PAPER

NJC
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Neutron diffraction investigations of L- and D-alanine at different temperatures: the search for structural evidence for parity violation

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Received (in Durham, UK) 23rd December 2004, Accepted 22nd August 2005
First published as an Advance Article on the web 7th September 2005

Single crystal neutron diffraction has been used in an investigation of the structures of the amino acids L- and D-alanine. The aim of the study was to look for proposed phase transitions around $T_c \approx 270$ K. Measurements of both structures at 295 K and 60 K—the neutron structure of D-alanine being determined for the first time—show no significant structural basis for this phase transition in alanine. Further, confirmatory, investigation of the structure of D-alanine at temperatures of 240, 250, 260 and 300 K also showed no significant changes in bond lengths or angles. We can thus offer no structural support to other physical measurements, which are indicative of the observable effect of parity violation of the electroweak force in these phase transitions.

Introduction

The physical-chemical basis for the selection of chiral molecules in naturally occurring macromolecules is a fascinating problem that is not understood (reviewed in refs. 1, 2). Protein molecules are composed of L-amino acids while polynucleotides and polysaccharides contain only D-sugars. Clearly once living processes had selected a distinct chirality, the complex machinery of ribosomal protein synthesis and the stereoselectivity of enzymes ensure that such chirality is perpetuated. There are a few exceptions such as in the bacterial cell wall where D-amino acids are linked to the polysaccharide component by selective enzymes. Structural studies on the pyridoxal phosphate dependent alanine racemase from *B. stearothermophilus* have demonstrated the specificity requirements for recognition and reaction at the catalytic site.[3] Exceptionally a DL-racemase also exists in mammalian brain leading to the formation of D-serine as a receptor ligand.[4,5]

Quantum mechanical calculations based solely on electrostatic energies show equal energies for D- and L-amino acids since no chirality is implied in the electrostatic energy term. Inclusion of the parity violating weak interaction mediated by the very short range Z^0 bosons gave results that showed L-amino acids are stabilised with respect to D-amino acids with an energy difference of 10^{-14} J mol^{-1}.[6–8] The very small energy difference corresponds to a preference for only 1 molecule in 10^{17} at room temperature. The smallness of this value has prompted chemists to doubt that the parity violating term could give rise to the chirality of macromolecules observed in nature. Several authors have addressed ways in which the small energy difference might be amplified. One possibility is that the subtle parity violating energy difference (PVED) might be amplified by a type of Bose condensation phenomenon that gives rise to a second order phase transition below a certain critical temperature T_c and promotes the conversion of the very slightly less stable D-enantiomer to the more stable L-enantiomer.[9,10] Calculations of the likely critical temperature, using analogies to the Barden, Cooper, Schrieffer (BCS) theory of superconductivity, suggested a $T_c = 250$ K.

A number of experiments[11–13] have been reported that have detected some indication of parity violating phase transitions. Specific heat measurements by differential scanning calorimetry showed differences around 260 K for D-alanine and D-valine crystals; temperature dependent magnetic susceptibility measurements showed a difference in the magnetic susceptibility (χ) as a function of temperature between the D- and L-enantiomers; laser Raman spectra of L- and D-alanine showed that the second order C_α–H deformation modes of D-alanine vanished at 270 K (but reappeared at 100 K) while L-alanine shows no such phenomenon; and solid state NMR measurements on D-and L-alanine crystals showed differences in behaviour between the two enantiomers. More recently some of these experimental results have been questioned.[14]

Amino acids are known to racemise under basic and acidic conditions and at neutral pH with measurable rates at temperatures above 373 K. The rate of racemisation is related to the electronegativity and the size of the amino acid side chain. The rate constant for alanine in aqueous solution at 413 K is 2.0×10^{-6} s^{-1}.[15] The initial step is generally assumed to be loss of a proton from the α-methine carbon, resulting in the formation of a resonance stabilised planar α-carbanion. Calculations of possible transition states for the unimolecular gas

DOI: 10.1039/b419295h

phase racemisation of alanine have suggested a path in which the hydrogen atom migrates from the α-methine carbon to the amino group. Racemisation then occurs when another proton from the amino group migrates back to the chiral carbon centre.[14] In both the aqueous phase and the gas phase there is the expectation of lengthening of the C–H bond of the α-carbon atom in the early stages of racemisation.

