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Acetylglycine-*N*-methylamide

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Abstract. $C_5H_{10}N_2O_2$, monoclinic, $C2/c$, $Z=4$, $a=8{\cdot}352\ (3)$, $b=4{\cdot}934\ (3)$, $c=17{\cdot}642\ (8)$ Å, $\beta=94{\cdot}47\ (8)°$; $D_m=1{\cdot}19$, $D_x=1{\cdot}193$ g cm^{-3}. The final R value is 0·128 for 559 observed reflexions. The crystal exhibits an orientational disorder with an apparent molecular symmetry of 2. The dihedral angle between two peptide planes is 97°. The torsion angles ψ and φ are 109° and −21°, respectively. The conformation of the peptide backbone is very close to that of polyglycine II.

Introduction. Infrared spectra of this compound have been studied by Moriwaki, Tsuboi, Shimanouchi & Mizushima (1959) and by Koyama & Shimanouchi (1968), but the conformation of the molecule has not been determined in detail.

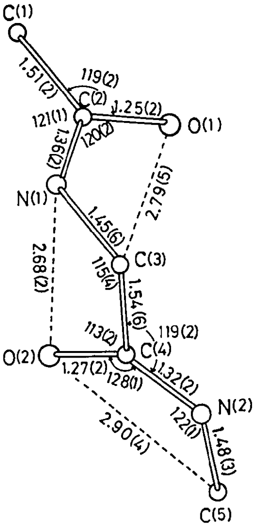

Fig. 1. Interatomic distances (Å) and angles (°) with their estimated standard deviations.

The sample was supplied by Professor Tsuboi and Dr Koyama, and recrystallized from ethyl acetate. The crystals are colourless flat plates with a well developed {001} form and are easily cleaved. Cell dimensions were calibrated with copper powder lines superposed on Weissenberg photographs. Intensity data were collected from integrated equi-inclination Weissenberg photographs around the a and b axes, $0kl \sim 5kl$, $h0l \sim h3l$, and around [110] for the zero layer with Cu $K\alpha$ radiation. The intensities were estimated visually. No absorption correction was applied.

Since the molecule has neither a centre of symmetry nor a twofold axis, the structure analysis was attempted on the basis of the space group Cc. A trial structure was deduced from a sharpened Patterson map and packing considerations. Block-diagonal least-squares refinement with isotropic temperature factors gave an R of 0·27. Three more cycles of full-matrix least-squares with anisotropic temperature factors reduced R to 0·16. Although the refinement had converged at this stage, there were several improbable bond distances, such as 1·95 for C–C and 1·11 Å for C–N. An examination of a difference map and the thermal-vibration ellipsoids of the atoms suggested that the crystal exhibits an orientational disorder with the apparent molecular symmetry of 2 coincident with a twofold axis in the space group $C2/c$. However, refinement of the parameters in $C2/c$ was unsuccessful ($R=0{\cdot}23$). Therefore, the refinement of the disordered model in Cc was continued by full-matrix least-squares calculations. R dropped to 0·12. Although several improbable bond lengths were again obtained, the average values of the corresponding bond distances between two mole-

Table 1. *Atomic parameters with their estimated standard deviations*

The anisotropic temperature factors are of the form: $\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

(*a*) Heavy atoms (all values are $\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−1746 (19)	4924 (37)	795 (9)	191 (17)	556 (58)	27 (3)	81 (28)	8 (6)	−17 (12)
C(2)	−581 (19)	5699 (24)	1455 (9)	194 (24)	307 (41)	55 (5)	25 (23)	36 (8)	9 (9)
C(3)	98 (67)	8495 (13)	2599 (27)	99 (32)	341 (21)	58 (14)	−25 (24)	−7 (19)	7 (10)
C(4)	288 (10)	6398 (24)	3249 (8)	83 (11)	241 (38)	57 (4)	−67 (15)	30 (6)	−23 (8)
C(5)	1981 (34)	4309 (56)	4286 (16)	403 (48)	828 (122)	49 (6)	52 (45)	33 (11)	66 (19)
N(1)	−962 (8)	7662 (15)	1951 (5)	99 (7)	442 (29)	63 (3)	68 (16)	5 (5)	39 (8)
N(2)	1641 (7)	6360 (15)	3684 (4)	109 (8)	568 (37)	58 (3)	−14 (15)	20 (4)	−75 (9)
O(1)	797 (20)	4698 (39)	1501 (6)	120 (10)	520 (34)	47 (5)	154 (14)	17 (8)	18 (15)
O(2)	−853 (21)	4700 (40)	3229 (6)	143 (11)	521 (34)	46 (5)	162 (14)	18 (8)	1 (14)

