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N-Acetylglycyl-L-lysine Methyl Ester Acetate*

BY D. M. SALUNKE AND M. VIJAYAN

Molecular Biophysics Unit, Indian Institute of Science, Bangalore-560 012, *India*

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Abstract. $C_{11}H_{22}N_3O_4^+.C_2H_3O_2^-$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}511\,(2)$, $b = 14{\cdot}588\,(4)$, $c = 21{\cdot}109\,(4)$ Å, $Z = 4$. The structure has been solved using *MULTAN* and refined to $R = 0{\cdot}079$ for 993 observed reflections. The fully extended lysine side chain in the molecule is staggered between the main-chain amino and carbonyl groups. The dipeptide molecules in the crystal structure are arranged in twofold helices centred on 2_1 screw axes. These helices are interconnected through interactions involving the acetate and the side-chain amino groups. Each acetate group bridges two adjacent side-chain amino groups, related by an **a** translation, giving rise to an infinitely long chain of alternating negatively charged carboxylate and positively charged amino groups.

Introduction. The crystal structure of the acetate of the protected dipeptide *N*-acetylglycyl-L-lysine methyl ester is reported here as part of a programme of X-ray studies of crystalline complexes involving amino acids and peptides (Bhat, Sudhakar & Vijayan, 1980; Sudhakar, Bhat & Vijayan, 1980, and references therein). The programme is aimed at exploring, at atomic resolution, the possible geometrical features of the interactions of the amino acid residues in proteins among themselves as well as with other molecules. In this context, the present structure was expected to provide, among other things, a possible geometrical description of the interactions of the amino group in the lysyl side chain, which in fact is the only positively charged group in the dipeptide, with a free carboxylate ion in a protein-like environment.

Elongated rectangular crystals of the compound, obtained commercially from Sigma Chemical Co., USA, were grown by slow evaporation of a solution in methanol. The intensity data were collected on a CAD-4 computer-controlled diffractometer from a specimen of approximate dimensions $0{\cdot}15 \times 0{\cdot}18 \times 0{\cdot}90$ mm using graphite-monochromated Cu $K\alpha$ radiation up to a Bragg angle of 65°. Of the 1351 reflections measured in this range, 993 had $I > 2\sigma(I)$ and were subsequently used for structure refinement. The data were corrected for Lorentz and polarization factors. The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the block-diagonal structure-factor least-squares method. The heavy atoms and the H atoms were given anisotropic and isotropic temperature factors respectively. The refinement converged at $R = 0{\cdot}079$. The weighting scheme was of the form $1/(a + bF_o + cF_o^2)$ where $a = 1{\cdot}00$, $b = -0{\cdot}107$ and $c = 0{\cdot}0039$. The scattering factors for the non-hydrogen atoms and the H atoms were taken from Cromer & Waber (1965) and Stewart, Davidson & Simpson (1965) respectively. The final coordinates of the non-hydrogen atoms are given in Table 1.*

* X-ray Studies on Crystalline Complexes Involving Amino Acids and Peptides. VI. Part V: Sudhakar, Bhat & Vijayan (1980).

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36202 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* (*Hamilton*, 1959) *of the non-hydrogen atoms*

Estimated standard deviations are given in parentheses.

	x	*y*	*z*	B_{eq} (Å^2)
C(1)	5121 (21)	982 (6)	5804 (5)	3·1 (3)
C(2)	5592 (20)	1945 (5)	5988 (4)	3·8 (5)
O(3)	4324 (14)	2381 (4)	6363 (3)	4·5 (4)
N(4)	7542 (16)	2347 (3)	5722 (3)	3·6 (4)
C(5)	8126 (19)	3284 (6)	5878 (4)	3·7 (5)
C(6)	6186 (18)	3945 (6)	5638 (4)	3·0 (4)
O(7)	4940 (14)	3818 (4)	5178 (3)	4·2 (4)
N(8)	5995 (14)	4726 (5)	5996 (3)	3·2 (4)
C(9)	4217 (17)	5414 (6)	5805 (4)	3·4 (4)
C(10)	4804 (22)	5913 (6)	5189 (5)	4·7 (5)
O(11)	3362 (16)	6341 (6)	4896 (4)	5·3 (5)
O(12)	7152 (13)	5850 (4)	5025 (3)	4·2 (4)
C(13)	7853 (24)	6327 (8)	4443 (5)	5·1 (6)
C(14)	3913 (21)	6142 (6)	6322 (5)	4·2 (5)
C(15)	6024 (18)	6752 (6)	6482 (4)	3·5 (4)
C(16)	5361 (20)	7414 (6)	7013 (4)	3·8 (5)
C(17)	7439 (22)	8040 (6)	7179 (4)	4·2 (5)
N(18)	6810 (15)	8660 (5)	7715 (3)	3·2 (4)
C(19)	9966 (22)	5595 (8)	8033 (5)	4·4 (5)
C(20)	8336 (17)	5032 (6)	7606 (4)	3·1 (4)
O(21)	6184 (14)	4897 (5)	7808 (3)	4·4 (4)
O(22)	9077 (12)	4708 (5)	7099 (3)	3·2 (3)