The aim of this work is to complement the available data on possible differences between D- and L-alanine by obtaining accurate neutron diffraction data from crystals at temperatures above and below the putative phase transition point. In this way we hope to be able to observe any geometric or structural changes involving the hydrogen atoms, to which neutron diffraction will be particularly sensitive. Our work also allows a direct comparison between the D- and L-structures—prior to this work there had been no reported neutron study of the D-enantiomer.

Experimental

L- and D-alanine were obtained from Sigma. The single crystals were grown at room temperature (295 K) by slow evaporation from an aqueous solution of L- or D-alanine at approximate concentration of 250 mg ml^{-1}. The initial neutron diffraction data were collected using standard procedures, on the SXD instrument at the ISIS spallation neutron source at the Rutherford Appleton Laboratory.†[16] Data were obtained for both L- and D-alanine at 295 K and 60 K (see Table 1).

The structure factor sets were used for structural refinement, initially in GSAS[18] and completed in SHELXL-97.[19] Refinement was carried out, on F^2, using the coordinates from the previous room temperature neutron diffraction study of L-alanine[20] as a starting model. These coordinates were inverted to offer a starting point for the D-alanine refinement. The refined parameters from each room temperature determination were then used as starting parameters for the 60 K refinements. In the final refinement at each temperature, positional and anisotropic thermal parameters were refined for all atoms, including the hydrogens. The refinements all converged satisfactorily using this model, the final refinement comprising 118 parameters. The resulting structures are shown in Fig. 1, with bond lengths and angles from the refinement given in Tables 2 and 3. Data collection parameters, refined atomic coordinates and ADPs are available as ESI.‡

Results and discussion

The refined structure of L-alanine at 295 K is in good agreement with the previous determination[20] though of slightly lower precision than that comprehensive study using monochromatic neutron data collection.

Table 1 Refinement data for the extreme temperature (60 K, 295 K; SXD experiment) determinations of the structure of L- and D-alanine ($C_3H_7NO_2$, molecular weight 75.08)

	L-Alanine	L-Alanine	D-Alanine	D-Alanine
T/K	60	295	60	295
a/Å	5.940 (2)	6.036 (3)	5.942(2)	6.025(3)
b/Å	12.274(4)	12.342(5)	12.261(4)	12.324(5)
c/Å	5.806(2)	5.788(3)	5.785(2)	5.783(3)
V/Å^3	423.3	431.2	421.5	429.4
N_{total}	5261	2482	4306	2058
N_{unique} (R_{int})	2023	1008	1968	836
$N_{parameters}$	118	118	118	118
$R(F)$	0.060	0.083	0.086	0.095
wR_2 (F^2)	0.111	0.144	0.156	0.159

Comparison of the determined structures show the following general features:

(i) The room temperature structures of L- and D-alanine agree well with each other with no significant differences in geometry or thermal parameters (ADPs).

(ii) The low temperature (60 K) structures of the two enantiomers are likewise very similar.

(iii) For each enantiomer, the only significant changes between the determinations at the two temperatures are the natural reduction of the ADPs as the temperature is lowered. There are once again no significant geometrical changes apparent across the phase transition for either amino acid structure.

Given the "null" nature of this result, and in view of the evidence from other physical measurements, the structure of D-alanine has subsequently been determined at temperatures closer to the putative transition temperature on the VIVALDI instrument at the Institut-Laue Langevin.§ This has allowed the structure to be refined at 240 K, 250 K, 260 K and 300 K. The results of the VIVALDI study will be published in full elsewhere—the preliminary findings are presented here (Tables 2b and 3b) in confirmation of the SXD results showing no significant structural changes in this material beyond those attributable to changes in the data collection temperature.

