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Supporting information for article:

On the stacking disorder of dl-norleucine

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S1. Validation of the force field and DFT-D calculations

The molecular structure of a single molecule from the single crystals of the α - and β -phases from DL-norleucine were compared with a single molecule of the crystal structures optimised by Dreiding force field and DFT-D (Table S1).

Table S1 Comparison of the experimental molecular structure of DL-norleucine with force field and DFT-D optimised molecular structure.

Bond length / Å	α -phase			β -phase		
	observed ^a	DFT-D	Force field	observed ^b	DFT-D	Force field
O1-C1	1.249(2)	1.266	1.245	1.248(1)	1.266	1.245
O2-C1	1.256(2)	1.278	1.243	1.262(1)	1.277	1.243
N1-C2	1.488(2)	1.488	1.461	1.487(1)	1.489	1.461
C1-C2	1.521(3)	1.529	1.465	1.528(1)	1.529	1.465
C2-C3	1.528(3)	1.532	1.546	1.529(1)	1.532	1.546
C3-C4	1.513(3)	1.526	1.545	1.526(2)	1.526	1.545
C4-C5	1.502(4)	1.524	1.543	1.517(2)	1.524	1.543
C5-C6	1.509(5)	1.525	1.538	1.521(2)	1.525	1.538
Angle / °						
O1-C1-O2	125.8(2)	125.31	114.70	126.1(1)	125.25	114.70
O1-C1-C2	117.1(2)	117.31	123.27	117.0(1)	117.04	123.27
O2-C1-C2	117.0(2)	117.29	122.02	116.8(1)	117.63	122.02
N1-C2-C1	109.3(2)	108.94	108.56	108.8(1)	108.71	108.59
N1-C2-C3	110.9(2)	110.65	112.94	110.7(1)	110.43	112.92
C1-C2-C3	109.3(2)	109.41	110.55	109.0(1)	109.56	110.56
C4-C3-C2	116.4(2)	114.09	114.05	115.4(1)	114.03	114.02
C5-C4-C3	113.7(2)	112.50	111.44	112.7(1)	112.65	111.46

C4-C5-C6	114.3(3)	112.52	112.21	113.1(1)	112.34	112.17
Torsion angle / °						
O1-C1-C2-N1	-30.59	-31.34	-47.94	-31.1(1)	-33.48	-48.10
O2-C1-C2-N1	153.22	151.92	133.47	152.7(1)	149.59	133.29
N1-C2-C3-C4	-53.51	-51.67	-55.06	-52.7(1)	-52.05	-55.23
C1-C2-C3-C4	-174.07	-171.70	-176.95	-172.3(1)	-171.76	-177.11
C2-C3-C4-C5	-177.76	-179.79	-174.72	-177.9(1)	-178.35	-174.86
C3-C4-C5-C6	-174.30	-173.60	-174.85	-174.6(1)	-176.11	-175.08

^a Harding *et al.* (1995)

^b Dalhus & Görbitz (1996)

The Dreiding force field describes the molecular structure of both phases of DL-norleucine in a reliable way. The force field is sufficiently adapted to norleucine. The DFT-D geometry of the molecule is in similarly good agreement with the experimental molecular structure.

R.m.s. cartesian displacement (r.m.s.c.d.) values of non-hydrogen atoms were additionally calculated after the method of van de Streek and Neumann (2010) (van de Streek, Neumann, 2010). An r.m.s.c.d. value above 0.25 Å “either indicates an incorrect experimental crystal structure or reveal interesting structural features”. The calculated r.m.s.c.d. values are given in Table S2.

Table S2 R.m.s. cartesian displacement values of force field and DFT-D optimised crystal structures of DL-norleucine.

Crystal structure	Stacking sequence	R.m.s.c.d. value / Å	
		Force field	DFT-D
α-phase	L	0.206	0.147
β-phase	LM	0.200	0.081

The calculated r.m.s.c.d. values of the force field as well as the DFT-D calculations are far below 0.25 Å. Therefore both methods can be used for the geometry optimisation of ordered models of DL-norleucine.