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Discussion. The bond lengths and angles in the structure are normal and do not merit comment. The torsional angles that define the main-chain and the side-chain conformation of the protected dipeptide (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are given in Table 2. As can be seen from the table, the glycyl residue falls in the region corresponding to the collagen structure in conformational space whereas the lysyl residue falls in the region corresponding to the right-handed helices. The peptide groups in the molecule are *trans* and planar within experimental error. Descriptions of the side chain of lysine are available so far from the crystal structures of L-lysine.HCl.$2H_2O$ (Wright & Marsh, 1962), L-lysine L-aspartate (Bhat & Vijayan, 1976) and DL-lysine.HCl (Bhaduri & Saha, 1979). In the first two of these structures, as well as in the present structure, the side chain has an extended all-*trans* conformation which appears to be energetically the most favourable (Bhat, Sasisekharan & Vijayan, 1979). The main difference between the present structure and those reported earlier pertains to the value of χ^1 which defines the orientation of the side chain with respect to the amino N and the carbonyl (or carboxyl in amino acids) C atoms. Sterically the most favourable value of χ^1 is around $-60°$ with C^γ *trans* to the C atom and *gauche* to the N atom. The observed conformation of the lysine molecule in L-lysine.HCl.$2H_2O$ and L-lysine L-aspartate corresponds to this possibility. The next most favourable conformation with C^γ *trans* to the N atom and *gauche* to the C atom ($\chi^1 \sim 180°$) is observed in DL-lysine.HCl. In the present structure, however, χ^1 is around 60°, corresponding to the sterically least favourable conformation with C^γ staggered between the C and the N atoms.

Table 2. *Torsional angles and hydrogen-bond parameters*

φ_1	C(2)–N(4)–C(5)–C(6)	−66·0 (1·1)°
ψ_1	N(4)–C(5)–C(6)–N(8)	151·5 (0·8)
φ_2	C(6)–N(8)–C(9)–C(10)	−68·9 (1·0)
ψ_2^*	N(8)–C(9)–C(10)–O(12)	−19·1 (1·2)
ω_0	C(1)–C(2)–N(4)–C(5)	−179·9 (0·8)
ω_1	C(5)–C(6)–N(8)–C(9)	179·1 (0·7)
ω_2^*	C(9)–C(10)–O(12)–C(13)	−179·1 (0·8)
χ^1	N(8)–C(9)–C(14)–C(15)	64·9 (1·1)
χ^2	C(9)–C(14)–C(15)–C(16)	−179·1 (0·8)
χ^3	C(14)–C(15)–C(16)–C(17)	−179·5 (0·8)
χ^4	C(15)–C(16)–C(17)–N(18)	−177·7 (0·8)

N(4)···O(7)^b	2·87 (1) Å	H1(N4)–N(4)···O(7)	13 (7)°
N(8)···O(22)^a	2·88 (1)	H1(N8)–N(8)···O(22)	10 (5)
N(18)···O(3)^c	2·76 (1)	H1(N18)–N(18)···O(3)	11 (5)
N(18)···O(22)^d	2·76 (1)	H2(N18)–N(18)···O(22)	12 (8)
N(18)···O(21)^c	2·68 (1)	H3(N18)–N(18)···O(21)	13 (4)

Symmetry code: (*a*) *x*,*y*,*z*; (*b*) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (*c*) $1-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; (*d*) $2-x, \frac{1}{2}+y, 1\frac{1}{2}-z$.

* O(12) is considered to be equivalent to a N atom in the definition of these torsion angles.

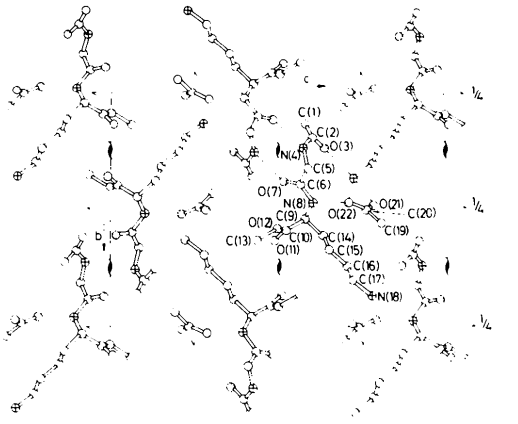

Fig. 1. Crystal structure as viewed along the *a* axis. The broken lines indicate a set of crystallographically non-equivalent hydrogen bonds.

