

## Deformation Electron Density of $\alpha$ -Glycylglycine at 82 K. I. The Neutron Diffraction Study\*

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A neutron diffraction study of  $\alpha$ -glycylglycine,  $C_4H_8N_2O_3$ , has been carried out at 82 K. Intensities of 3341 reflections were measured at the Brookhaven National Laboratory High Flux Beam Reactor, and the structure was refined to a final  $R(F^2)$  of 0.030. The crystal was cooled in a cryostat employing liquid nitrogen as cryogen. The temperature at the crystal was 82.3 K with a maximum long-term variation of 0.4 K. The crystals are monoclinic, space group  $P2_1/c$ , with a cell of dimensions:  $a = 8.025$  (2),  $b = 9.543$  (4),  $c = 7.788$  (2) Å,  $\beta = 106.50$  (2)° at 82 K. The main purpose of the investigation was to obtain precise information on the positional and thermal parameters of the nuclei in the molecule. The bond distances between heavy atoms have been determined with estimated standard deviations in the range 0.0005–0.0007 Å; the corresponding values for heavy atom–H distances are 0.0009–0.0010 Å.

### Introduction

The recent improvement in the precision of diffraction techniques has increased the interest in the application of diffraction data to direct studies of electron distributions in solids (Coppens, 1975). The present work is the first part of an experimental determination of the deformation electron density in the peptide  $\alpha$ -glycylglycine based on separate neutron and X-ray experiments at 82 K. The main purpose of the neutron study was to obtain accurate information on the positional and thermal parameters of the nuclei in the molecule. The results of the X-ray study and the deformation electron densities will be discussed in a subsequent paper (Kvick, Koetzle & Stevens, 1978).

The crystal and molecular structure of perdeutero- $\alpha$ -glycylglycine was determined earlier (Freeman, Paul & Sabine, 1970) by neutron diffraction at room temperature. Our study has been performed at 82 K with the intention of reducing the thermal motion in the crystal. In electron-density studies it is important to minimize anharmonic contributions to the thermal motion and also to reduce the smearing of the experimental difference-electron densities.

### Experimental

#### *Crystal growth*

Crystals of  $\alpha$ -glycylglycine suitable for neutron diffraction were grown from solution. Small, well formed, seed crystals of  $\alpha$ -glycylglycine were grown by slow evaporation of aqueous *n*-propanol at 40°C. These were used as seeds for growing larger crystals by evaporation of a saturated aqueous solution of  $\alpha$ -glycylglycine at about +5°C. A plate-like crystal of dimensions 3.22 × 3.18 × 0.58 mm between the parallel faces was used for the data collection. The crystal is bounded by six faces of the forms {100} and {011}.

#### *Crystal data*

Crystal data are given in Table 1. The cell-dimensions were determined at 82 K from X-ray

Table 1. *Crystal data*

$\alpha$ -Glycylglycine, $C_4H_8N_2O_3$
FW 132.12
Space group $P2_1/c$
$a = 8.025$ (2) Å at 82 K
$b = 9.543$ (4)
$c = 7.788$ (2)
$\beta = 106.50$ (2)°
$U = 571.86$ Å <sup>3</sup> , $Z = 4$
$D_x = 1.534$ g cm <sup>-3</sup> , $\mu = 1.570$ cm <sup>-1</sup>

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diffraction data (Kvick, Koetzle & Stevens, 1978). The linear absorption coefficient,  $\mu = 1.570 \text{ cm}^{-1}$ , was determined experimentally by measuring the attenuation of a narrow beam of neutrons passing through the  $\alpha$ -glycylglycine crystal of known thickness. Assuming absorption cross-sections for C, N and O as tabulated in *International Tables for X-ray Crystallography* (1962) the mean incoherent scattering cross-section for H in  $\alpha$ -glycylglycine was found to be 25.5 barn at a neutron wavelength of 1.0164 Å.

