An Experimental Study of the Influence of Temperature on a Hydrogen-Bonded System: The Crystal Structure of γ-Glycine at 83 K and 298 K by Neutron Diffraction*

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Abstract

Neutron diffraction studies of γ-glycine, $C_2H_5NO_2$, have been carried out at 83 K and 298 K using the same crystal. Intensities of 2235 (83 K) and 1426 (298 K) reflections were measured at the Brookhaven National Laboratory High Flux Beam Reactor and the structures were refined by full-matrix least-squares techniques to yield final agreement factors of $R(F^2)_{83K} = 0.024$ and $R(F^2)_{298K} = 0.025$. The crystal was assigned space group $P3_2$ with a cell of dimensions: $a = 7.046$ (3), $c = 5.491$ (2) Å at 298 K and $a = 6.975$ (2), $c = 5.473$ (2) Å at 83 ± 0.5 K. The observed thermal parameters have been analyzed according to a general rigid-body model in order to study the effect of cooling on the molecular dimensions and on the thermal motion of the atoms. Large differences in the hydrogen-bond distances were found. The N···O hydrogen-bond lengths were observed to be 0.02–0.05 Å longer at room temperature than at 83 K. These differences are accompanied by substantial changes in the lattice constants. The a and b axes contract more upon cooling than does the c axis, and this observation may be related to the fact that the largest principal axis of libration of the molecules lies nearly along c.

Introduction

Glycine is known to crystallize in three different forms. The common α form has been studied by neutron diffraction (Jönsson & Kvick, 1972), whereas the β and γ forms, which are reported to transform into the α form

upon heating, have only been investigated by means of X-ray diffraction (Iitaka, 1960, 1961). Here we report the neutron diffraction studies of γ-glycine at 298 K and 83 K. The main purpose of the investigations was to obtain accurate positional and thermal parameters for the nuclei and to study the effect of temperature on the structure. This work is part of a systematic investigation of amino acids by neutron diffraction performed at Brookhaven National Laboratory (Koetzle & Lehmann, 1976).

Experimental

Crystal data

A crystal of γ-glycine suitable for study by neutron diffraction was kindly supplied by Professor E. R. Lippincott of the University of Maryland. The irregularly shaped crystal had a volume of 22·5 mm^3 and was slightly elongated along the crystallographic c direction. The crystal shape was approximated by the ten rational boundary planes $(1\bar{1}0)$, $(\bar{1}00)$, $(1\bar{2}0)$, $(\bar{3}50)$, (001), $(00\bar{1})$, $(10,0,\bar{1})$, (312), $(1\bar{3}2)$, and $(13\bar{2})$.

Crystal data are given in Table 1. The cell dimensions were determined by least-squares fitting to observed θ values of 45 and 28 reflections measured at 298 K and 83 K respectively. The linear absorption

Table 1. *Crystal data*

γ-Glycine, $C_2H_5NO_2$
M_r 75·067
Space group $P3_2$; $Z = 3$

	298 K	83 K	Δ
a	7·046 (3) Å	6·975 (2) Å	0·071 Å
c	5·491 (2)	5·473 (2)	0·018
U	236·1 (2) Å³	230·6 (2) Å³	5·5 Å³
D_m	1·584 Mg m⁻³	1·621 Mg m⁻³	0·037 Mg m⁻³
μ	0·164 mm⁻¹		

coefficient $\mu = 0.164$ mm^{-1} was determined assuming absorption cross-sections for C, N and O atoms as tabulated in *International Tables for X-ray Crystallography* (1962) and with the mean incoherent scattering cross-section of 2.55×10^3 fm^2 for H. This latter value was that determined experimentally in α-glycylglycine at $\lambda = 1.0164$ Å (Kvick, Al-Karaghouli & Koetzle, 1977).

Experimental conditions

Measurements at the two temperatures were carried out at the High Flux Beam Reactor at Brookhaven National Laboratory. The 298 K data were collected with the crystal mounted on a glass fiber with the normal to the (001) plane approximately along the φ axis of the four-circle diffractometer. The data were obtained at a neutron wavelength of $\lambda = 1.0204$ Å (based on KBr, $a = 6.600$ Å). The 83 K data were collected at a neutron wavelength of 0.9109 Å, with the crystal oriented in a similar fashion. In this case the crystal was mounted on an aluminum pin, enclosed in a thin-walled quartz thimble, and placed inside a liquid-nitrogen-cooled cryostat. The aluminum sample holder was attached to a copper block which was in direct contact with the cryogen. A platinum-resistance thermometer used to monitor the temperature of the copper block registered 82 ± 0.5 K. The recorded temperatures were calibrated (Kvick *et al.*, 1977) with reference to a magnetic phase transition in an FeF$_2$ crystal and the temperature at the crystal position was shown to be approximately 0.8 K higher than that recorded in the copper block. The actual temperature in the present experiment was therefore 83 ± 0.5 K.

