Bistability and the Phase Transition in 1,3,2-Dithiazolo[4,5-b]pyrazin-2-yl

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Spin state crossovers in transition metal complexes can be accompanied by magnetic hysteresis,[1] and these bistable materials have been actively pursued because of their potential applications in magneto-thermal switching and information storage devices.[2] However, while the magnetic signature of the bistability is well established, the underlying structural causes, i.e., the nature of the intermolecular interactions that generate the necessary cooperativity, are not well understood.

Chart 1

TPDTA, 1   TDTA, 2   PDTA, 3
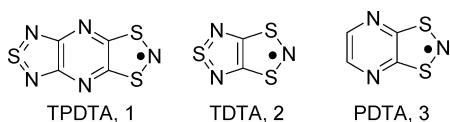
Recently, magnetic hysteresis has been observed in a number of molecular radicals,[3] including the three 1,3,2-dithiazolyls **1**−**3** (Chart 1).[4−6] The bistability initially observed in TPDTA[4] and TDTA[5] provided dramatic manifestations, particularly for TDTA, of the coexistence over a wide temperature range of two solid state structures, one based on diamagnetic dimers ($S = 0$), the other on essentially paramagnetic radicals ($S = 1/2$). In TPDTA the mechanism of the phase interconversion was described in terms of a tectonic plate slippage of π-stacked layers (Scheme 1),[4] while for TDTA a "domino cascade" of slipped radical π-stacks has been suggested.[6]

Scheme 1
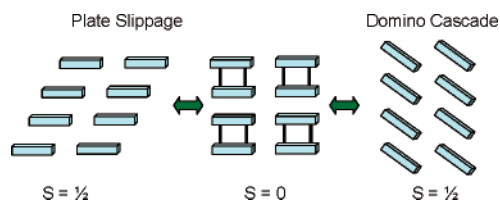
Variable-temperature magnetic susceptibility measurements (χ) on PDTA reveal a regime of bistability spanning 46 K, with $T_C{\downarrow} = 297(1)$ K and $T_C{\uparrow} = 343(1)$ K (Figure 1).[6] The similarity in the magnetic response and in the temperature range and width to that found for TDTA[5] prompted us to consider a similar interconversion pathway. To explore this possibility we have determined the crystal structures of the high- and low-temperature (HT and LT) phases of PDTA at 323 K,[7] i.e., near the midpoint of the bistable region. The HT phase was generated by heating a crystal of LT form to
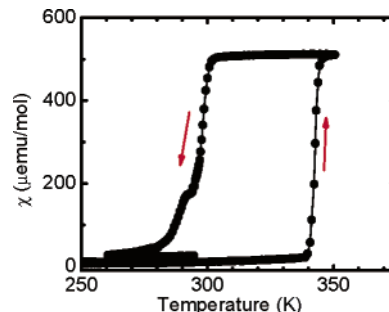

Figure 1. Magnetic susceptibility (χ) of PDTA as a function of T (K).

85 °C for 5 min and then cooling the transformed crystal to 50 °C for data collection.

While the space group and cell dimensions of the two phases are different,[7] the appearances of the two structures, when viewed down the stacking directions, are very similar. In both cases, the PDTA molecules (radicals or dimers) are aligned head-to-tail into chains running along [0,0,1] in the HT phase and along [0,1,0] in the LT phase. In HT-PDTA, this arrangement affords rows of radicals along [1,0,0], while in LT-PDTA the analogous rows run parallel to the cell diagonal vector [0,1,1].
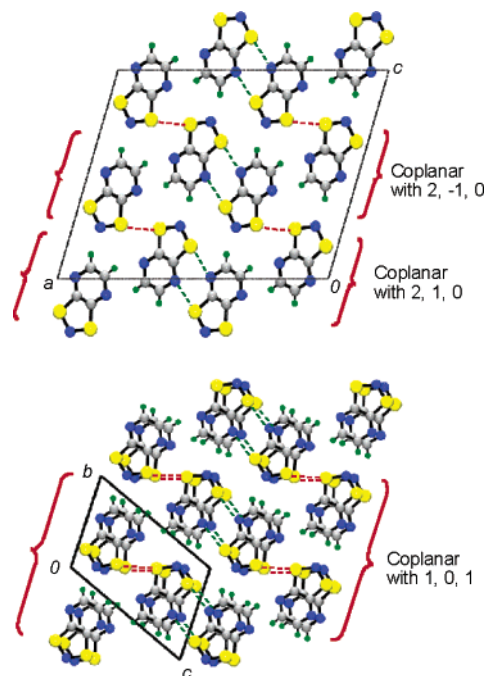

Figure 2. Packing of HT-PDTA (above) and LT-PDTA (below), showing lateral S- - -S and six-center S- - -N contacts.

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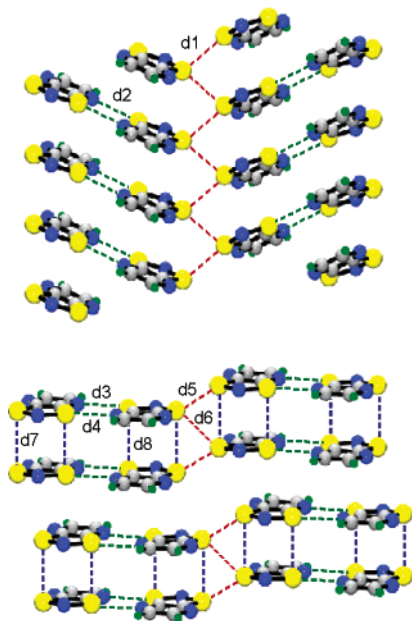[§] University of Louisville.

