Room-Temperature Magnetic Bistability in Organic Radical Crystals

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A large first-order magnetic phase transition in an organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl, is described. The transition occurs with a wide thermal hysteresis loop over the temperature range 230 to 305 kelvin. The high-temperature phase is paramagnetic, and its structure consists of a uniform one-dimensional stacking of the radical. The low-temperature phase is diamagnetic because of strong dimerization along the stacking direction. The results may have applications in thermal sensors, switching units, and information storage media based on organic radical crystals.

The magnetic properties of organic radical crystals have been studied for a long time. Such materials provide excellent models of quasi–one-dimensional (1D) magnets because of the 1D stacking of the anisotropic π-orbitals in their crystals. One of the most successful demonstrations of the usefulness of the organic radicals was the discovery of the so-called spin-Peierls transition (*1*) in the antiferromagnetic spin chain of ionized tetrathiafulvalene, TTF^+, in $(TTF)[CuS_4C_4(CF_3)_4]$ in 1975 (*2*). Uniform antiferromagnetic chains of Heisenberg $S = 1/2$ spins allow a gapless excitation of a paramagnetic spin wave, resulting in a transition to a dimerized state with a spin gap, as the temperature is lowered to a point at which the stabilization of the spin system caused by formation of the spin gap overcomes the elastic energy. The spin-Peierls transition is intrinsically second-order, but specific organic-radical insulators with 1D molecular stacking exhibit first-order phase transitions accompanied by lattice dimerization (*3–7*). Although their similarity to the spin-Peierls transition has been recognized, there has been no systematic discussion of the difference between the first- and second-order transitions. Here, we report an unusual first-order phase transition in an organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA), which occurs with a surprisingly wide hysteresis loop and with a drastic change in magnetism.

TTTA was prepared by a modification of the method described in (*8*). Its single crystals were obtained by vacuum sublimation. The magnetic measurements were carried out on a Quantum Design MPMS-XL SQUID (superconducting quantum interference device) susceptometer. The diamagnetic correction was performed using a diamagnetic susceptibility that was evaluated by assuming that TTTA was in a nonmagnetic state in the range 100 to 150 K. The x-ray diffraction data collection was performed with graphite-monochromated Mo Kα radiation on a Rigaku AFC5S four-circle diffractometer for the high-temperature (HT) phase and on a Rigaku R-AXIS-IV imaging-plate system for the low-temperature (LT) phase.

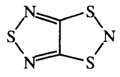
The magnetic and structural properties of TTTA can be better understood in the context of the molecular orbital calculations of the PM3/UHF method (*9*). The calculation indicated two characteristics: (i) The unpaired electron of TTTA is localized on the -S-N-S- moiety, and (ii) TTTA has a strong electric polarization that leaves positive polarized charges on the S atoms and negative polarized charges on the N atoms.

We examined the temperature dependence of the paramagnetic susceptibilities, χ_p, for a polycrystalline sample of TTTA (Fig. 1). As the sample is cooled from room temperature, χ_p shows a slight decrease. At 230 K, χ_p begins to quickly decrease, becoming zero at 170 K. TTTA is diamagnetic below this temperature. When heated from a low temperature below 150 K, χ_p is nearly zero over the range 150 to 230 K. Above 200 K, χ_p shows a very slight increase followed by a sudden increase at 305 K to a value that is almost the same as the initial value. The magnetic measurements indicated a first-order phase transition with a surprisingly wide hysteresis loop ($T_{c\downarrow} = 230$ K and $T_{c\uparrow} = 305$ K). Therefore, the material exhibits a room-temperature bistability in its magnetic properties. We repeated the cycles several times, but there was little change in the hysteresis loop. The hysteresis behavior of TTTA was confirmed by means of electron paramagnetic resonance spectroscopy. It is worth noting that the material is thermochromic as well, changing color in the phase transition; the HT and LT phases are purple and green, respectively.

The samples in the HT and LT phases were isolated by annealing at 40°C and at liquid nitrogen temperature for several hours, respectively. We carried out crystal structure analyses for the two phases at room temperature. We found that the HT phase was identical to the structure reported in (*8*).