Data collection and reduction

Intensity data were collected using a θ–2θ step-scan technique on a four-circle diffractometer operated under the Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & Van Norton, 1966). The following scan intervals were used: (298 K) $\Delta 2\theta = 4.6°$ for $d^* \leq 0.55$ Å^{-1}; $\Delta 2\theta = 2.95$ (1 + 1.03 tan θ)° for $0.55 \leq d^* \leq 1.40$ Å^{-1}; (83 K) $\Delta 2\theta = 2.6°$ for $d^* \leq 0.65$ Å^{-1}; $\Delta 2\theta = 2.0$ (1 + 1.1 tan θ)° for $0.65 \leq d^* \leq 1.50$ Å^{-1}. The step size in 2θ was chosen to give approximately 50 steps in each scan. Intensities of two reflections were monitored at regular intervals to provide a check on experimental stability. Observed variations are consistent with counting statistics.

Background corrections were made by a method (Lehmann & Larsen, 1974) which divides the step scan into peak and background such that $\sigma(I)/I$ is minimized. I is the net 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 numerical integration over

a Gaussian grid with a total of 640 points ($\mu = 0.164$ mm^{-1}). Calculated transmission factors fell in the range 0.624 to 0.710.

Structure refinements

The starting parameters for the refinement of the structure of γ-glycine were those given by Iitaka (1961). Initial positions for the H atoms were obtained from difference Fourier maps. The structure was refined with a version of the least-squares program *ORFLS* (Busing, Martin & Levy, 1962) modified to include 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:

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

where $\sigma_c^2(F_o^2)$ is based on counting statistics, $k' = 0.02$ and $k'' = 4000$ and 2000 for the final cycles of refinement with the 83 K and 298 K data, respectively. The constant term k'' was included in order to give lower weight to weak reflections, most of which had F_o^2 greater than $|F_c|^2$, possibly due to multiple scattering. All measured reflections, even those with $F_o^2 \leq 0$, were included in the refinements. A summary of pertinent refinement parameters is given in Table 2. Comparison of refinements incorporating anisotropic and isotropic extinction models and employing both Lorentzian and Gaussian distributions (Becker & Coppens, 1975) showed that the fit was not improved by using the anisotropic extinction model. The intensities of equivalent reflections and associated absorption-weighted mean path lengths were therefore averaged.

An isotropic mosaic-spread-dominated type I extinction model with Gaussian distribution was used in the final cycles of refinement. Final values of the extinction parameter g were found to be 3.34 (9) $\times 10^3$

Table 2. *Experimental and refinement parameters*

	83 K	298 K
Wavelength of neutron beam	0.9109 Å	1.0204 Å
Monochromator	Be (002)	Ge (220)
Number of reflections measured*	2235	1426
Number of independent reflections (n)	546	440
R_A,† (agreement factor for averaging)	0.035	0.031
$\sin \theta / \lambda_{max}$	0.76 Å^{-1}	0.68 Å^{-1}
Number of parameters refined (m)	92	92
Overall scale factor (k)	57.8 (2)	39.6 (2)
$R(F^2)$†	0.024	0.025
$R_w(F^2)$†	0.035	0.035
$R(F)$†	0.014	0.017
S†	1.62	1.39
Most significant extinction correction (divides F_o)	0.51 (342)	0.42 (110)

* At each temperature, a hemisphere of reciprocal space ($l \geq 0$) was explored.

† $R_{Av} = \sum (\sum_{i=1}^{n} |F_{o,i}^2 - \langle F_o \rangle^2|)/\sum n' \langle F_o^2 \rangle$; $R(F^2) = \sum |F_o^2 - k^2|F_c|^2|/\sum F_o^2$; $R_w(F^2) = [\sum w(F_o^2 - k^2|F_c|^2)^2/\sum wF_o^4]^{1/2}$; $R(F) = \sum |F_o - k|F_c||/\sum F_o$ ($F_o^2 \geq 0$ only); $S = [\sum w(F_o^2 - k^2|F_c|^2)^2/(m-n)]^{1/2}$.