#### Experimental conditions

During the data collection the crystal was kept at a mean temperature of 82.3 K with a maximum observed variation of 0.4 K. The cooling was accomplished with a cryostat with liquid nitrogen as cryogen. The crystal was mounted on a small aluminium pin, which was attached to a copper block in direct contact with the cryogen.

The cryostat was placed on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor. The supply Dewar containing the cryogen is an integral part of the cryostat, and transfer lines were therefore not necessary. The sample was enclosed in an aluminium container and the space around the crystal was evacuated before operation. The temperature of the copper block was monitored regularly with a platinum resistance thermometer. The recorded temperatures were calibrated using a crystal of  $\text{FeF}_2$  as a probe. A single crystal of  $\text{FeF}_2$  was mounted in the cryostat in the same manner as the  $\alpha$ -glycylglycine crystal, and the scattered neutron intensity from the {100} plane was measured at intervals of  $0.25^\circ$  in the temperature range 75–80 K to observe the magnetic phase transition of  $\text{FeF}_2$  with  $T_N = 78.38(1) \text{ K}$  (Hutchings, Schulhof & Guggenheim, 1972). In our experiment the scattered intensity for the 100 reflection changed by a factor of 60 over a temperature range of  $2^\circ$ . The observed temperature for the magnetic phase transition showed that the difference in temperature between the crystal and the copper block, where the thermometer was mounted, was  $0.8^\circ$ .

#### Data collection and reduction

Intensity data were collected using a  $\theta$ - $2\theta$  scan technique with the diffractometer operated under the Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & Van Norton, 1966). The scan interval was  $\Delta 2\theta = 2.4^\circ$  for  $d^* \leq 0.5 \text{ \AA}^{-1}$  and  $\Delta 2\theta = 1.15(1 + 4 \tan \theta)^\circ$  for  $0.5 < d^* < 1.5 \text{ \AA}^{-1}$ . The step size was chosen to give approximately 60 steps in each scan. Data were collected over a complete hemisphere of reciprocal space out to  $\sin \theta/\lambda = 0.716 \text{ \AA}^{-1}$  ( $\lambda = 1.0164 \text{ \AA}$ ). Two standard reflections were measured at regular intervals to provide a check on

crystal and electronic stability. Only variations expected from counting statistics could be observed.

Background corrections were made using a method (Lehmann & Larsen, 1974) which separates the peak and the background in such a way that  $\sigma(I)/I$  is minimized.  $I$  is the integrated intensity and  $\sigma(I)$  its e.s.d. based on counting statistics. Squared structure amplitudes were obtained as  $F_o^2 = I \sin 2\theta$  and were corrected for absorption by the Gaussian integration method using a grid of 384 points. The crystal shape was represented by six rational boundary planes. The transmission factors fell in the range 0.633 to 0.910 for the 3571 collected data.

Owing to diffraction from the aluminium vacuum shroud of the cryostat a few low-angle-reflection intensities were affected by non-uniform background.  $2\theta$  scans with the experimental set-up, but with the glycylglycine crystal removed, showed significant diffraction from aluminium in the following  $\theta$  regions: 10.9–11.6, 12.8–13.3, 13.7–14.3 and 16.0–16.4°. Reflections in these regions were thus down-weighted in subsequent calculations to compensate for the uncertainties in the background corrections.

#### Structure refinement

The starting parameters for the refinements of the structure of  $\alpha$ -glycylglycine were the final parameters from the neutron analysis of perdeutero- $\alpha$ -glycylglycine as refined by Griffin & Coppens (1975). The structure was refined with the full-matrix least-squares program *LINEX 74* including the extinction treatment according to Becker & Coppens (1974, 1975). The function minimized was  $\sum w(|F_o|^2 - k^2|F_c|^2)^2$ , where  $w$  denotes the weight given to each reflection, and  $k$  the overall scale factor. The weight  $w$  is inversely proportional to the estimated variance of an observation:

$$w^{-1} = \sigma_c^2(F_o^2) + (k' F_o^2)^2 = \sigma^2(F_o^2),$$

where  $\sigma_c(F_o^2)$  is based on counting statistics and  $k' = 0.016$  in the final cycles of refinement. The standard deviation of an observation of unit weight is

$$s = [\sum w(|F_o|^2 - k^2|F_c|^2)^2 / (m - n)]^{1/2} = 1.54,$$

where  $m$  is the total number of observations (3083) and  $n$  is the total number of variable parameters (162).