The crystal structure of L-alanine is known from X-ray,[28] low temperature high resolution X-ray[29] and neutron diffraction data.[20] The basic features of that structure, and the closely related DL-alanine,[30] are again found here for both the L- and D-alanine determinations and will not be discussed further here.

† The crystals used on SXD at ISIS were of dimensions 4 × 2 × 2 mm^3 (L-alanine) and 7 × 4 × 1.5 mm^3 (D-alanine). For data collection at 295 K and 60 K the crystal was mounted inside a closed cycle refrigerator offering rotation about a vertical (ω) axis, and yielding temperature control of better than ±1 K throughout the experiment. Data were collected on SXD,[16] now incorporating a large array of 11 position-sensitive detectors, using the time-of-flight Laue diffraction method.[16,17] This method uses a wavelength-sorted white neutron beam, along with large area position-sensitive detectors, to allow a large volume of reciprocal space to be measured in a single crystal setting (a "frame"). The full data collection comprises a series of such frames, each collected with a stationary crystal-detector arrangement. A total of 5–6 frames, each containing information from seven of the eleven detectors, were collected at each temperature, with exposure times for each frame varying from around 120–750 minutes. The intensities were extracted and reduced to structure factors using standard SXD procedures.[17]

‡ CCDC reference numbers 278464–278467. See http://dx.doi.org/10.1039/b419295h for crystallographic data in CIF or other electronic format.

§ The crystal used at VIVALDI at the ILL was of dimensions 2.5 × 1.5 × 1.0 mm^3 (D-alanine). Data collection for D-alanine crystals at 240 K, 250 K, 260 K and 300 K were carried out at the VIVALDI (Very Intense Vertical Axis Laue Diffractometer) neutron beam line at the Institut Laue-Langevin, Grenoble, France[24] VIVALDI operates in Laue geometry, with the stationary crystal illuminated by a broad and continuous part of the incident thermal neutron spectrum. VIVALDI is equipped with a large neutron sensitive image plate detector that is mounted on a cylindrical drum camera that encircles the sample. The very large (> 2π Sr) angular acceptance means that virtually all discrete and continuous components of diffraction are then stimulated and recorded simultaneously[25,26]. On VIVALDI, the D-alanine crystal was mounted on an alignment stage of an Edwards Displex cryostat with b^* parallel to the spindle axis and c^* parallel to the neutron beam. Data sets were collected at 240 K, 250 K, 260 K and 300 K. Each data set comprised 5 Laue diffraction images collected at 20° intervals in rotation of the crystal perpendicular to the incident beam. Exposure times ranged between 120–180 minutes per image. Diffraction patterns were indexed, matched to a wavelength range of 0.9–3.1 and to a d_{min} of 0.7 Å, and integrated using a version of LAUEGEN of the Daresbury Laboratory Laue Suite[27] modified to account for the cylindrical geometry of the detector. Data collected at each temperature were scaled together and wavelength-normalised (to account for the spectral distribution) using the program LSCALE. Final scaling and merging of the data were performed with AGROVATA of the CCP4 suite. Full details of the VIVALDI determinations will be published elsewhere.

