

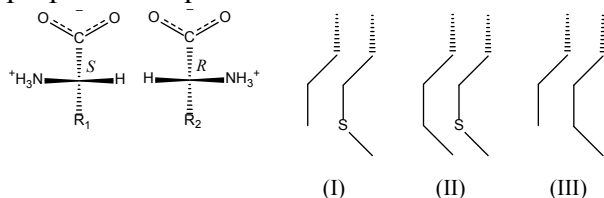
Poster Presentations

[MS24-01] Intricate temperature-induced phase transitions for amino acid quasiracemates.

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The racemates of certain amino acids with linear side chains undergo unique solid-state phase transitions involving not just changes to the side-chain conformations, but also major rearrangements of the stacking of layers in the crystals. For DL-aminobutyric acid,[1] DL-norvaline[2] and DL-nor-leucine,[3] two transitions have been found upon heating (or cooling), from $P2_1/c$ to $C2/c$ and then back to $P2_1/c$.^{*} For DL-methionine, only the transition from the low-temperature β form ($P2_1/c$) to the α form ($C2/c$) at 326 K has been described.[4] We report here the first investigation of similar properties in quasiracemates.



The three selected complexes, L-norvaline:D-methionine (I), L-norleucine:D-methionine (II) and L-norvaline:D-norleucine (III), each proved to have very complex phase behaviour with Differential Scanning Calorimetry (DSC) measurements indicating three to five transitions in the temperature range between 105 and 400 K. Subsequent single-crystal data collections right above and below each transition identified essentially three different types of structural changes: 1. Formal space group transitions from $P2_1$ to $C2$ or opposite (corresponding to $P2_1/c$ and $C2/c$ for the regular racemates), 2. Transitions from ordered side chains to disordered side chains, or between phases of various degree of disorder, 3. Changes of cell parameters without change to space group or disorder type (although

with shifts in rotamer populations). An observed transition may involve any one of these three phenomena, or combinations between them. On the other hand, side-chain disorder may also develop over an extended temperature range and hence be not detected by DSC.

The amount of structural information revealed here, based on 20 data sets collected between 105 and 390 K, permit a discussion of these phase transitions at an unprecedented level of detail, supported by Raman spectroscopy studies.

^{*}Both transitions are incomplete for DL-aminobutyric acid; for DL-norvaline the space group for the low-temperature phase has not been established.

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