The 162 parameters included the scale factor, 51 positional and 102 anisotropic thermal parameters, the neutron scattering lengths for the two N atoms and six anisotropic extinction components. In the final cycles, 55 reflections with  $(F_o^2 - k^2 F_c^2) / \sigma(F_o^2) > 3$  and  $k^2 F_c^2 < 10\sigma(F_o^2)$  that were considered to be contaminated by multiple-scattering effects were eliminated from the refinement. Otherwise all reflections, even those with  $F_o^2 < 0$ , were included. Because of the extinction, only

Table 2. Final fractional coordinates ( $\times 10^5$ ) and thermal parameters ( $\times 10^4$ )

The anisotropic Debye–Waller factor is given by  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

	$b$ ( $\times 10^{-16}$ cm)	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	6648	-34291 (4)	9378 (4)	-10259 (4)	85 (1)	80 (2)	82 (1)	-4 (1)	-3 (1)	11 (1)
C(2)	6648	-48473 (4)	17023 (3)	-24211 (4)	75 (1)	62 (1)	79 (1)	-3 (1)	-7 (1)	-2 (1)
C(3)	6648	-76396 (5)	15740 (4)	-46619 (5)	97 (2)	75 (2)	114 (2)	15 (1)	-27 (1)	-15 (1)
C(4)	6648	-86174 (4)	5525 (4)	-61005 (4)	83 (1)	76 (1)	65 (1)	0 (1)	-1 (1)	2 (1)
N(1)	9296 (19)	-17528 (3)	16815 (3)	-7774 (3)	81 (1)	81 (1)	82 (1)	-3 (1)	-6 (1)	-5 (1)
N(2)	9309 (20)	-61677 (3)	9251 (2)	-33752 (3)	84 (1)	66 (1)	102 (1)	-4 (1)	-19 (1)	-2 (1)
O(1)	5803	-47763 (5)	29929 (4)	-25685 (6)	120 (2)	60 (2)	147 (2)	-8 (1)	-26 (1)	-1 (1)
O(2)	5803	-82543 (5)	-7320 (4)	-58919 (5)	149 (2)	72 (2)	82 (2)	-4 (1)	4 (1)	-1 (1)
O(3)	5803	-97204 (6)	10907 (5)	-74022 (5)	147 (2)	141 (2)	89 (2)	23 (1)	-39 (1)	13 (1)
H(1)	-3740	-19038 (11)	27451 (8)	-5949 (12)	238 (4)	131 (3)	299 (4)	-1 (3)	40 (3)	-15 (3)
H(2)	-3740	-8551 (10)	13206 (9)	3794 (11)	178 (3)	241 (4)	188 (3)	11 (3)	-25 (3)	30 (3)
H(3)	-3740	-13235 (11)	15154 (9)	-19153 (11)	223 (4)	278 (4)	197 (4)	-14 (3)	82 (3)	-12 (3)
H(4)	-3740	-37719 (11)	9772 (10)	2450 (10)	247 (4)	372 (5)	161 (3)	-20 (3)	70 (3)	38 (3)
H(5)	-3740	-32988 (11)	-1551 (8)	-13966 (12)	254 (4)	123 (3)	311 (4)	4 (3)	13 (3)	-14 (3)
H(6)	-3740	-60998 (10)	-1421 (8)	-33279 (11)	229 (4)	120 (3)	282 (4)	-6 (3)	-11 (3)	4 (3)
H(7)	-3740	-85617 (12)	19951 (11)	-39787 (13)	250 (4)	396 (5)	281 (4)	137 (4)	10 (3)	-125 (4)
H(8)	-3740	-71812 (13)	24497 (9)	-53219 (13)	320 (4)	197 (4)	349 (5)	-71 (3)	-43 (4)	96 (3)

