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Temperature-induced phase transitions for amino acids with linear side chains

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Two polymorphs are known to exist under ambient conditions for a number of amino acids (three for glycine). While investigations at high pressure have revealed a number of additional polymorphs, temperature-induced changes are rare. Low-temperature structures with modified side-chain conformations were identified for L- and DL-cysteine. Furthermore, racemates with linear side chains, such as DL-methionine and the non-standard DL-aminobutyric acid (DL-Abu), DL-aminopentanoic acid (DL-norvaline, DL-Nva) and DL-aminohexanoic acid (DL-norleucine, DL-Nle), undergo major crystalline rearrangements on transitions between P21/c and C2/c space groups [1], some of them entropy driven (disordering). As for the corresponding enantio-pure amino acids, we recently described related P21 and I2 structures at 105 K for L-Abu, both with Z' = 4 [2]. A short side-chain C–C bond (1.426 Å) in the only available CSD entry for L-Nle (at 298 K) [3] lead us to suspect that disorder could have been overlooked in the original refinement. L-Nva has not been described previously. We now present single-crystal X-ray determinations between 105 and 405 K for L-Abu, L-Nva and L-Nle, showing phase behavior of unprecedented complexity. For L-Abu and L-Nva we find three different forms in this temperature interval, while four different phases were found for L-Nle. Its known C2 structure with Z' = 1 prevails between 200 and 390 K, and the side chain is indeed disordered 2:1 over two positions. Above 390 K disorder is extensive; the space group remains C2 but cell parameters change. Upon cooling new low-temperature forms are observed at 200 and 170 K. Both are modulated, but to a different extent: data collected at 100 K reveal an almost commensurate phase, while the 180 K phase is fully incommensurate. This is, to our knowledge, the first observation of modulated structures for an amino acid, and also the first observations of major crystalline rearrangements akin to those seen for the corresponding racemates.

[1] *C. H. Görbitz, F. Alebachew, V. Petříček, J. Phys. Chem. B, 2012, 116, 10715-10721.,* ***[2]*** *C. H. Görbitz, Acta Crystallogr., 2010, B66, 253-259.,* ***[3]*** *K. Torii, Y. Iitaka, Acta Crystallogr., 1973, B29, 2799-2807.*

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