Table 3. *Final fractional coordinates* ($\times 10^5$; *for* H *atoms* $\times 10^4$)

The first line refers to the 83 K experiment, the second to the 298 K experiment and the third gives the differences between the 298 K and 83 K parameters.

	x	y	z
N	24435 (6)	2851 (7)	50381 (−)†
	24619 (10)	2926 (11)	50381 (−)†
	184	75	0†
O(1)	23261 (10)	1233 (11)	1382 (16)
	23324 (17)	1150 (20)	1487 (25)
	63	−83	105
O(2)	54367 (11)	−320 (13)	−1729 (16)
	54233 (21)	−91 (28)	−1667 (26)
	−134	229	62
C(1)	39201 (9)	−128 (9)	10245 (15)
	39219 (14)	21 (15)	10248 (20)
	18	149	3
C(2)	39750 (10)	−2730 (10)	37867 (15)
	39876 (16)	−2403 (19)	37887 (19)
	126	327	20
H(1)	2502 (2)	162 (3)	6949 (3)
	2519 (4)	170 (4)	6945 (4)
	17	8	−4
H(2)	2916 (3)	1919 (2)	4600 (3)
	2915 (4)	1902 (4)	4610 (4)
	−1	−17	10
H(3)	830 (2)	−741 (3)	4457 (3)
	871 (4)	−730 (4)	4455 (4)
	41	11	−2
H(4)	5639 (3)	770 (3)	4520 (3)
	5627 (4)	811 (7)	4496 (5)
	−12	41	−24
H(5)	3458 (3)	−1999 (3)	4198 (4)
	3486 (7)	−1947 (5)	4196 (6)
	28	52	−2

† Coordinate held constant to fix the origin in the c direction.

and $2 \cdot 80$ (8) $\times 10^3$ for the data measured at 83 K and 298 K respectively. These values correspond to mosaic spreads of $17 \cdot 4$ and $20 \cdot 8''$.

The neutron scattering lengths for C, O and H atoms were taken to be $6 \cdot 648$, $5 \cdot 803$ and $-3 \cdot 740$ fm respectively (Shull, 1972). The neutron scattering lengths for N were refined and were found to be $b_N(298$ K$) = 9 \cdot 34$ (5) fm and $b_N(83$ K$) = 9 \cdot 29$ (5) fm. These values are consistent with the mean value of $9 \cdot 17$ (9) fm given by Kvick, Koetzle, Thomas & Takusagawa (1974), and agree with that of $9 \cdot 36$ (2) fm recently quoted by Koester (1977).

The refined atomic parameters are listed in Table 3.*

Discussion

The crystal structure of γ-glycine has been discussed by Iitaka (1961). Here we will consider only those aspects

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34520 (10 pp.). Copies may be obtained through The Exeuctive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the structure specifically concerning the H atoms, and features which are affected by thermal motion.

The structure is illustrated in Figs. 1 and 2. It can be described as consisting of glycine molecules linked by two hydrogen bonds [N—H(1)$\cdots$O(1), N—H(2)$\cdots$O(2)] to form helices around the crystallographic 3_2 screw axes. A third lateral hydrogen bond [N—H(3)$\cdots$O(1)] connects the helices, thus forming a three-dimensional network.

It is interesting to note that in γ-glycine all molecules are oriented in the same fashion. In α-glycine and in the β form, the molecules are oriented to form antiparallel double layers and alternating antiparallel layers, respectively.

Analysis of the thermal motion

Rigid-body motions described by T, L and S tensors (Schomaker & Trueblood, 1968) have been fit to the observed atomic thermal parameters at the two temperatures. Atoms were selected to comprise the rigid body as follows, (I): non-hydrogen atoms, (II): entire molecule, (III): C(2), N, H(1), H(2), H(3); the results are presented in Table 4. Since the rigid-body fit with model (I) was better than with model (II), the results for model (I) were used to derive the bond distances corrected for effects of libration (Table 5) used in the discussion below. For each analysis all elements of the S tensor were small thus indicating little correlation of translations and librations.
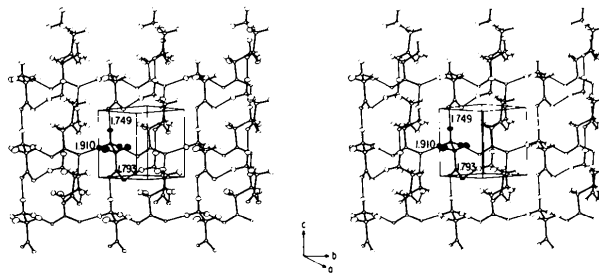