repeated measurements of identical reflections were averaged. The final agreement factors are:

$$R(F^2) = \Sigma |F_o^2 - k^2|F_c|^2| / \Sigma |F_o|^2 = 0.030$$

$$R_w(F^2) = [\Sigma w|F_o^2 - k^2|F_c|^2| / \Sigma wF_o^4]^{1/2} = 0.042.$$

The corresponding conventional  $R(F)$  is 0.019 if the 272 reflections with  $I \leq 3\sigma(I)$  are excluded.

The anisotropic extinction model employed was the mosaic-spread-dominated type I model with a Lorentzian distribution (Becker & Coppens, 1975) and anisotropy of mosaic spread described according to Thornley & Nelmes (1974). Values of the mosaic-spread tensor  $Z$  ( $\times 10^8$ ) are as follows:  $Z_{11} = 0.109$  (6),  $Z_{22} = 0.521$  (21),  $Z_{33} = 0.420$  (15),  $Z_{12} = -0.074$  (9),  $Z_{13} = -0.053$  (7),  $Z_{23} = -0.074$  (12).

The neutron scattering lengths for the N atoms were found to be  $b_{N(1)} = 0.930$  (2) and  $b_{N(2)} = 0.931$  (2)  $\times 10^{-12}$  cm. These values are mutually consistent and also in quite good agreement with the mean experimental value of  $0.917$  (9)  $\times 10^{-12}$  cm given by Kvik, Koetzle, Thomas & Takusagawa (1974). Scattering lengths for C, O and H atoms were taken to be 0.6648, 0.5803, and  $-0.3740 \times 10^{-12}$  cm respectively (Shull, 1972). Fourier syntheses were calculated based on  $F_o$  and values of  $(F_o - F_c)$  from the final cycle of refinement. The largest peak in the difference synthesis corresponds to a scattering density of  $0.054 \times 10^{-12}$  cm  $\text{\AA}^{-3}$ . This residual density is less than 1% of the mean peak density at a C atom in the  $F_o$  synthesis ( $5.94 \times 10^{-12}$  cm  $\text{\AA}^{-3}$ ).

The refined atomic parameters are listed in Table 2.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32831 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

All calculations were carried out on the CDC 7600 and CDC 6600 computers at Brookhaven National Laboratory.

## Discussion

### The molecular structure

The molecular structure is illustrated in Fig. 1, which also defines the atomic notation used throughout this paper. Complete geometrical details and standard deviations are listed in Table 3.

The bond distances agree reasonably well with the values found for  $\alpha$ -glycylglycine at room temperature (Hughes, 1968), the largest differences being elongations of the C(2)–N(2) and C(4)–O(3) bonds of 0.016 and 0.019  $\text{\AA}$  respectively. The torsional angles are given in Table 4.

The best least-squares plane through the atoms C(1), C(2), O(1) and N(2) is given in Table 5, and it can be noticed that the atoms are not coplanar, deviations being as large as 0.016  $\text{\AA}$  from the least-squares plane. The carboxylate end [C(3), C(4), O(3), O(4)] is planar, however, with a dihedral angle of  $20.6^\circ$  with respect to the 'peptide' plane.

The C–H distances are all less than 0.004  $\text{\AA}$  from the mean value of 1.099  $\text{\AA}$  whereas the N–H distances vary considerably, as expected.