Table 1 (*cont.*)

(*b*) Hydrogen atoms (positional parameters $\times 10^3$)

	x	y	z	B(Å^2)
H(1)	−210	859	189	5·0
H(2)	251	785	360	5·0
H(3)	−19	1042	276	5·0
H(4)	133	864	233	5·0

cules related by the pseudo-twofold axis were found to be generally quite reasonable: C(1)–C(2) and C(1′)–C(2′), for example, were 1·44 and 1·64 Å, respectively, while their mean value was 1·54 Å. Moreover, each atomic parameter in one molecule had a strong correlation with the corresponding value in the related molecule. These observations strongly suggested that the true space group of this crystal is *C*2/*c*. Atomic positions in the disordered structure in the space group *Cc* were adjusted so as to conform to a strict twofold symmetry, and the refinement was carried out in *C*2/*c* again. *R* was reduced to 0·13, and the molecular dimensions were found to be reasonable within their estimated deviations. The atomic positions in the previous model (*C*2/*c*, $R=0{\cdot}23$) deviated slightly from those obtained in the new refinement. The refinement in the non-centrosymmetric space group *Cc* was quite effective for obtaining these shifts of positional parameters. Four hydrogen atom positions, other than those of the methyl groups, were calculated with C–H and N–H distances of 1·08 and 1·05 Å, respectively, but were not refined. Two more cycles of refinement were carried out for all the observed reflexions except six strong ones. The final *R* value was 0·119 (0·128 including these strong reflexions). The weighting scheme used was $w=1/(a+b|F_o|+c|F_o|^2)$, where $a=1{\cdot}25$, $b=0{\cdot}30$ and $c=0{\cdot}08$. Atomic scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The final atomic parameters are listed in Table 1.*

Discussion. Bond lengths and angles are shown in Fig. 1. They are in good agreement with the standard values for peptides (Pauling & Corey, 1953) and the values in other acetyl amino acid *N*-methylamides (Ichikawa & Iitaka, 1969; Matsuzaki & Iitaka, 1971). The molecule is composed of two peptide planes whose dihedral angle is 97°. The conformation of the peptide backbone is represented by two angles, ψ and φ (Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, 1966). The angle of internal rotation about N(1)–C(3), ψ, is 109° and C(2) is *gauche* to C(4). The angle φ about C(3)–C(4) is −21°, and N(1) is *trans* to N(2). This conformation is very close to that of polyglycine II proposed by Crick & Rich (1955).

The molecular arrangement is shown in Figs. 2 and 3. Intermolecular N–H···O hydrogen bonds extend along [110] and [$1\bar{1}0$] to form a two-dimensional network. This network holds the molecules together in sheets parallel to the (001) plane. This sheet structure

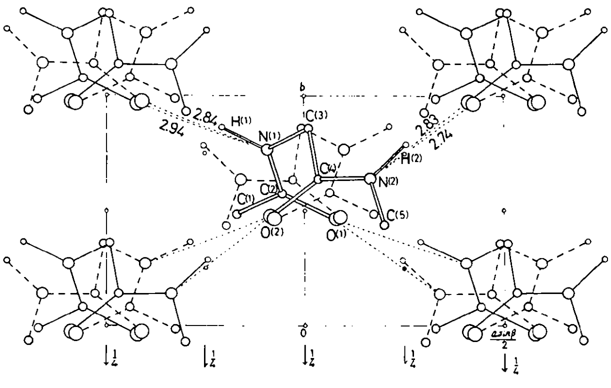

Fig. 2. Projection of the structure along the *c* axis. Molecules related by the *c* glide are omitted.