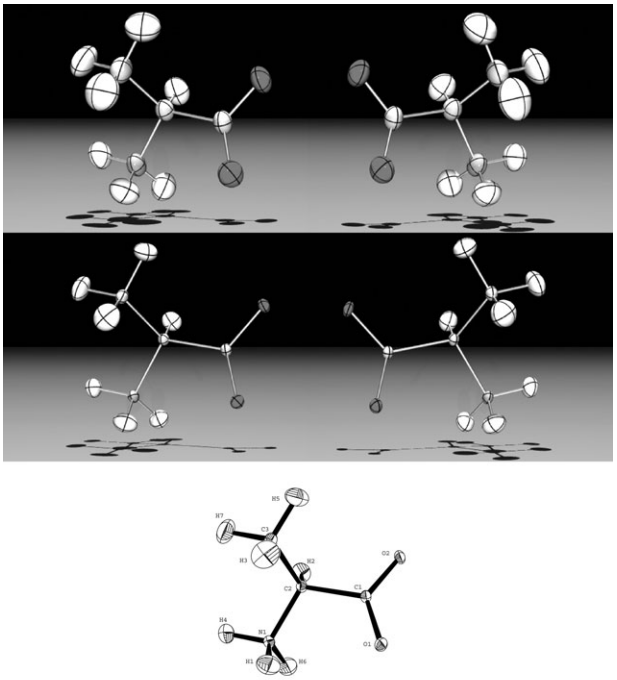

Fig. 1 ORTEP[21,22] views of the structures of L- and D-alanine determined by neutron diffraction at 295 K and 60 K, with the atomic numbering shown in the inset. (Top left) L-alanine at 295 K, (top right) D- at 295 K, (bottom left) L- at 60 K, (bottom right) D- at 60 K.

Table 2 Bond lengths for D- and L-alanine, from neutron diffraction experiments

(a) Bond lengths (Å)—SXD experiment[a]

Bond	L-Ala 60 K	L-Ala 295 K	D-Ala 60 K	D-Ala 295 K
C(1)–O(1)	1.249(1)	1.239(4)	1.249(2)	1.245(4)
	1.251	1.246	1.251	1.252
C(1)–O(2)	1.270(1)	1.260(3)	1.265(2)	1.259(5)
	1.272	1.266	1.267	1.265
C(1)–C(2)	1.538(1)	1.532(2)	1.536(2)	1.532(4)
	1.539	1.537	1.537	1.537
C(2)–N(1)	1.490(1)	1.484(3)	1.491(1)	1.491(3)
	1.492	1.492	1.493	1.499
C(2)–C(3)	1.529(1)	1.525(4)	1.525(2)	1.525(4)
	1.531	1.535	1.528	1.535
N(1)–H(1)	1.045(3)	1.033(6)	1.036(4)	1.031(7)
N(1)–H(4)	1.059(3)	1.054(5)	1.050(4)	1.071(8)
N(1)–H(6)	1.040(3)	1.048(8)	1.038(4)	1.036(7)
C(2)–H(2)	1.097(3)	1.090(5)	1.099(4)	1.098(8)
C(3)–H(3)	1.097(4)	1.085(8)	1.086(6)	1.114(10)
C(3)–H(5)	1.095(4)	1.092(11)	1.092(5)	1.095(11)
C(3)–H(7)	1.104(4)	1.085(7)	1.093(6)	1.093(13)

(b) Bond lengths (Å)—VIVALDI experiment for D-alanine

Bond	240 K	250 K	260 K	300 K
C(1)–O(1)	1.247(3)	1.245(2)	1.246(3)	1.244(4)
C(1)–O(2)	1.257(3)	1.259(3)	1.259(3)	1.255(4)
C_α(2)–C(1)	1.535(4)	1.535(3)	1.537(4)	1.536(4)
C_α(2)–N(1)	1.489(3)	1.485(2)	1.489(3)	1.484(3)
C_α(2)–C(3)	1.527(3)	1.524(2)	1.522(3)	1.515(3)
N(1)–H(1)	1.031(4)	1.035(4)	1.027(5)	1.028(6)
N(1)–H(4)	1.052(5)	1.052(4)	1.043(5)	1.054(6)
N(1)–H(6)	1.040(5)	1.042(4)	1.032(5)	1.028(6)
C_α(2)–H_α(2)	1.092(4)	1.097(4)	1.094(4)	1.091(5)
C(3)–H(3)	1.080(6)	1.080(6)	1.081(7)	1.074(8)
C(3)–H(5)	1.092(6)	1.095(6)	1.080(7)	1.085(8)
C(3)–H(7)	1.091(7)	1.111(7)	1.102(8)	1.082(9)

[a] The lower values for the heavy atom–heavy atom bond lengths are corrected for thermal motion effects (using the TLS method;[23] implemented in the THMA11 program in WinGX).[22]