The observed thermal parameters have been fitted to general rigid-body motions described by the T, L, and S tensors (Schomaker & Trueblood, 1968). When the entire glycylglycine molecule was taken as a rigid body, the largest principal axis of L corresponds to a libration of  $L_1 = 6.0^\circ$ , approximately about the long axis of the molecule, and the r.m.s. error of fit is  $(\Delta U_{ij}^2)^{1/2} = 0.005$   $\text{\AA}^2$ . When the H atoms are excluded from the rigid

Table 3. Bond distances (Å) and angles (°)

Distances	Uncorrected	Minimum correction	Rigid-body correction		Riding-motion correction
			A*	B†	
N(1)–C(1)	1.4842 (5)	1.4842	1.4856	1.4877	1.4842
N(1)–H(1)	1.0368 (9)	1.0418	1.0392	1.0425	1.0549
N(1)–H(2)	1.0396 (8)	1.0435	1.0408	1.0421	1.0557
N(1)–H(3)	1.0500 (8)	1.0552	1.0523	1.0557	1.0672
C(1)–C(2)	1.5185 (6)	1.5185	1.5207	1.5231	1.5193
C(1)–H(4)	1.1007 (9)	1.1077	1.1030	1.1065	1.1216
C(1)–H(5)	1.0950 (9)	1.1008	1.0974	1.1009	1.1142
C(2)–N(2)	1.3333 (5)	1.3334	1.3338	1.3347	1.3351
C(2)–O(1)	1.2398 (7)	1.2406	1.2427	1.2467	1.2452
N(2)–C(3)	1.4528 (5)	1.4528	1.4547	1.4566	1.4541
N(2)–H(6)	1.0200 (9)	1.0240	1.0224	1.0257	1.0371
C(3)–C(4)	1.5238 (6)	1.5241	1.5247	1.5266	1.5265
C(3)–H(7)	1.1026 (9)	1.1121	1.1051	1.1088	1.1293
C(3)–H(8)	1.0979 (10)	1.1071	1.1005	1.1040	1.1243
C(4)–O(2)	1.2598 (7)	1.2601	1.2630	1.2671	1.2630
C(4)–O(3)	1.2511 (6)	1.2524	1.2528	1.2545	1.2586
H(1)···H(2)		1.664 (1)	H(4)···H(5)	1.795 (1)	
H(1)···H(3)		1.710 (1)	H(7)···H(8)	1.780 (2)	
H(2)···H(3)		1.729 (1)			
Angles					
N(1)–C(1)–C(2)	109.33 (3)	N(2)–C(3)–C(4)	112.49 (3)	C(1)–N(1)–H(1)	110.44 (5)
N(1)–C(1)–H(4)	108.37 (5)	N(2)–C(3)–H(7)	110.37 (6)	C(1)–N(1)–H(2)	109.51 (5)
N(1)–C(1)–H(5)	109.82 (5)	N(2)–C(3)–H(8)	109.42 (6)	C(1)–N(1)–H(3)	108.68 (5)
C(2)–C(1)–H(4)	107.40 (5)	C(4)–C(3)–H(7)	108.17 (6)	H(1)–N(1)–H(2)	106.54 (7)
C(2)–C(1)–H(5)	112.16 (5)	C(4)–C(3)–H(8)	108.29 (6)	H(1)–N(1)–H(3)	110.04 (7)
H(4)–C(1)–H(5)	109.67 (7)	H(7)–C(3)–H(8)	107.97 (9)	H(2)–N(1)–H(3)	111.63 (7)
C(1)–C(2)–O(1)	119.92 (3)	C(3)–C(4)–O(2)	118.41 (3)	C(2)–N(2)–C(3)	120.60 (3)
C(1)–C(2)–N(2)	116.55 (3)	C(3)–C(4)–O(3)	115.55 (4)	C(2)–N(2)–H(6)	120.62 (5)
O(1)–C(2)–N(2)	123.45 (3)	O(2)–C(4)–O(3)	126.05 (4)	C(3)–N(2)–H(6)	118.37 (5)

\* Rigid body = non-hydrogen atoms.

