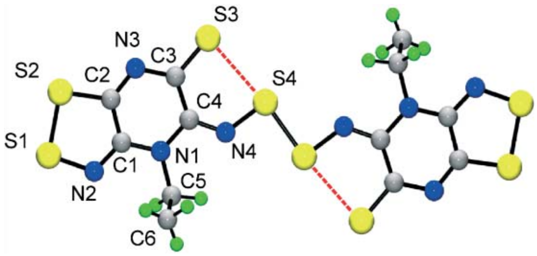

Fig. 4 The radical dimer β-[**2**]$_2$ (R_1 = Et), with atom numbering. Selected distances: S4–S4′ = 2.168(4), S3···S4 = 2.817(4), C3–S3 = 1.641(7) Å.

To date the known examples of 1,2,3-dithiazolyl dimers associate cofacially through their π-systems, and are linked *via* long (> 3.0 Å) transannular S···S contacts.[11] The observation of these new modes of dimerization is therefore unusual, but the

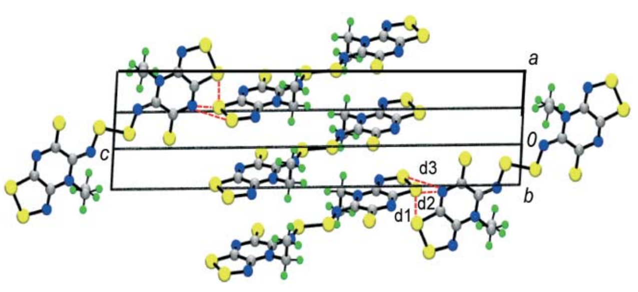

Fig. 5 Intersecting slipped π-stacks of β-[**2**]$_2$ (R_1 = Et), with inter-stack contacts: d1 = 3.226(3), d2 = 2.862(6), d3 = 3.011(6) Å.

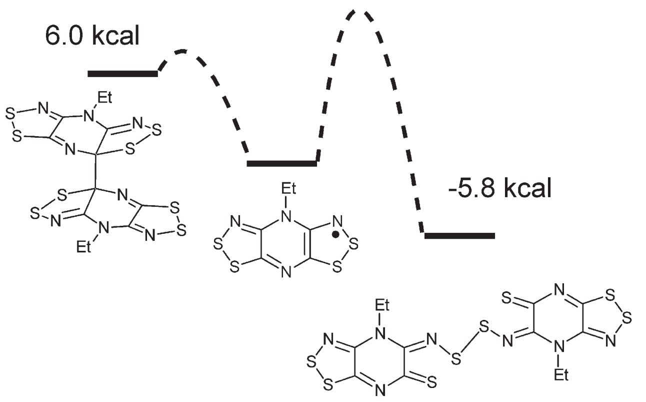

Fig. 6 B3LYP/6-31G** enthalpies of dimerization (per mole of dimer) for **2** (R_1 = Et).

occurrence of two *different* modes for the same radical is, to our knowledge, without precedent for a thiazyl radical (although a similar situation has recently been reported for spiro-biphenalenyls).[12] In the present case the C–C bonded α-dimer appears to be the kinetically favored product, as it readily crystallizes (from MeCN) at room temperature. Vaporization and recondensation of the radical leads to partial or complete conversion (depending on the landing zone temperature) to the more thermodynamically favored β-dimer. This interpretation is supported by the results of B3LYP/6-31G** calculations (performed with full geometry optimization) on **2**, α-[**2**]$_2$ and β-[**2**]$_2$ (R_1 = Et), which predict that association of the radical to the C–C dimer is, at the molecular level, an endothermic process (Fig. 6). Presumably the high lattice energy of the crystal structure, *i.e.*, the network of close S···S′ and S···N′ contacts, stabilizes the dimer in the solid state. By contrast radical association to the S–S bonded β-dimer is exothermic, but the process requires thermal activation, as might be expected from a reaction that requires a configurational ($\sigma \rightarrow \pi$) change,[10b] *i.e.*, is nominally symmetry forbidden.[13] However, the fact that **2** is readily detected by EPR when β-[**2**]$_2$ is dissolved in CH_2Cl_2 suggests that the interconversion barrier is not great.

The present results emphasize the potential diversity of the modes of dimerization available to heterocyclic thiazyl radicals, and the delicate energetic balance that exists between them. Which isomer is actually isolated depends in part on the associated lattice energy, but also on the degree of structural reorganization (activation energy) involved. It remains to be seen if changes in the nature of R_1 will alter the preferred mode of association of **2**, or indeed allow the isolation of materials which, like **1**, do not dimerize at all.

Notes and references

† Satisfactory chemical analyses (for C, H and N) were obtained for compounds **4**, **5**, [**2**][BF_4] (R_1 = Et) and β-[**2**]$_2$ (R_1 = Et).

‡ Crystal data at 298(2) K for α-[**2**]$_2$ (R_1 = Et): $C_{12}H_{10}N_8S_8$, M = 522.84, space group $P2_1/n$, a = 9.332(2), b = 7.4076(16), c = 14.207(3) Å, β = 100.594(3)°, V = 965.4(4) Å^3, Z = 2, D_{calcd} = 1.798 g cm^{-3}, μ = 0.944 mm^{-1}; 128 parameters were refined using 2203 unique reflections to give R = 0.0382 and R_w = 0.0899. Crystal data at 298(2) K for β-[**2**]$_2$ (R_1 = Et): $C_{12}H_{10}N_8S_8$, M = 522.84, space group $P2_1/c$, a = 4.5411(15), b = 7.583(2), c = 27.391(9) Å, β = 94.050(5)°, V = 940.9(5) Å^3, Z = 2, D_{calcd} = 1.845 g cm^{-3}, μ = 0.969 mm^{-1}; 128 parameters were refined using 2000 unique reflections to give R = 0.0718 and R_w = 0.0913. CCDC 292072–292073. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517098b

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