Table 3 Bond angles for D- and L-alanine, from neutron diffraction experiments

(a) Bond angles (°)—SXD experiment

Angle	L-Ala 60 K	L-Ala 295 K	D-Ala 60 K	D-Ala 295 K
H(6)–N(1)–H(4)	108.6(2)	108.4(4)	108.1(3)	108.0(6)
H(6)–N(1)–C(2)	108.8(2)	109.5(4)	109.0(2)	109.6(5)
H(6)–N(1)–H(1)	109.9(2)	109.8(6)	109.8(3)	110.0(6)
H(4)–N(1)–C(2)	109.5(2)	109.5(4)	109.0(2)	109.4(4)
H(4)–N(1)–H(1)	108.2(3)	108.1(4)	108.6(4)	107.4(6)
C(2)–N(1)–H(1)	111.7(2)	111.5(4)	112.2(3)	112.4(5)
H(2)–C(2)–N(1)	107.0(2)	106.2(3)	107.5(2)	107.4(4)
H(2)–C(2)–C(1)	108.3(2)	108.0(3)	107.9(2)	107.7(5)
H(2)–C(2)–C(3)	110.5(2)	111.3(4)	110.7(2)	110.4(4)
N(1)–C(2)–C(1)	110.1(1)	110.1(2)	109.8(1)	110.3(2)
N(1)–C(2)–C(3)	109.8(1)	109.8(2)	109.8(1)	110.0(2)
C(1)–C(2)–C(3)	111.1(1)	111.3(2)	110.9(1)	110.9(2)
O(2)–C(1)–C(2)	115.9(1)	116.1(2)	115.7(1)	115.9(3)
O(2)–C(1)–O(1)	125.7(1)	125.2(2)	125.8(1)	126.0(3)
C(2)–C(1)–O(1)	118.4(1)	118.7(2)	118.5(1)	118.2(3)
C(2)–C(3)–H(7)	110.0(2)	110.8(5)	109.8(3)	110.3(7)
C(2)–C(3)–H(5)	110.6(2)	110.8(6)	110.6(3)	112.0(7)
C(2)–C(3)–H(3)	110.8(2)	110.9(7)	111.0(3)	110.0(6)
H(7)–C(3)–H(5)	109.1(3)	109.6(8)	108.4(4)	107.7(9)
H(7)–C(3)–H(3)	108.1(3)	107.2(7)	107.8(5)	107.4(10)
H(5)–C(3)–H(3)	108.2(3)	107.4(8)	109.3(4)	109.2(10)

(b) Bond angles (°)—VIVALDI experiment (D-alanine)

Angle	240 K	250 K	260 K	300 K
O(1)–C(1)–O(2)	125.6(2)	125.7(2)	125.8(3)	125.1(3)
O(1)–C(1)–C(2)	118.0(2)	118.17(18)	118.1(2)	118.5(3)
O(2)–C(1)–C(2)	116.4(2)	116.09(17)	116.1(2)	116.4(2)
N(1)–C(2)–C(3)	110.08(17)	109.92(15)	109.96(18)	109.9(2)
N(1)–C(2)–C(1)	110.29(17)	110.17(15)	110.02(18)	110.3(2)
C(3)–C(2)–C(1)	110.88(17)	110.69(15)	110.85(18)	110.9(2)
N(1)–C(2)–H(2)	107.4(3)	106.9(3)	106.6(3)	106.9(4)
C(3)–C(2)–H(2)	110.0(3)	110.6(3)	110.6(3)	110.3(4)
C(1)–C(2)–H(2)	108.1(3)	108.5(3)	108.8(4)	108.4(4)
C(2)–C(3)–H(3)	110.8(4)	111.2(3)	110.8(4)	110.7(5)
C(2)–C(3)–H(5)	110.4(4)	110.8(4)	110.2(5)	110.0(5)
H(3)–C(3)–H(5)	109.1(6)	109.1(5)	108.0(6)	108.8(8)
C(2)–C(3)–H(7)	109.7(4)	110.1(3)	110.0(4)	110.1(5)
H(3)–C(3)–H(7)	108.4(6)	107.4(5)	109.3(6)	108.1(8)
H(5)–C(3)–H(7)	108.3(6)	108.0(5)	108.5(6)	109.0(8)
C(2)–N(1)–H(1)	111.0(3)	111.2(3)	110.7(3)	110.9(4)
C(2)–N(1)–H(4)	109.4(3)	109.5(3)	109.4(3)	109.9(4)
H(1)–N(1)–H(4)	108.3(4)	108.3(4)	109.0(4)	108.0(5)
C(2)–N(1)–H(6)	109.0(3)	109.1(3)	108.8(3)	108.2(4)
H(1)–N(1)–H(6)	110.7(4)	110.4(4)	110.7(5)	110.6(6)
H(4)–N(1)–H(6)	108.5(4)	108.2(4)	108.2(4)	109.2(5)

