

Low-Melting Organic Salts: Phase Transitions, Twinning, and Disorder. Victor G. Young, Jr.,¹ Wesley A. Henderson,² Stefano Passerini,³ Paul C. Trulove², Hugh C. De Long²; ¹X-Ray Crystallographic Laboratory, Chemistry Dept., Univ. of Minnesota, Minneapolis, MN 55455; ²United States Naval Academy, Dept. of Chemistry, Annapolis, MD 21402; ³ENEA, Casaccia Research Center, Via Anguillarese 301, 00060 Rome, Italy.

Low-melting organic salts often exhibit complex temperature-dependent properties. Below melting temperatures these are best described as crystalline materials with liquid-like properties where some or all of the cations and/or anions are disordered. At yet lower temperatures, as monitored by DSC, these undergo stepwise phase transitions to ordered systems where some are twinned by non-merohedry and have high Z' structures. Many of these have intermediate phases with both ordered and/or disordered species. For example,¹ the salt $\text{PYR}_{12}\text{TFSI}$ undergoes four known solid-solid phase transitions before melting at 91°C. At -120°C, the crystal structure consists of ordered ions (Phase IV). This crystal structure is found in space group $P\bar{1}$ with $Z'=8$ as a non-merohedral twin. Above the phase transition at -85°C all of the PYR_{12}^+ and TFSI^- ions become disordered forming a plastic crystalline phase (Phase III). This crystal structure is found in space group $P2_1/n$ with $Z'=2$ as a non-twinned, single crystal. The crystal structures of both Phase II and Phase I have not been determined due to their inherent liquid-like properties. The structures and phase behavior of several new low-melting organic salts will be presented in this paper.

¹Wesley A. Henderson, Victor G. Young, Jr., Stefano Passerini, Paul C. Trulove, and Hugh C. DeLong, Chem. Mater. (2006) **18**, 934.