In the HT phase, TTTA molecules form a polar 1D stacking column along the *b* axis with strong intercolumn interactions (Fig. 2A). In the column the stacking is regular and the overlap between the neighboring molecules is slightly shifted. One column is surrounded by six neighbors with short S···N and S···S contacts, probably caused by electrostatic interactions. Because the polar stacking column includes the short contact between the -S-N-S- moieties on which the unpaired electrons are populated, the intracolumn magnetic interaction would be stronger than the intercolumn interaction. The magnetic behavior of the HT phase can be interpreted by the model of a 1D antiferromagnetic chain (*10*), modified by the addition of a mean-field correlation to account for the intercolumn interactions. The dashed curve in Fig. 1 is the theoretical best fit with the parameters $J/k_B = -320$ K and $J'/k_B = -60$ K, where J and J' are the intra- and intercolumn exchange coupling constants, respectively, and k_B is the Boltzmann constant.

The molecular structures in the LT and HT phases are almost the same, but there is a crucial difference in molecular packing. The molecular planes are all parallel in the LT phase (Fig. 2B), whereas the unit cell of the



TTTA

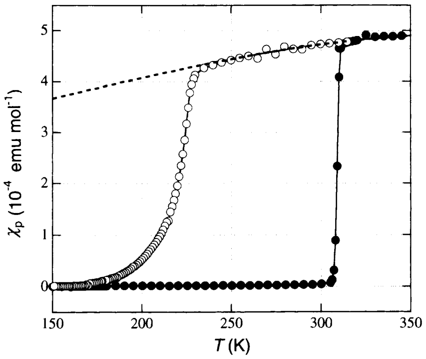


Fig. 1. Temperature dependence of the paramagnetic susceptibility, χ_p, for a polycrystalline sample of TTTA upon cooling (open circles) and upon heating (closed circles). The behavior clearly indicates a first-order phase transition with wide thermal hysteresis: $T_{c\downarrow} = 230$ K and $T_{c\uparrow} = 305$ K. The dashed curve is the theoretical best fit of the 1D antiferromagnetic chain of $J/k_B = -320$ K and $J'/k_B = -60$ K.

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HT phase includes two molecular-plane orientations (Fig. 2A). In addition, TTTA molecules are strongly dimerized in the LT phase along the stacking direction (Fig. 2B). By analyzing the magnetic data for the LT phase with the Bleaney-Bowers equation (*11*), we estimate the intradimer exchange coupling constant to be $J/k_B = -1300$ K, which is much larger than the *J* value in the HT phase.

The phenomena found in this study are similar to those in the spin-Peierls transition (*1*), which is caused by instability in the 1D antiferromagnetic chains of the $S = ½$ Heisenberg spins toward lattice dimerization. The phase transition in TTTA should be partially explained by the instability, but it is important to discuss the cause of the wide thermal hysteresis or the molecular bistability of TTTA. It is notable that the temperature dependence of χ_p for the HT phase indicates a strong intercolumn interaction. In the field of molecular magnetism, spectacular examples of molecular bistability include the specific Fe(II) spin-crossover complexes, in which the transitions between a diamagnetic state ($S = 0$) and a paramagnetic state ($S = 2$) occur with wide thermal hysteresis in the vicinity of room temperature (*12*). Because the Fe(II) sites are bridged by ligands in such specific complexes, it is believed that the intersite interactions bring about the hysteresis (*13*). The strong intercolumn interactions in TTTA possibly cooperate with the instability and result in the first-order phase transition. Another possible cause can be seen in the nearest-neighbor intermolecular arrangements (Fig. 2C). The two molecules exhibit a slipped overlap along the shorter molecular axis in the HT phase, but they are completely eclipsed in the LT phase. The geometry in the LT phase maximizes the exchange energy, because of the overlap between the molecular orbitals of the unpaired electrons, but it suffers electrostatic repulsion caused by the encounters of the polarized charges of the same sign. These phenomena can be explained by assuming that the gain in exchange energy overcomes the loss in electrostatic energy in this phase, and that the structure of the HT phase is obtained by a balance between the two kinds of energies. The competition between the exchange and electrostatic energies in the dimers may create a potential barrier between the structures of the LT and HT phases, resulting in the hysteresis loop.

There has been considerable interest in molecular bistability (*14, 15*), which means the property of a molecular assembly existing under two stable (or metastable) electronic states in a given range of external parameters (temperature, pressure, etc.), for the purpose of its application to electronic devices such as thermal sensors, switching units, and information storage media. Our results strongly suggest the possibility of magnetic molecular bistability in the low-dimensional structures of the heterocyclic thiazyl radicals, which possess strong intermolecular interactions and electric polarization effects.