All of the available hydrogen atoms are involved in N–H···O hydrogen bonds, as shown in Table 4. It can be seen that the geometry of these hydrogen bonds is similar in all the alanine structures determined. It is worthy of note that the N–H covalent bonds in these hydrogen bonds are all somewhat elongated (to ~1.05 Å from the more normal N–H covalent distance of 1.00 Å). This effect is a consequence of the zwitterionic nature of the alanine molecule.

The variation in the hydrogen bond geometry with temperature was previously discussed by Destro *et al.*[29] In that work a slight expansion of the *c*-axis between the room temperature neutron study and the 23 K X-ray study was noted, along with the fact that all three hydrogen bonds in the structure contracted by about the same degree (N···O separations reduced by 0.019 Å). This was taken to imply that there was some slight rearrangement of the molecular structure on cooling. This possible effect, believed to be significant since the N–H···O

Table 4 Hydrogen bond geometry (in Å and °, from SXD experiment)

	D-H	H···A	D-H-A	D···A		
N1–H6	1.048(8)	1.819(8)	162.2(6)	2.836(4)	O2 [$x + 1/2, -y + 1/2, -z - 1$]	L 295 K
N1–H6	1.036(7)	1.823(9)	163.2(7)	2.831(4)	O2 [$x + 1/2, -y + 1/2, -z - 1$]	D 295 K
N1–H6	1.040(3)	1.808(4)	162.5(3)	2.818(1)	O2 [$x + 1/2, -y + 1/2, -z - 1$]	L 60 K
N1–H6	1.038(4)	1.807(4)	162.6(3)	2.815(2)	O2 [$x + 1/2, -y + 1/2, -z - 1$]	D 60 K
N1–H4	1.054(5)	1.766(6)	168.6(5)	2.808(3)	O2 [$x, y, z - 1$]	L 295 K
N1–H4	1.071(8)	1.752(9)	168.1(6)	2.809(5)	O2 [$x, y, z - 1$]	D 295 K
N1–H4	1.059(3)	1.751(3)	169.0(2)	2.799(1)	O2 [$x, y, z - 1$]	L 60 K
N1–H4	1.050(4)	1.751(4)	169.8(3)	2.791(2)	O2 [$x, y, z - 1$]	D 60 K
N1–H1	1.033(6)	1.861(6)	162.0(5)	2.861(3)	O1 [$-x - 1/2, -y, z - 1/2$]	L 295 K
N1–H1	1.031(7)	1.855(8)	162.3(7)	2.855(4)	O1 [$-x - 1/2, -y, z - 1/2$]	D 295 K
N1–H1	1.045(3)	1.828(4)	161.3(3)	2.838(2)	O1 [$-x - 1/2, -y, z - 1/2$]	L 60 K
N1–H1	1.036(4)	1.832(4)	161.8(4)	2.834(2)	O1 [$-x - 1/2, -y, z - 1/2$]	D 60 K

Table 5 C–H···O contacts (in Å and °, from SXD experiment)