Figure 3. Stacking of radicals in the (1,0,−1) plane of HT-PDTA (above) and of dimers in the (0,1,0) plane of LT-PDTA (below).

Closer inspection of the two structures reveals significant differences. In the LT phase, all the molecules are coplanar with the (1,0,0) plane. By contrast, in the HT form, the mean planes of alternate radicals along [0,0,1], which are related by the *c*-glide, are rotated clockwise and counterclockwise, so that they lie coplanar with the (2,1,0) and (2,−1,0) planes, respectively.

The consequences of the alternating inclination of rings on π-stacking in the HT phase is illustrated in Figure 3, which shows a view of the (1,0,−1) plane, with slipped stacks of centrosymmetric pairs of radicals linked laterally by six-center intermolecular S- - -N contacts ($d2 = 3.000(5)$ Å). By contrast, an analogous view of the stacking in the LT phase, i.e., perpendicular to the (0,1,0) plane, reveals nearly superimposed stacks of π-dimers, with internal S—S bonds $d7$ (3.341(2) Å) and $d8$ (3.295(2) Å) that quench the spins of the radicals. As in the HT phase, lateral six-center S- - -N bridges $d3$ and $d4$ (2.941(4) and 2.957(4) Å) bridge adjacent radicals. In both phases, adjacent stacks of radical/dimer pairs are out-of-register and bridged by close interstack S- - -S contacts ($d1 = 3.546(4)$, $d5 = 3.370(2)$, and $d6 = 3.437(3)$ Å).

An understanding of the reversibility of the phase change and the cooperative effects necessary to induce hysteresis in PDTA emerges from a consideration of how the slipped stacks of the HT structure evolve into nearly superimposed stacks of the LT form. As in the case of TDTA, we invoke a domino cascade pathway (Figure 4). The difference between the two systems is that in this case it is the intermolecular S- - -S contacts that serve as hinges on which the molecular plates swing. The trigger that sets off the cooperative process in either direction is the cleavage of the six-center S- - -N contacts. Once these bridges are broken, the two rings are free to rotate (step A), up and down, with retention of inversion symmetry, until they are realigned with new partners with which they can form pairwise S- - -N contacts. This domino cascade allows for the perfect interconversion of slipped and superimposed radical π-stacks (step B). The subsequent formation of dimers, and doubling of the cell repeat distance along the stacking direction, provide what little enthalpy change there is in the overall sequence (step C). That the dimers are not actually superimposed in LT-PDTA indicates
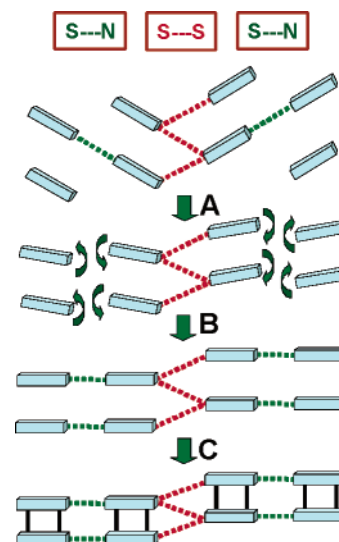

Figure 4. Domino cascade conversion of HT-PDTA to LT-PDTA, involving cleavage of S- - -N bridges (A), plate rotation about S- - -S hinges (B), and reformation of S- - -N bridges and dimerization (C).

that some minor lateral slippage also occurs, but this is unlikely to influence the energy barrier for the overall rearrangement.

Whether these dithiazolyl radical/dimer bistabilities will lead to useful device applications remains to be seen.[8] In the meantime, the understanding that the present results provide of the molecular design features necessary to induce hysteresis augurs well for the development of new magnetically bistable materials based on heterocyclic radicals.

Supporting Information Available: Crystallographic details in CIF format for the two structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for PDTA at 323(2) K: $C_4H_2N_3S$, $M = 156.21$. HT phase, monoclinic, space group C2/c, with $a = 20.526(14)$, $b = 3.718(3)$, $c = 15.506(10)$ Å, $\beta = 106.681(10)°$, $V = 1133.7(13)$ Å^3, $Z = 8$, $D_{calcd} = 1.830$ g cm^{-3}, $\mu = 0.826$ mm^{-1}; 82 parameters were refined using 590 unique reflections to give $R = 0.0792$ and $R_w = 0.1566$. LT phase, triclinic, space group P1, with $a = 7.0520(13)$, $b = 7.9277(13)$, $c = 11.4931(14)$ Å, $\alpha = 69.953(2)$, $\beta = 75.202(11)$, $\gamma = 76.340(10)°$, $V = 575.72(16)$ Å^3, $Z = 4$, $D_{calcd} = 1.802$ g cm^{-3}, $\mu = 0.813$ mm^{-1}; 165 parameters were refined using 1794 unique reflections to give $R = 0.0565$ and $R_w = 0.0993$.
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