approximately planar [C(4)—O(4)—C(1′)—C(2′) = −178, O(4)—C(1′)—C(2′)—C(3′) = −173, C(1′)—C(2′)—C(3′)—C(4′) = 0°].

The crystal-packing diagram (Fig. 3) shows the presence of intermolecular hydrogen bonding between the O(9) hydrogen and the O(3) carbonyl oxygen along the *a* axis. The O(3)···O(9) hydrogen-bonding distance is 2·93 Å.

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L-Arginyl-L-glutamic Acid Dihydrate, $C_{11}H_{21}N_5O_5.2H_2O$

BY J. PANDIT, T. P. SESHADRI AND M. A. VISWAMITRA

Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science, Bangalore 560012, India

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Abstract. $M_r = 339{\cdot}35$, monoclinic, $P2_1$, $a = 11{\cdot}028\,(2)$, $b = 9{\cdot}583\,(2)$, $c = 16{\cdot}010\,(2)$ Å, $\beta = 96{\cdot}57\,(1)°$, $U = 1680{\cdot}85$ Å^3, $Z = 4$, $D_m = 1{\cdot}37$, $D_x = 1{\cdot}34$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 0{\cdot}85$ mm^{-1}, $F(000) = 728$, $T = 300$ K, $R = 0{\cdot}085$ for 2845 diffractometer-measured reflections $[F_o > 3\sigma(F_o)]$. The two molecules in the asymmetric unit have similar conformations except for a static disorder at the C^β and C^γ positions in one of the glutamic-acid side chains. An interesting feature of the crystal structure is a pair of hydrogen bonds between the guanidinium and γ-carboxylate groups of neighbouring molecules. This is the first such specific interaction observed between side chains of arginine and glutamic acid.

Introduction. The arginine side chain is expected to play an important role in the specific recognition process between nucleic acids and proteins. In view of this interest we have initiated a study of arginine-containing peptides and their complexes with nucleotides. We report here the first description of the crystal and molecular structure of an arginine-containing peptide.

Experimental. Thin, needle-like crystal, 0·075 × 0·075 × 0·625 mm, from aqueous solution of the compound (obtained from Bachem Inc.) by diffusion of ethanol; preliminary crystal data from rotation and Weissenberg photographs with Cu $K\alpha$ radiation, cell dimensions from 25 strong reflections, Enraf–Nonius CAD-4 diffractometer; density measurements (flotation in acetone/bromoform) indicated two molecules of the compound and four water molecules in the asymmetric unit, ω–2θ scans up to $\theta = 75°$, h −13–13, k 0–12, l 0–20, $\bar{2}10$ and $\bar{1}22$ monitored periodically, crystal stable to X-rays, correction for Lorentz and polarization but not for absorption; structure solved with *MULTAN* (Germain, Main, & Woolfson, 1971) and refined with *SHELX* (Sheldrick, 1976), block-diagonal least squares, isotropic, $R = 14{\cdot}8\%$. At this stage, other bond distances were normal, but C^α—C^β in the Glu side chain of molecule *B* was 1·84 Å. The difference map exhibited two peaks in the vicinity of C^β and C^γ, suggesting positional disorder. These two atoms were assigned two different positions corresponding to the positions indicated on the difference map [similar situations have been reported in the literature, for example a bond length 0·3 Å greater than expected in the structure of *p*-(*N*-methylbenzylidene)-*p*-methylaniline (Berstein, Bar & Christensen, 1976)]. Four cycles anisotropic refinement on *F* (temperature factor

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and occupancy for disordered atoms kept fixed in alternate cycles) indicated occupancies of disordered atoms all nearly 0·5; subsequent full-matrix refinement with half occupancies for these atoms, 26 out of the 50 H atoms located from difference Fourier map, the rest, except for those on the disordered side chain, fixed stereochemically, H atoms included in the last two cycles of refinement, $R = 8{\cdot}48\%$, $R_w = 8{\cdot}5\%$, $w = 1$, electron density in final difference map $\leq 0{\cdot}3$ e Å^{-3}, max. shift/e.s.d. = 3·438, av. shift/e.s.d. = 0·503, scattering factors from Cromer & Mann (1968), molecular diagrams drawn with *ORTEP* (Johnson, 1976).*