† Rigid body = entire molecule.

body, the corresponding results are  $L_1 = 3.9^\circ$  and  $(\Delta U_{ij}^2)^{1/2} = 0.001 \text{ \AA}^2$ . Bond distances have been corrected for the effects of thermal motion, using these rigid-body models as well as the 'minimum' and 'riding'

Table 4. Torsional angles (°)

	Angle	IUPAC–IUB designation*	
N-terminal	H(1)–N(1)–C(1)–C(2)	$\varphi_1^1$	48.94 (6)
	H(2)–N(1)–C(1)–C(2)	$\varphi_1^2$	165.96 (5)
	H(3)–N(1)–C(1)–C(2)	$\varphi_1^3$	–71.86 (6)
	N(1)–C(1)–C(2)–N(2)	$\psi_1$	150.98 (3)
Peptide bond	C(1)–C(2)–N(2)–C(3)	$\omega$	176.09 (3)
C-terminal	C(2)–N(2)–C(3)–C(4)	$\varphi_2$	157.12 (3)
	N(2)–C(3)–C(4)–O(2)	$\psi_1^1$	10.67 (5)
	N(2)–C(3)–C(4)–O(3)	$\psi_1^2$	–169.06 (3)

\* IUPAC–IUB Commission on Biochemical Nomenclature (1970).

Table 5. Deviations (Å) from the best least-squares plane through the peptide plane as defined by atoms C(1), C(2), N(2) and O(1)

The equation of the plane\* is

$$5.745676x - 1.293444y - 6.697605z + 1.399793 = 0$$

(x, y, z are the fractional coordinates of a point in the coordinate system defined by the cell.)

C(1)	–0.0047 (3)	O(3)	0.6314
C(2)	0.0161 (3)	H(1)	0.3493
N(2)	–0.0031 (2)	H(2)	0.4836
O(1)	–0.0114 (4)	H(3)	1.7261
		H(4)	–1.0579
C(3)	–0.0709	H(5)	0.4599
C(4)	0.4629	H(6)	0.1423
N(1)	0.6959	H(7)	–0.1128
O(2)	0.6980	H(8)	0.5213

\* The equation of the plane through the four atoms in the carboxylate group is:

$$6.990323x + 1.068338y - 5.497832z - 2.609649 = 0.$$

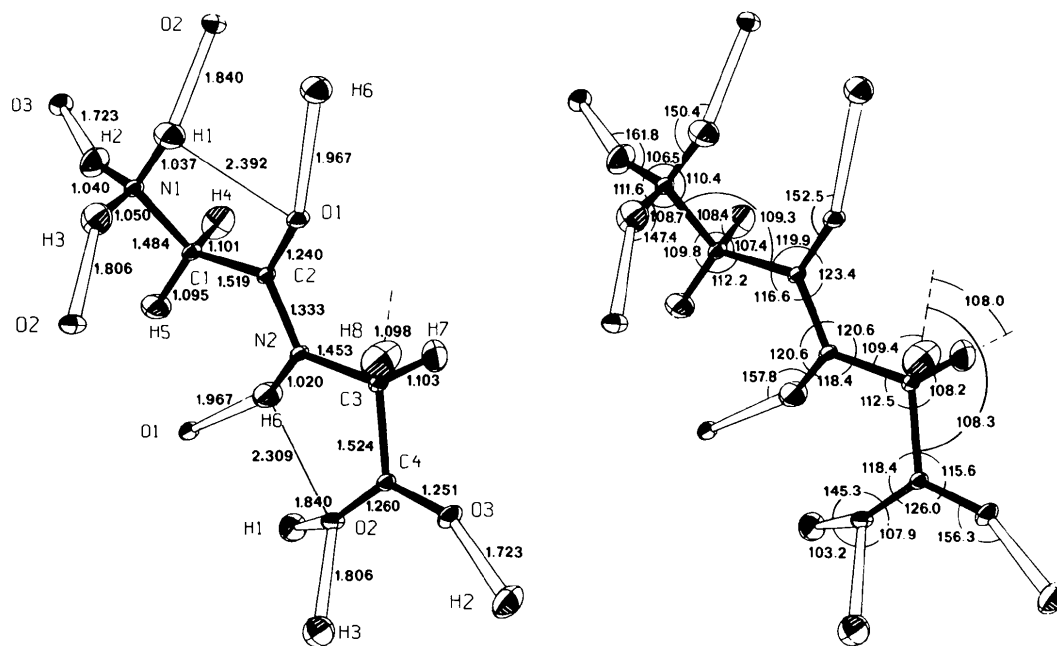


Fig. 1. Bond distances and angles. Standard deviations are given in Table 3. Covalent bonds are filled and hydrogen bonds are open; other short contacts are represented by solid lines. The thermal ellipsoids are drawn at the 90% probability level.

corrections of Busing & Levy (1964). These corrected distances are included in Table 3.