Fig. 1. A stereoscopic illustration of the molecular packing viewed normal to the hydrogen-bonded chains. This and other diagrams in this paper were produced with *ORTEP* II (Johnson, 1976).
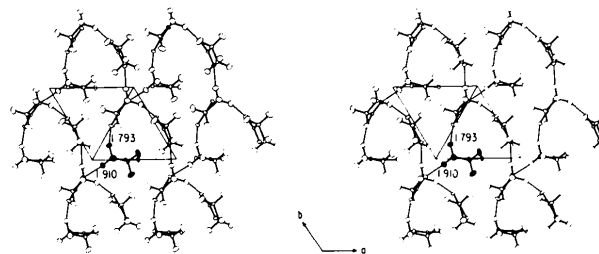

Fig. 2. A stereoscopic representation of the structure viewed down the crystallographic c axis.

Table 4. Rigid-body analyses of thermal motion

The units for the mean-square amplitude of translation (T), libration (L) and r.m.s. fit, $\langle\Delta U^2\rangle^{1/2}$, are 0·0001 Å², 0·0001 rad², and 0·0001 Å², respectively. The e.s.d.'s quoted for the diagonal terms of T and L in the ab^*c system were obtained from the least-squares fit of the group parameters to the appropriate set of unit-weighted individual-atom U_{ij}'s. Standard deviations for these components in the special axial system were obtained by the usual propagation-of-error procedure.

Rigid body	Coordinate system†	Temperature (K)	T_x	T_y	T_z	L_x	L_y	L_z	$\langle\Delta U^2\rangle^{1/2}$
(I) C(1), C(2),	x‖C(1)–C(2) bond	298	123 (4)	195 (54)	154 (8)	159 (103)	28 (11)	65 (99)	5
N, O(1),	y⊥C(1)–C(2)–N plane	83	44 (2)	73 (19)	60 (3)	47 (37)	7 (4)	17 (36)	2
O(2)	z = x × y	Diff.‡	79 (4)	122 (57)	94 (9)	112 (109)	21 (12)	48 (105)	–
	x‖a	298	142 (5)	208 (59)	122 (4)	53 (108)	25 (3)	174 (105)	5
	y‖b*	83	57 (2)	77 (21)	44 (2)	12 (39)	7 (1)	52 (38)	2
	z‖c	Diff.‡	85 (5)	131 (63)	78 (4)	41 (115)	18 (3)	122 (112)	–
(II) Entire	x‖C(1)–C(2) bond	298	177 (16)	188 (24)	199 (19)	200 (14)	24 (8)	81 (10)	
molecule	y⊥C(1)–C(2)–N plane	83	89 (14)	56 (20)	97 (16)	91 (12)	13 (6)	45 (8)	
	z = x × y	Diff.‡	88 (22)	132 (31)	102 (25)	109 (18)	11 (10)	36 (13)	
	x‖a	298	185 (19)	197 (25)	182 (16)	66 (10)	21 (8)	218 (15)	37
	y‖b*	83	91 (16)	59 (20)	92 (14)	38 (9)	12 (6)	99 (12)	31
	z‖c	Diff.‡	94 (25)	138 (32)	90 (21)	28 (13)	9 (10)	119 (19)	–
(III) C(2), N,	x‖C(2)–N bond	298	222 (27)	227 (26)	164 (24)	126 (64)	43 (45)	148 (53)	21
H(1), H(2),	y⊥C(1)–C(2)–N plane	83	116 (26)	101 (26)	70 (24)	114 (63)	38 (44)	65 (52)	21
H(3)	z = x × y	Diff.‡	106 (37)	126 (37)	94 (34)	12 (90)	5 (63)	83 (74)	–
	x‖a	298	217 (26)	238 (27)	157 (21)	121 (64)	41 (40)	155 (40)	21
	y‖b*	83	110 (26)	104 (26)	72 (21)	94 (63)	41 (39)	81 (39)	21
	z‖c	Diff.‡	107 (37)	134 (37)	85 (30)	27 (90)	0 (56)	74 (56)	–

† The origin of each coordinate system is defined by the geometrical center of the atoms included in the rigid body.
‡ Diff. = difference between values obtained at 298 K and 83 K.