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for* C, N *and* O *atoms*

E.s.d.'s are in parentheses. $U_{\rm eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Molecule *A*				
N(1)	10513 (6)	6736 (9)	2183 (4)	29 (2)
C(2)	10822 (8)	6948 (8)	3106 (5)	28 (2)
C(3)	12056 (7)	7646 (9)	3329 (5)	29 (3)
C(4)	13125 (8)	6842 (11)	3049 (6)	43 (3)
C(5)	14341 (9)	7549 (11)	3354 (7)	46 (3)
N(6)	15409 (7)	6801 (9)	3144 (5)	40 (2)
C(7)	15922 (8)	5720 (10)	3595 (6)	34 (3)
N(8)	15541 (8)	5354 (9)	4326 (5)	42 (3)
N(9)	16829 (7)	5056 (9)	3296 (5)	39 (3)
C(10)	9824 (7)	7848 (8)	3401 (5)	24 (2)
O(11)	9441 (6)	8882 (6)	2970 (4)	34 (2)
N(12)	9407 (6)	7477 (7)	4098 (4)	24 (2)
C(13)	8418 (7)	8211 (9)	4458 (5)	26 (2)
C(14)	8159 (7)	7397 (9)	5249 (6)	29 (2)
C(15)	7167 (9)	8042 (11)	5688 (6)	44 (3)
C(16)	6831 (9)	7218 (11)	6437 (6)	39 (3)
O(17)	7627 (6)	6485 (8)	6857 (5)	46 (2)
O(18)	5778 (7)	7354 (12)	6613 (5)	70 (3)
C(19)	8803 (8)	9763 (9)	4701 (6)	30 (3)
O(20)	8023 (7)	10667 (7)	4505 (6)	63 (3)
O(21)	9819 (6)	9942 (7)	5090 (5)	42 (2)
Molecule *B*				
N(1)	10084 (6)	6690 (7)	7231 (4)	30 (2)
C(2)	10402 (7)	6926 (8)	8160 (5)	27 (2)
C(3)	11649 (9)	7573 (10)	8377 (7)	39 (3)
C(4)	12722 (8)	6773 (9)	8080 (5)	34 (3)
C(5)	13894 (8)	7472 (11)	8388 (6)	42 (3)
N(6)	14976 (6)	6824 (9)	8129 (4)	38 (2)
C(7)	15555 (7)	5744 (9)	8521 (5)	31 (2)
N(8)	15200 (8)	5229 (9)	9233 (5)	47 (3)
N(9)	16497 (7)	5178 (9)	8190 (5)	41 (2)
C(10)	9439 (7)	7946 (8)	8436 (5)	29 (2)
O(11)	9026 (6)	8882 (6)	7947 (4)	38 (2)
N(12)	9102 (7)	7748 (7)	9184 (5)	34 (2)
C(13)	8179 (10)	8670 (9)	9476 (8)	51 (4)
C(14*X*)	8103 (16)	8217 (16)	10494 (12)	18 (5)
C(15*X*)	7452 (16)	6822 (17)	10511 (9)	29 (5)
C(14*Y*)	7355 (22)	8024 (24)	10062 (12)	47 (7)
C(15*Y*)	8202 (20)	7780 (28)	10865 (13)	45 (8)
C(16)	7319 (12)	6667 (14)	11458 (8)	64 (5)
O(17)	8100 (6)	6229 (7)	12000 (4)	44 (2)
O(18)	6233 (8)	6820 (13)	11558 (5)	89 (4)
C(19)	8757 (8)	10182 (9)	9657 (6)	33 (3)
O(20)	7985 (6)	11136 (7)	9511 (5)	66 (2)
O(21)	9838 (7)	10318 (7)	9920 (6)	45 (3)
O*W*(1)	18617 (6)	3678 (7)	9030 (4)	42 (2)
O*W*(2)	15736 (7)	2220 (9)	9526 (5)	60 (3)
O*W*(3)	18725 (6)	3180 (7)	3962 (4)	41 (2)
O*W*(4)	15978 (7)	2167 (10)	4661 (5)	62 (3)

Discussion. The final atomic parameters are given in Table 1.

The α-amino and the guanidyl groups are protonated and hence positively charged, whereas the α-carboxyl and the γ-carboxyl groups are deprotonated and negatively charged. The bond lengths and angles (Fig. 1), apart from those involving disordered atoms, are comparable to the corresponding values observed in other structures containing arginine or glutamic acid. C(13*B*)—C(14*X*) and C(15*Y*)—C(16*B*) lie outside the range expected for a normal C—C single bond. As already mentioned, these atoms are disordered.

The arginyl and glutamyl side chains are extended on opposite sides of the peptide backbone (Fig. 2). The peptide bond is essentially planar in both molecules, with conformational angles (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) $\omega = -178{\cdot}2\ (7)°$ in molecule *A* and $-179{\cdot}2\ (7)°$ in *B*.