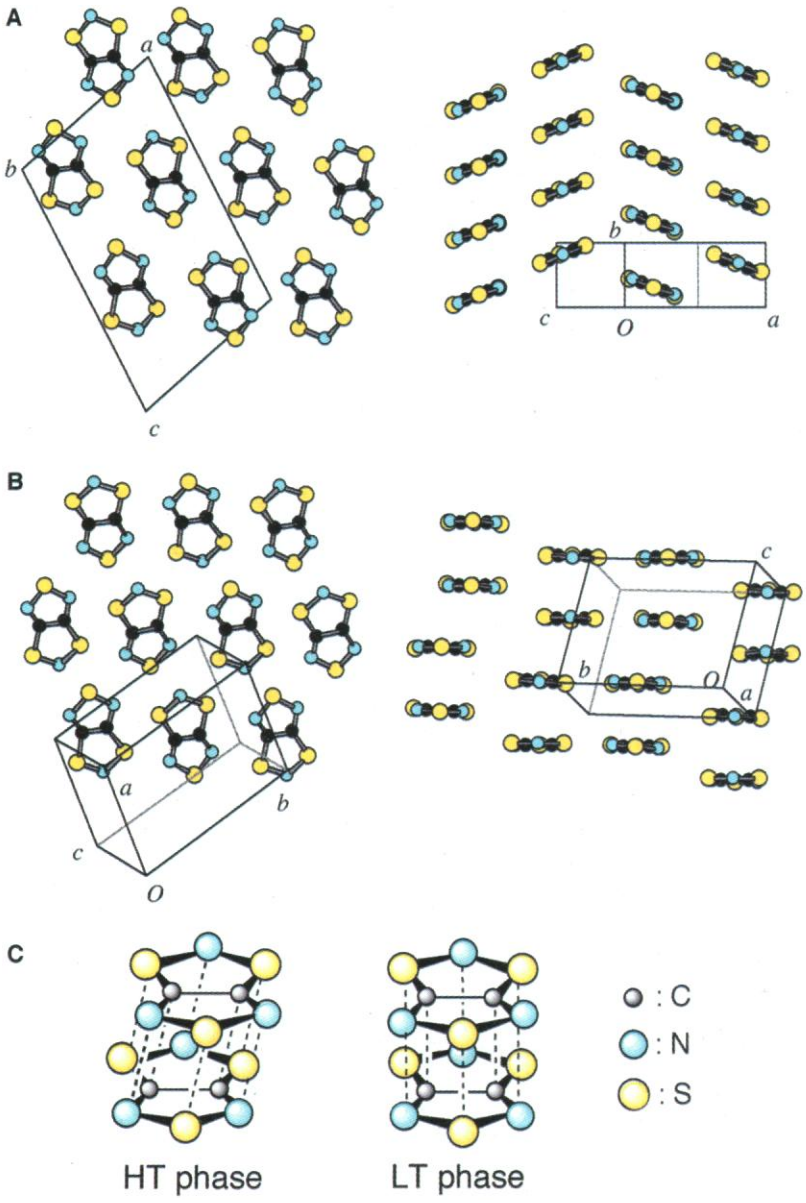

Fig. 2. (**A**) Top and side views of the columnar structures of TTTA in the HT phase. (**B**) Top and side views of the columnar structures of TTTA in the LT phase. (**C**) Nearest-neighbor intermolecular arrangements of TTTA in the HT and LT phases. Crystal data for the HT phase: monoclinic $P2_1/c$, $a = 9.4 \pm 0.1$ Å, $b = 3.71 \pm 0.01$ Å, $c = 15.064 \pm 0.007$ Å, $\beta = 104.66° \pm 0.06°$, $V = 510 \pm 1$ Å^3, $Z = 4$, $R = 5.0\%$. Crystal data for the LT phase: triclinic $P_{\bar{1}}$ with $a = 7.5205 \pm 0.0004$ Å, $b = 10.0319 \pm 0.0008$ Å, $c = 7.0162 \pm 0.0004$ Å, $\alpha = 100.572° \pm 0.005°$, $\beta = 97.009° \pm 0.007°$, $\gamma = 77.584° \pm 0.004°$, $V = 506.30 \pm 0.06$ Å^3, $Z = 4$, $R = 6.5\%$, $\mu = 13.1$ cm^{-1}.

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16. We thank M. Ogata for helpful discussion. Supported by a grant-in-aid for scientific research from the Ministry of Education, Science, and Culture, Japan.

28 June 1999; accepted 31 August 1999

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