Table 5. Covalent bond lengths (Å) and angles (°)

Values in square brackets have been corrected for rigid-body motion.

	83 K	298 K	α-Glycine 298 K*
C(1)–O(1)	1·259 (1) [1·263]	1·258 (1) [1·271]	1·250 (1) [1·261]
C(1)–O(2)	1·250 (1) [1·252]	1·247 (2) [1·255]	1·251 (1) [1·261]
C(2)–N	1·476 (1) [1·478]	1·473 (1) [1·483]	1·476 (1) [1·490]
C(1)–C(2)	1·525 (1) [1·527]	1·531 (1) [1·538]	1·526 (1) [1·539]
N–H(1)	1·052 (2) [1·053]	1·053 (1) [1·058]	1·054 (2) [1·062]
H–H(2)	1·044 (1) [1·047]	1·040 (2) [1·052]	1·025 (2) [1·033]
N–H(3)	1·037 (1) [1·040]	1·034 (2) [1·042]	1·037 (2) [1·042]
C(2)–H(4)	1·092 (2) [1·095]	1·086 (3) [1·097]	1·089 (2) [1·099]
C(2)–H(5)	1·094 (2) [1·097]	1·093 (3) [1·106]	1·090 (2) [1·099]
C(2)–C(1)–O(1)	117·8 (1)	117·7 (1)	117·5 (1)
C(2)–C(1)–O(2)	116·5 (1)	116·5 (1)	117·1 (1)
O(1)–C(1)–O(2)	125·6 (1)	125·8 (1)	125·5 (1)
C(1)–C(2)–N	111·3 (1)	111·5 (1)	111·9 (1)
C(2)–N–H(1)	112·2 (1)	112·3 (1)	112·1 (1)
C(2)–N–H(2)	107·8 (1)	107·9 (1)	110·4 (1)
C(2)–N–H(3)	110·8 (1)	110·7 (1)	111·7 (1)
H(1)–N–H(2)	108·3 (1)	108·1 (2)	107·1 (2)
H(1)–N–H(3)	108·8 (1)	108·9 (2)	108·7 (2)
H(2)–N–H(3)	108·9 (1)	108·9 (2)	106·6 (2)
C(1)–C(2)–H(4)	111·5 (1)	110·1 (2)	110·5 (1)
C(1)–C(2)–H(5)	108·7 (1)	108·3 (2)	108·8 (1)
N–C(2)–H(4)	108·8 (1)	108·8 (2)	109·1 (1)
N–C(2)–H(5)	108·1 (1)	108·0 (2)	108·5 (1)
H(4)–C(2)–H(5)	108·3 (2)	109·0 (3)	108·0 (2)

* Jönsson & Kvick (1972).

The thermal-motion analyses show that the molecule librates considerably around an axis approximately parallel to the crystallographic c axis. This direction also closely coincides with the C(1)–C(2) and N—H(1)···O(1) bond directions. The values associated with the principal axes of the librational tensor (L) are found to be 0·0195 (0·0058), 0·0036 (0·0008) and

0·0022 (0·0006) rad² (values in parentheses refer to the 83 K study). The largest librational motion is evidently reduced from 8·0 to 4·4° by cooling the crystal from 298 K to 83 K.

Thermal expansion in cell dimensions is caused by the anharmonic terms in the intermolecular potential. It has also been shown (Williams, 1972) that the thermal expansion is proportional to the mean-square amplitude of vibration with a proportionality factor depending on the anharmonicity. The observed anisotropy of L therefore suggests that the unit cell may be expected to shrink least along the c axis or helix direction upon cooling. In fact, the proportional change in a is approximately three times that of the c dimension (refer to Table 1).

The translational motion is more isotropic with values along the principal axes of the translational tensor (T) of 0·0210 (0·0078), 0·0142 (0·0057) and 0·0120 (0·0043) Å². These axes coincide closely with the crystallographic b*, a and c directions, respectively.