Considerable flexibility has been observed in the conformation of the arginine side chain (Bhat & Vijayan, 1977). In the present structure, the conformation is similar to that observed in arginine–HBr

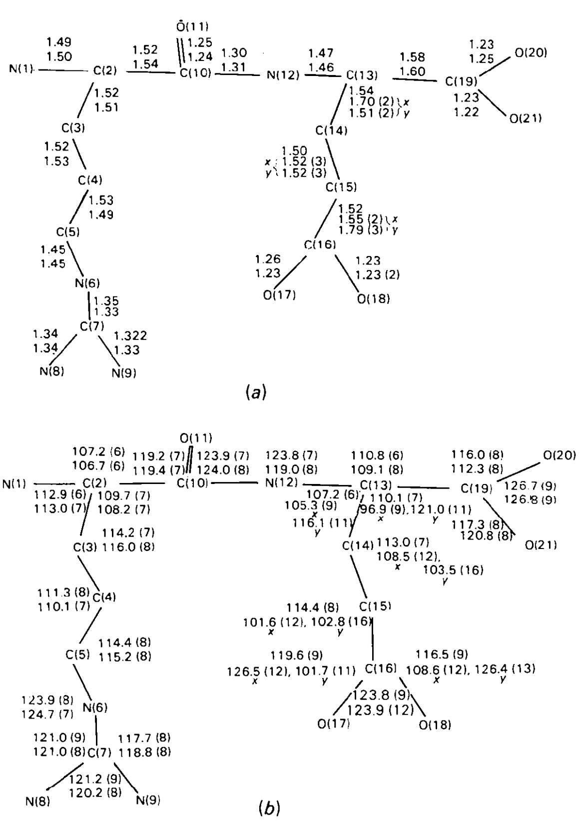

Fig. 1. (*a*) Bond distances (Å) for molecule *A* (upper) and molecule *B* (lower). E.s.d.'s are 0·01 Å unless otherwise indicated. *X* and *Y* refer to the two different positions of the disordered atoms. (*b*) Bond angles (°) for molecule *A* (upper) and molecule *B* (lower) with e.s.d.'s in parentheses. *X* and *Y* refer to the two different positions of the disordered atoms.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and torsion angles and figures illustrating the disorder and molecular packing have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38642 (23 pp.). Copies may be obtained through The Executive Secretary, 5 Abbey Square, Chester CH1 2HU, England.

(Mazumdar & Srinivasan, 1966) and arginine–HCl (Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970).

The glutamic-acid side chain in molecule *A* assumes an extended conformation with the torsion angles χ^1 and χ^2 about C^α—C^β and C^β—C^γ both nearly 180°. The dihedral angles χ^{31} and χ^{32}, which describe the conformation of the carboxyl group about the C^γ—C^δ bond, are 29·7 (13) and −152·5 (9)°, respectively. These are significantly different from the usually observed values of 0 and 180° (Bhat & Vijayan, 1977). The γ-carboxyl group is involved in four strong hydrogen bonds in the extended crystal structure. The present conformation seems to have the optimum geometry for forming these interactions.

The disorder in the Glu side chain of molecule *B* leads to two different conformations for the side chain (labelled *X* and *Y*), both of which are different from the conformation in molecule *A*.* In conformation *X*, χ^1 and χ^2 are −73·3 (13) and −173·2 (11)°, while in conformation *Y* they are 69·3 (17) and −167·2 (13)°. Both of these fall in the range of energetically favourable conformations according to the classical energy calculations of Ponnuswamy & Sasisekharan (1971). In molecule *A* χ^1 and χ^2 are 179·6 (7) and 176·3 (8)°.

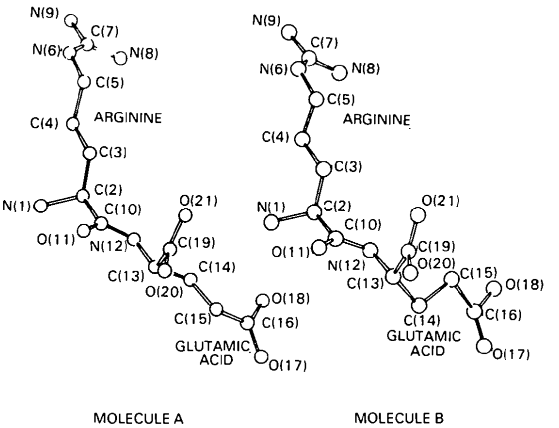

Fig. 2. View along **b** of the two independent molecules in the asymmetric unit.

