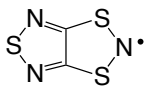
First and Second Order Phase Transitions in Dithiazolyl- based Materials

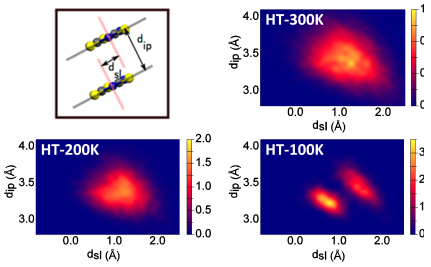
Sergi VELA, Fernando Mota, Juan J. Novoa, Mercè Deumal, and Jordi Ribas

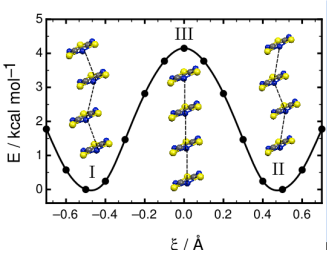
Departament de Química Física and IQTCUB, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1, 08028-Barcelona, Spain

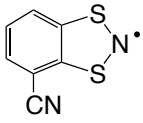
Recent years have witnessed a growing interest in the use of organic radicals as building blocks for functional molecular materials.[1] In this context, bistable materials are being intensively pursued for their potential applications as thermal sensors as well as memory and switching devices.[2] The family of DTA-based radicals has provided the most promising candidate towards this goal, the TTTA, which presents a diamagnetic-paramagnetic (order-disorder) phase transition with a hysteresis cycle at room temperature.[3] In contrast, other radicals of the same family (such as 2-NCBDTA) present the same kind of transition but without hysteresis loop.[4] Interestingly, the main structural features of the two phases are common in all cases; the LT phase always presents stacks of dimerized radicals, while in the HT phase these stacks are regular, (*i.e.* show no sign of dimerization). In order to identify the main characteristics that define the shape of the transition, we have performed first-principles molecular dynamic simulations on TTTA and 2-NCBDTA crystals. The analysis of these results reveals the presence of a second-order phase transition in both radicals that is concomitant with a first-order transition in the case of TTTA. Our computations thus suggest a new general mechanism justifying the presence of bistability in these crystals, where the paramagnetic-diamagnetic transition is caused by the important difference in entropy between the HT and LT structures, originated in the high vibrational disorder of the HT phase.



TTTA







2-NCBDTA

1. I. Ratera, J. Veciana, *Chem. Soc. Rev.* **41** 303–349 (2012).
2. O. Kahn, C.J. Martinez, *Science*, **279** 44-48 (1998).
3. W. Fujita and K. Awaga, *Science*, **286** 261-262 (1999)
4. A. Alberola, R. J. Collis and J. M. Rawson, *Inorganic Chemistry*, **45** 1903-1905. (2006)