Structure	T/K	C_α–H2/Å	H2···O1/Å	C_α···O1/Å	C_α–H2···O1/°
L-Alanine	295	1.090(5)	2.438(6)	3.474(3)	158.3(5)
	60	1.097(3)	2.390(3)	3.445(2)	160.6(2)
D-Alanine	295	1.098(8)	2.419(8)	3.472(4)	160.0(6)
	60	1.099(4)	2.378(4)	3.436(2)	161.0(3)
L-Alanine[a]	*RT*	1.093(2)	2.429	3.472	159.5

[a] Ref. 20.

hydrogen bond approximately parallel to the ***c*** direction contracts to the same degree as the others in spite of the slight expansion of the *c*-axis on cooling, is apparently reproduced here, though the degree of shortening is not so consistent in our determinations. Any changes we see are marginal and do not lend themselves to a simple systematic explanation such as that advanced in the above X-ray study. We do not eliminate the possibility, but conclude that any effect is very subtle and does not seem to depend on the detailed hydrogen atom geometry.

The network of C–H···O non-bonded interactions has also been examined, and is presented in Table 5. These involve the hydrogen of the C_α–H bond interacting with a carboxylate oxygen from a neighbouring molecule. Similar conclusions hold as for the N–H···O hydrogen bonds, at the level of accuracy obtained in these experiments.

The conformation of the zwitterionic structure of L-alanine can be characterized by three torsion angles; where θ defines the angle between the O_2C and C_α–H_α planes, ω defines the NH_3^+ conformation and ψ the CO_2^- conformation. The dihedral angle θ has been considered in possible models for parity violation[31] which have shown a θ dependence for both the parity violating and parity conserving energy terms.

Table 6 Torsional angles (°) defining the conformation of the alanine molecule

	D-Ala 295 K	L-Ala 295 K	D-Ala 60 K	L-Ala 60 K
θ (O_2C/C_α–H_α)	−44.4(5)	45.8(5)	−45.1(2)	45.5(2)
ω(N–C–C–O)	18.2(3)	−18.8(3)	18.1(1)	−18.3(1)
ψ (H–N–C–C)	−58.7(5)	59.0(4)	−58.2(3)	58.0(2)

	D-Ala 240 K	D-Ala 250 K	D-Ala 260 K	D-Ala 300 K
θ (O_2C/C_α–H_α)	−44.3	−44.9	−45.1	−43.4
ω(N–C–C–O)	18.4	18.5	18.5	18.6
ψ (H–N–C–C)	−59.0	−58.3	−58.3	−60.2

Examination of the temperature and enantiomer dependence of θ (Table 6) once again shows no significant or systematic variation within the accuracy of our neutron diffraction data. The values of θ vary from 43.4° to 45.7° for the different experimental structures of D- and L-alanine. These values are close to the optimum value for the contribution of the parity violating term for neutral L-alanine in the gas phase and solution and higher than optimum values obtained for the zwitterionic form which is around 15°.[31] However the conformation is more likely to be a consequence of the need to achieve a staggered conformation around the C_α–C bond, as shown by the dominant parity-conserving energies in the above calculations.

Conclusions

We have made accurate determinations of the structure of both L- and D-alanine above and below the proposed 270 K phase transition, using single crystal neutron diffraction. These show there to be no significant geometric changes between enantiomers as a function of temperature. Thus we have determined no structural basis for the previously observed anomalies in DSC, magnetisation, Raman and NMR measurements.[11–13]

This is in agreement with the findings from a variable temperature X-ray diffraction study of D-valine[32] and L-alanine[33] and our neutron work suggests there to be no significant effect of the hydrogen atom geometry on this situation. We must therefore seek alternative explanations for a possible structural basis for the putative ~270 K phase transition in amino acids. It may be that this transition can only take place in solution, or at least not in the crystalline state where the very small differences in energies between the D-and L-configurations may be masked by crystal lattice energy terms. The neutron diffraction studies presented here provide an experimental evaluation of one of the possible mechanisms for the origin of chirality in nature.

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