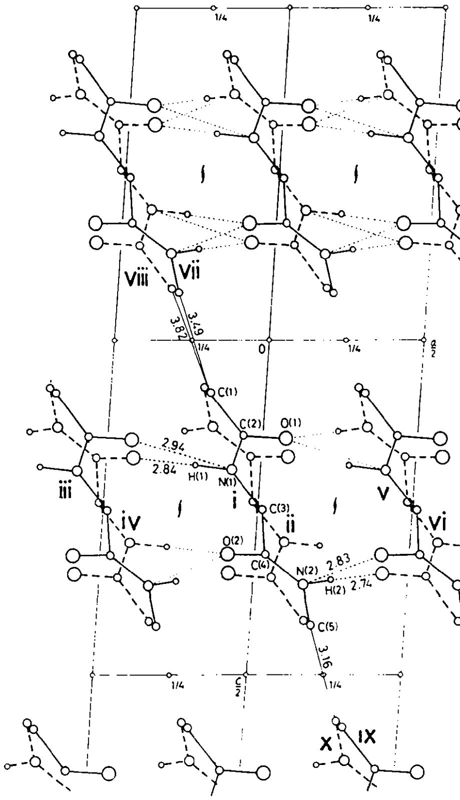

Fig. 3. Projection of the structure along the *b* axis. Symmetry operators: (i) x,y,z; (ii) $-x,y,-z+\frac{1}{2}$; (iii) $x-\frac{1}{2},y+\frac{1}{2},z$; (iv) $-x-\frac{1}{2},y+\frac{1}{2},-z+\frac{1}{2}$; (v) $x+\frac{1}{2},y+\frac{1}{2},z$; (vi) $-x+\frac{1}{2},y+\frac{1}{2},-z+\frac{1}{2}$; (vii) $x-\frac{1}{2},-y+\frac{1}{2},z-\frac{1}{2}$; (viii) $-x-\frac{1}{2},-y+\frac{1}{2},-z$; (ix) $x+\frac{1}{2},-y+\frac{1}{2},z+\frac{1}{2}$; (x) $-x+\frac{1}{2},-y+\frac{1}{2},-z+1$.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30579 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

reasonably explains the pronounced cleavage parallel to (001).

Molecule i (see Fig. 3) can form N–H···O hydrogen bonds with either of the molecules iii and iv and also with either v or vi in a disordered state. However, hydrogen-bond distances of $N(1^{i})\cdots O(2^{iv})$ (2·84) and of $N(2^{i})\cdots O(1^{vi})$ (2·74 Å) are slightly shorter than those of $N(1^{i})\cdots O(1^{iii})$ (2·94) and $N(2^{i})\cdots O(2^{v})$ (2·83 Å). Therefore it is likely that molecule i prefers to occupy the position in the neighbourhood of iv rather than of iii. On the other hand, an abnormally short methyl–methyl contact is found between i and x [$C(5^{i})\cdots C(5^{x})$, 3·16 Å]. Molecule i, therefore, should prefer also to occupy the site in the neighbourhood of molecule ix rather than x. This arrangement of the molecule, with i situated in the neighbourhood of iv, vi and ix, corresponds to the space group $P2_1/n$, which must be the basic structure in an ordered state. The crystal is probably partially ordered; diffuse spots are observed at the reciprocal lattice points forbidden by the space group $C2/c$: hkl with $h+k$ odd and $h0l$ with h and l odd.

All crystallographic computations were performed on the HITAC 5020E and 8800 computers of the Computer Centre of the University of Tokyo using the program system UNICS (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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1,1,1-Trimethylhydrazinium 3-Carbomethoxy-5-pyrazolecarboxylate

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Abstract. $[(CH_3)_3NNH_2^+]$ $[CH_3OCO\text{–}(C_3N_2H_2)\text{–}COO^-]$, $(C_9H_{16}N_4O_4)$, $M=244·16$, monoclinic, $C2/c$, $a=18·227(2)$, $b=8·019(1)$, $c=18·284(2)$ Å, $\beta=113·68(1)°$ $V=2447·5$ Å^3, $Z=8$, $D_x=1·325$, $D_m=1·327$ g cm^{-3}. Full-matrix least-squares refinement of 1669 reflections $[I>3\sigma(I)]$ collected with θ–2θ scans on a Syntex $P2_1$ diffractometer yielded a final R of 0·043. Multiple hydrogen bonds are found between the cations and anions.

Introduction. The space group and approximate unit-cell dimensions were determined from a study carried out on a Syntex $P2_1$ diffractometer. The cell parameters were later refined using the Bragg angles of Cu $K\alpha_1$ peaks of 24 high-angle reflections measured on a GE XRD-5 diffractometer (Cu $K\alpha_1=1·54050$ Å). A crystal which measured $0·27\times0·31\times0·26$ mm perpendicular to (111), $(1\bar{1}1)$ and $(10\bar{1})$, respectively, was selected for mounting on the Syntex diffractometer. Molybdenum $K\alpha$ radiation (0·71069 Å) monochromatized by a graphite crystal was used for data collection. The θ–2θ scan technique was employed with scans ranging from 1° below the $K\alpha_1$ peak to 1° above the $K\alpha_2$ peak and with scan rates determined in the following way. A preliminary two second count was made using the stationary-crystal–stationary-counter technique. All reflections with counts below 150 were collected at the minimum scan rate of 1° min^{-1}; all those above 1500 were collected at the maximum rate of 5° min^{-1}; and the remainder were collected at a rate specified by the algorithm: scan rate = 0·002963 × preliminary count + 0·5556. Background measurements were taken at both ends of the scan range, each for a time equal to one-half of the scan time. Four standard reflections were monitored every 46 reflections; no intensity change was observed throughout the data-collection period. In