The thermal-motion analysis employing model (III), where the atoms C(2), N, H(1), H(2) and H(3) constitute the rigid body, shows interesting details. At 298 K this rigid body librates as a part of the entire molecule (i.e. major axis of libration parallel to the c-axis direction). This motion is considerably reduced at the lower temperature. This segment of the molecule, however, also shows large independent librations around the C(2)—N bond direction, and this libration is hardly affected by the reduction in temperature. The
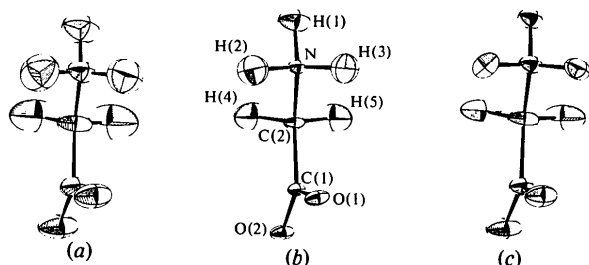
Fig. 3. Molecular conformation in γ-glycine with thermal ellipsoids drawn to enclose 74% probability. (a) 298K, (b) 83 K, (c) difference ellipsoids generated from $U_{ij}(298$ K$) - U_{ij}(83$ K$)$.

results presented in Table 4 show that the mean-square amplitude of librational motion around the c direction is reduced from 0·0155 to 0·0081 rad^2 whereas the motion around the C(2)—N direction is only reduced from 0·0126 to 0·0114 rad^2. This observation can partly be understood in terms of the large zero-point vibrations for the H atoms and is in agreement with the results of a normal coordinate analysis on γ-glycine (Destrade, Garrigou-Lagrange & Forel, 1971). This analysis shows the existence of a low-frequency torsional mode (13·6 mm^{-1}) around the C—C direction and a torsional mode of higher frequency (55·3 mm^{-1}) around the C—N direction. It is well known that the reduction of the vibrational mean-square amplitudes of atoms caused by a decrease in temperature is considerably larger for low-frequency vibrations.

The thermal motions of the atoms are illustrated in Fig. 3 where the thermal ellipsoids at the 74% probability level are given for the two temperatures. The effect of cooling is illustrated by difference ellipsoids generated from $U_{ij}($diff.$) = U_{ij}(298$ K$) - U_{ij}(83$ K$)$.

The molecular structure

The glycine molecule is in the amphionic (zwitterion) form. The atomic notation used in this paper is given in Fig. 3. The intramolecular distances and angles are presented in Table 5. The covalent bond distances and angles observed at the two temperatures are in excellent agreement [R_d = $\sum$ distances (83 K)/$\sum$ distances (298 K) = 1·001]. The agreement, however, worsens slightly when the rigid-body correction is applied (R_d = 0·995) indicating that in this case the rigid-body model for correcting bond distances results in a minor overcorrection.

The geometrical details of the glycine molecule in the γ-glycine structure only deviate from those found in α-glycine for the bonds affected by the difference in hydrogen bonding in the two structures.

The plane through the atoms C(1), C(2), N is given in Table 6, together with the torsion angles. The dihedral angle between the planes defined by atoms

Table 6. *Deviations* (Å) *from the plane defined by atoms* C(1), C(2) *and* N, *and torsional angles* (°)

The equations of the plane are

$$0·29445X + 0·95280Y + 0·07393Z - 0·84052 = 0 \ (83 \text{ K}),$$
$$0·28358X + 0·95649Y + 0·06810Z - 0·82324 = 0 \ (298 \text{ K}).$$

(X, Y, Z are the atomic coordinates of a point in the orthogonal coordinate system defined by the a^*, b and c directions.)

	83 K	298 K		83 K	298 K
N	0	0	H(1)	0·0311 (18)	−0·0240 (25)
C(1)	0	0	H(2)	0·8519 (13)	−0·8529 (25)
C(2)	0	0	H(3)	−0·8401 (18)	0·8345 (25)
O(1)	−0·2989 (7)	−0·2960 (12)	H(4)	0·8646 (19)	−0·8628 (42)
O(2)	0·2540 (8)	0·2497 (17)	H(5)	−0·9057 (19)	0·9105 (33)

Torsion angles are defined according to the IUPAC–IUB Commission on Biochemical Nomenclature (1970) convention.