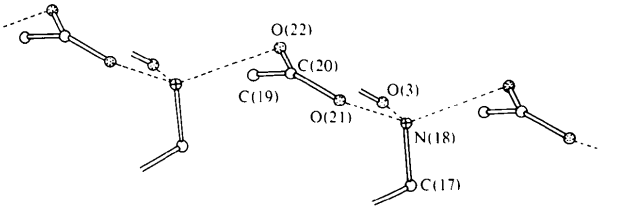

Fig. 2. The arrangement of the side-chain amino and the acetate groups in the crystal structure. The broken lines indicate hydrogen bonds.

The crystal structure of the compound is given in Fig. 1. The parameters of the hydrogen bonds which contribute to the stability of the structure are listed in Table 2. The dipeptide molecules are arranged into twofold helices centred on 2_1 screw axes parallel to the *a* axis. These helices are stabilized by hydrogen bonds between peptide amino and carbonyl groups. The adjacent helices are interconnected through interactions involving the side-chain amino group of lysine and the acetate group. As can be seen from Fig. 2, each acetate group bridges two adjacent side-chain amino groups, related by an **a** translation, giving rise to an infinitely long chain of alternating negatively charged carboxylates and positively charged amino groups. The observed arrangement is of interest in relation to the possible modes of interactions of the lysine side chain with carboxylate groups.

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2-Amino-7-methoxy-3*H*-phenoxazin-3-one

BY R. G. BUCKLEY, J. CHARALAMBOUS AND K. HENRICK

Department of Chemistry, The Polytechnic of North London, London N7 8DB, England

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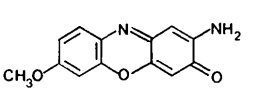
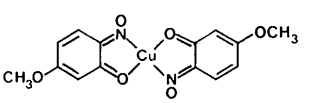
Abstract. $C_{13}H_{10}N_2O_3$, M_r = 242·23, monoclinic, $P2_1/n$ [equivalent positions $\pm(x, y, z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$], a = 21·976 (3), b = 3·901 (4), c = 12·523 (3) Å, β = 95·68 (2)°, U = 1068·3 (1·4) Å^3, Z = 4, D_c = 1·506 Mg m^{-3}, μ (Mo $K\alpha$) = 0·067 mm^{-1}, $F(000)$ = 504. The structure was solved from diffractometer data by direct methods and refined to R = 0·052 for 598 observed reflections. The phenoxazinone ring is almost planar and its geometry closely resembles that of the same heterocyclic fragment in the structure of the antibiotic actinomycin.

Introduction. In parallel with our chemical studies on the synthetic potential of the reactions of metal complexes of 2-nitrosophenols (monoximes of 1,2-quinones) with phosphines, amines and phenols (Charalambous, Kensett & Jenkins, 1977), we are investigating the X-ray structures of the heterocyclic products of these reactions. The phenoxazinone (1) reported here was obtained from the reaction of bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) (2) with 1,2-diaminoethane. Phenoxazines are of interest both as dyestuffs (Ionescu & Mantsch, 1967) and as natural products which show biological activity such as the antibiotics of the actinomycin group (Brockmann & Muxfeldt, 1958).



(1)



(2)

Data were collected from a crystal 0·38 × 0·10 × 0·02 mm. 1918 intensities were recorded ($3·0 \le \theta \le 30·0°$) on a Philips PW1100 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, a θ–2θ scan mode, and a constant scan width of 0·80°. Lp corrections were applied. No absorption correction was made. Equivalent reflections were averaged to give 598 unique observed intensities [$F > 6\sigma(F)$]. Cell dimensions were derived from the angular measurements of 25 strong reflections ($10·0 < \theta < 15·0°$). The structure was solved by multisolution Σ_2 sign expansion for terms with $E > 1·2$. All the non-hydrogen atoms were located from the E map with the second-highest combined figure of merit (2·766). The structure was refined by full-matrix least-squares calculations using isotropic thermal parameters. All the H atoms were located from a difference map and were included in the refinement without constraints. Neutral-atom scattering factors were used (Cromer & Mann, 1968). The refinement converged to R = 0·052 and $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|$ = 0·045 with $w = 1/(\sigma^2 F_o)$. The final coordinates are listed in Table 1, bond lengths and angles in Table 2.* Computations were performed with *SHELX* 76 (Sheldrick, 1976).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36204 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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