High-pressure crystal structures of organic radical molecules for applications in molecular electronics

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Over the last 10 years, pressures of only a few gigapascals have been shown to modify and re-arrange intermolecular contacts in the organic solid state, such as hydrogen bonds and van der Waals contacts, leading to extensive phase diversity. Several interesting physical phenomena have been observed in small radical molecules, including semiconductor–insulator phase transitions and magnetic bistability.[1] Applications of these phenomena span modern microelectronics, providing potential lightweight organic alternatives to current electronic components. Organic radicals are emerging as species of interest in molecular electronics and molecular materials science. This naturally draws attention to the properties of these molecules in the bulk crystalline phase and the potential to manipulate these in response to external influences, such as light, temperature and pressure. Of particular interest in this work are the 6-oxo-verdazyl radicals (Figure 1), where the synthetic pathways and single molecule properties of 6-oxo-verdazyl analogue compounds have been previously studied.[2,3] A structure-property relationship with respect to pressure has not yet been observed for this class of organic radical. This area of materials chemistry discovery is therefore ripe for exploration.

In this work, high-pressure crystal structures of the 1,3-tolyl-5-phenyl-6- oxo-verdazyl radical (Figure 1) have been obtained at the Australian Synchrotron at pressures ranging from 0 to 3.3 GPa. Here we describe the effects on the crystal structure upon application of pressure, and a comprehensive analysis of the resulting changes in intermolecular interactions. Analysis of electrical and magnetic properties provide an insight into the viability of these organic radical crystals as components in future electronics. We completed this analysis using a suite of computational techniques including periodic density functional theory (DFT) and *ab initio* calculations. Magnetic susceptibility and electrical conductance measurements were also conducted to supplement this analysis.

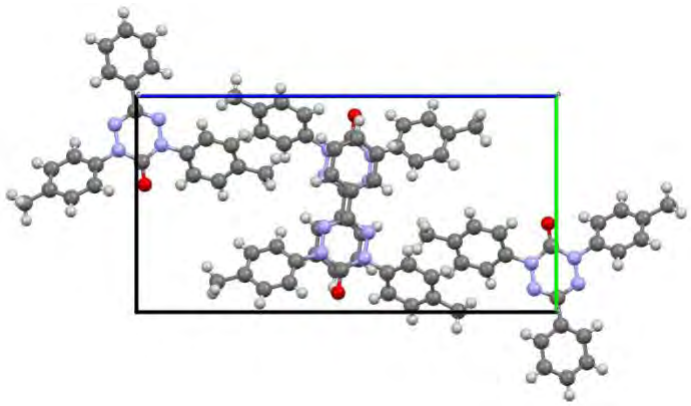

Figure 1. Crystal structure of 1,3-tolyl-5-phenyl-6-oxo-verdazyl radical

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