	83 K	298 K
H(1)–N–C(2)–C(1)	−178·2 (1)	−178·6 (1)
H(2)–N–C(2)–C(1)	−59·0 (1)	−59·6 (1)
H(3)–N–C(2)–C(1)	60·1 (1)	59·5 (1)
N–C(2)–C(1)–O(1)	−15·6 (1)	−15·4 (1)
N–C(2)–C(1)–O(2)	166·9 (1)	167·1 (1)

C(1), O(1), O(2) and by C(1), C(2), N is 14·5° at 83 K (14·3° at 298 K). These values are slightly smaller than the corresponding angle of 18·9° in α-glycine (Jönsson & Kvick, 1972).

Hydrogen bonds

The geometrical details of the three unique hydrogen bonds are given in Table 7 and illustrated in Fig. 4. The most obvious differences in the bond lengths at the two temperatures can be found in the hydrogen-bond parameters. The differences in N···O distances for the three bonds are 0·16 (3), 0·028 (3) and 0·045 (2) Å, while for the corresponding H···O distances the differences are 0·014 (4), 0·035 (4) and 0·050 (4) Å. The smallest difference occurs for the hydrogen bond N—H(1)···O(1) lying approximately parallel to the crystallographic c axis.

The structure is further stabilized by two short N···O contacts. The shortest contact [2·885 (1) Å at

Table 7. *Distances* (Å) *and angles* (°) *for the hydrogen bonds*

Symmetry code: (i) $x, y, z - 1$; (ii) $1 - x + y, 1 - x, \frac{1}{3} + z$; (iii) $-x + y, -x, \frac{1}{3} + z$.

	N–H···O	N···O	N–H	H···O	∠N–H···O
83 K	N–H(1)···O(1)^i	2·793 (2)	1·052 (2)	1·749 (2)	171·2 (1)
298 K		2·809 (2)	1·053 (2)	1·763 (3)	171·3 (1)
Diff.*		0·016 (3)	0·001 (3)	0·014 (4)	0·1 (1)
83 K	N–H(2)···O(2)^{ii}	2·781 (2)	1·044 (1)	1·793 (2)	156·5 (1)
298 K		2·809 (2)	1·040 (2)	1·828 (3)	155·8 (1)
Diff.*		0·028 (3)	−0·004 (2)	0·035 (4)	−0·7 (1)
83 K	N–H(3)···O(1)^{iii}	2·942 (1)	1·037 (1)	1·910 (2)	172·7 (1)
298 K		2·987 (2)	1·034 (2)	1·960 (3)	171·9 (1)
Diff.*		0·045 (2)	−0·003 (2)	0·050 (4)	−0·8 (1)

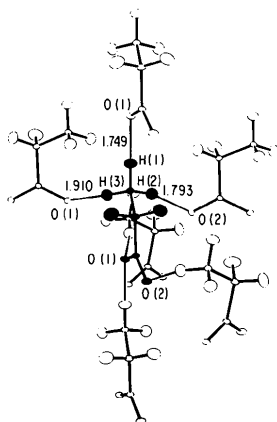* Differences between distances and angles observed at 298 K and 83 K.

Fig. 4. An illustration of the six hydrogen bonds around one molecule.

83 K] is found between the N atom and the O(1) atom $(-y, x - y, \frac{2}{3} + z)$. This contact is not classified as a hydrogen bond since the three O···H distances [O(1)···H(1) 2·827 (2), O(1)···H(2) 2·532 (2), O(1)···H(3) 2·771 (2) Å] all are well within the range of normal van der Waals contacts. Another electrostatic interaction is found between the N atom and the O(2) atom at $(-y, x - y - 1·0, \frac{2}{3} + z)$ with a separation of 3·017 (2) Å [O(2)···H(1) = 2·847 (2), O(2)···H(3) = 2·659 (2) Å].

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X-ray Studies on Crystalline Complexes Involving Amino Acids.
IV. The Structure of L-Arginine L-Ascorbate*

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Abstract

L-Arginine ascorbate, $C_6H_{15}N_4O_2^+.C_6H_7O_6^-$, a 1:1 crystalline complex between the amino acid arginine and the vitamin ascorbic acid, crystallizes in the monoclinic space group $P2_1$ with two formula units in a cell of dimensions $a = 5·060$ (8), $b = 9·977$ (9), $c = 15·330$ (13) Å, $\beta = 97·5$ (2)°. The structure was solved by the symbolic addition procedure and refined to an R of 0·067 for 1501 photographically observed reflec-