The molecular structure seems to be stabilized by two intramolecular  $H\cdots O$  contacts. The sum of the van der Waals radii for O and H is considered to be 2.40 Å whereas both the  $H(1)\cdots O(1)$  and  $H(6)\cdots O(2)$  distances are shorter than this value [2.392 (1) and 2.309 (1) Å respectively], indicating interaction between these atoms.

#### Crystal packing

The crystal packing is illustrated stereoscopically in

Fig. 2, and has been described in detail by Biswas, Hughes, Sharma & Wilson (1968).

In summary the glycylglycine molecules form a layer-like structure with three hydrogen bonds within the layers and two hydrogen bonds joining the layers.

#### Hydrogen bonds

The geometrical details of the five  $N-H\cdots O$  hydrogen bonds are given in Table 6. All the bonds are considerably bent with  $N-H\cdots O$  angles varying from 147.37 (7) to 161.82 (8)°. There is no obvious correlation between the  $O\cdots H$  and  $N-H$  distances

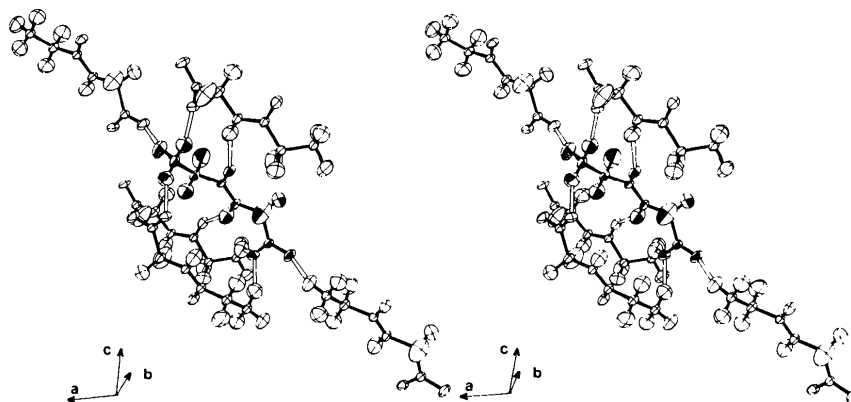


Fig. 2. A stereoscopic view of the crystal packing. Covalent bonds are filled and hydrogen bonds are open. The asymmetric unit is indicated by shaded ellipsoids. The thermal ellipsoids are drawn at the 90% probability level.

Table 6. Distances (Å) and angles (°) for the hydrogen bonds

N—H...O	N...O	N—H	H...O	∠N—H...O
N(1)—H(1)...O(2)	2.7889 (10)	1.0368 (9)	1.8399 (10)	150.42 (7)
N(1)—H(2)...O(3)	2.7300 (9)	1.0396 (8)	1.7230 (9)	161.82 (8)
N(1)—H(3)...O(2)	2.7492 (8)	1.0500 (8)	1.8059 (10)	147.37 (7)
N(2)—H(6)...O(1)	2.9373 (12)	1.0200 (9)	1.9673 (11)	157.84 (7)

around the  $-\text{NH}_3^+$  group, where the N—H bond lengths [1.0368 (9), 1.0396 (8) and 1.0500 (8) Å] have corresponding H...O bond lengths of 1.840 (1), 1.723 (1) and 1.806 (1) Å. The bond involving the peptide nitrogen, N(2)—H(6)...O(1), with an O(1)...H(6) distance of 1.967 (1) Å, is considerably longer than the bonds donated by the ammonium group.

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