S2. Lattice-energy minimisations using force fields

Results of the lattice energy minimisations using force fields with models containing four double layers ($c' = 4c_0$) are shown in Table S3. Models including a mixture of L, M, A and B layers are less favourable by nearly $1 \text{ kJ}\cdot\text{mol}^{-1}$. The stacking sequences LAMB, LBMA and LAMA increase the energy by about $2 \text{ kJ}\cdot\text{mol}^{-1}$.

Table S3 Results of the lattice-energy minimisations using force field on models containing four double layers ($c' = 4c_0$, $Z = 16$).

Stacking sequence	Space group model ^h	Force field methods Relative energy / $\text{kJ}\cdot\text{mol}^{-1}$	Remarks
LLLL	$P2_1/a$, $Z = 4$	0.00	α -phase
LLLM	$P2_1/a$, $Z = 16$	0.02	
LMLM	$C2/c$, $Z = 8$	0.05	β -phase
LLMM	$A2/a$, $Z = 16$	0.02	
LLLA	$P2_1/a$, $Z = 16$	1.03	
LALA	$P2_1/c$, $Z = 4$	2.01	
LLAA	$P2_1/a$, $Z = 8$	1.03	
LLLB	$P2_1/a$, $Z = 16$	0.99	
LBLB	$A2/n$, $Z = 8$	1.92	
LLBB	$A2/a$, $Z = 16$	0.99	
LMAM	$P2_1/a$, $Z = 16$	1.01	
LMBM	$P2_1/a$, $Z = 16$	1.05	
LMAB	$P2/a$, $Z = 8$	1.01	
LAMB	$A2/a$, $Z = 16$	1.97	
LBAM	$P2/a$, $Z = 8$	1.01	
LBMA	$A2/a$, $Z = 16$	1.97	

LMAB	$P2/a, Z = 8$	1.01
LMBA	$A2/a, Z = 16$	1.05
LAAB	$Pa, Z = 16$	1.02
LABA	$P2_1/a, Z = 16$	1.05
LBAA	$Pa, Z = 16$	1.02
LAAM	$Pa, Z = 16$	1.02
LAMA	$P2_1/a, Z = 16$	1.97
LMAA	$Pa, Z = 16$	1.02
LBBA	$Pa, Z = 16$	1.02
LBAB	$P2_1/a, Z = 16$	1.01
LABB	$Pa, Z = 16$	1.02

S3. Local stacking probabilities

Assuming that the energy of a double layer is given by the neighbouring double layers in a finite distance, this double layer is considered to be the centre of a layer triple. Therefore the lattice-energy is calculated by the sum of the energies of the layer triples within a given model size.

For the stacking sequences, an additive combination of energies is assumed, i.e. the energy of a given double layer depends almost exclusively only on the arrangement of the neighbouring layers, whereas interactions with more distant double layers do not play a major role. For a given length of the local layer triple, we use a combinatorial approach to get the total number of possible local layer triples.

For a statistical examination of the energies of the layer triples, the Boltzmann distribution is used.

$$\frac{N_i}{N_j} = \frac{g_j}{g_i} e^{\frac{E_i - E_j}{kT}}$$

Using the energies of the layer triples, first the relative occupancy values N_i and afterwards stacking probabilities p_i for each local layer triple was calculated.

$$p_i = \frac{N_i}{\sum_{i=1}^n N_i}$$

As the basis we took the DFT-D optimised models LLL with $Z = 4$, LMLM with $Z = 8$ and LLMM with $Z = 16$. With these models a complete set of layer triples is given to describe all models containing

Dalhus, B., Görbitz, C. H. (1996). *Acta Cryst.* C52, 1761–1764.

Harding, M. M., Kariuki, B. M., Williams, L., Anwar, J. (1995). *Acta Cryst.* B51, 1059–1062.

Van de Streek, J., Neumann, M. A. (2010). *Acta Cryst.* B66, 544–558.