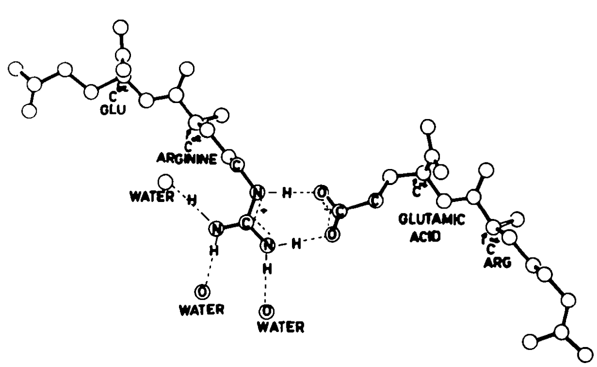

Fig. 3. Specific interaction between the guanidyl group and the γ-carboxylate group, viewed along the normal to the plane containing the interacting groups.

Table 2. *Hydrogen-bonding interactions*

Average e.s.d.'s are 0·01 Å and 5°.

A—H···*B*	*A*···*B* (Å)	∠*A*—H···*B*	Symmetry code for *B**	Unit-cell translation for *B*
N(1*A*)—H(1*A*)···O(17*B*)	2·69	171	(i)	0 0−1
N(1*A*)—H(2*A*)···O(11*B*)	2·79	150	(ii)	2−1 1
N(1*A*)—H(3*B*)···O*W*(1)	2·93	175	(ii)	3 0 1
N(6*A*)—H(11*A*)···O(18*B*)	2·79	171	(i)	1 0−1
N(8*A*)—H(12*A*)···O*W*(4)	3·01	163	(ii)	3 0 1
N(8*A*)—H(13*A*)···O*W*(4)	3·13	132	(i)	0 0 0
N(9*A*)—H(14*A*)···O(17*B*)	2·86	152	(i)	1 0−1
N(9*A*)—H(15*A*)···O*W*(3)	2·87	153	(i)	0 0 0
N(12*A*)—H(16*A*)···O(21*A*)	2·84	133	(ii)	2−1 1
N(1*B*)—H(1*B*)···O(17*A*)	2·71	170	(i)	0 0 0
N(1*B*)—H(2*B*)···O*W*(3)	2·83	177	(ii)	3 0 1
N(1*B*)—H(3*B*)···O(11*A*)	2·77	144	(ii)	2−1 1
N6(*B*)—H(11*B*)···O(18*A*)	2·73	175	(i)	1 0 0
N(8*B*)—H(12*B*)···O*W*(2)	2·97	143	(i)	0 0 0
N(8*B*)—H(13*B*)···O*W*(2)	3·02	162	(ii)	3 0 2
N(9*B*)—H(14*B*)···O*W*(1)	2·94	160	(i)	0 0 0
N(9*B*)—H(15*B*)···O(17*A*)	2·88	158	(i)	1 0 0
N(12*B*)—H(16*B*)···O(21*B*)	2·91	177	(ii)	2−1 2
O*W*(1)—H1*W*(1)···O(21*B*)	2·74	135	(ii)	3−1 2
O*W*(1)—H2*W*(1)···O(20*B*)	2·67	152	(i)	1−1 0
O*W*(2)—H1*W*(2)···O(18*B*)	2·65	162	(ii)	2−1 2
O*W*(2)—H2*W*(2)···O(20*B*)	2·69	176	(i)	1−1 0
O*W*(3)—H1*W*(3)···O(21*A*)	2·68	169	(ii)	3−1 1
O*W*(3)—H2*W*(3)···O(20*A*)	2·70	133	(i)	1−1 0
O*W*(4)—H1*W*(4)···O(18*A*)	2·65	173	(ii)	2−1 1
O*W*(4)—H2*W*(4)···O(20*A*)	2·71	172	(i)	1−1 0

* (i): x,y,z; (ii): $-x,\frac{1}{2}+y,-z$.

It is unusual to find disordered atoms in the middle of a side chain as seen here, rather than at the end. The main-chain α-carboxyl O atoms and the γ-carboxyl O atoms at the end of the Glu side chain are bound by strong hydrogen bonds which could explain why the disorder is confined to the C^β and C^γ atoms.

The crystal structure is stabilized by extensive hydrogen bonding and ionic interactions. Every possible proton donor or acceptor is involved in a hydrogen bond. Table 2 lists the parameters of the hydrogen bonds. A diagram showing the details of the molecular packing has been deposited.*

The guanidyl group of arginine can potentially donate five protons for H-bonding interactions (from one $N^\varepsilon H$ and two terminal NH_2 groups). Of these, $N^\varepsilon H$ and one NH_2 form a pair of nearly parallel hydrogen bonds with the γ-carboxylate group of Glu. The remaining NH_2 protons are involved in weak H bonds with water molecules (Fig. 3). This is the first time that such an interaction has been observed. In all other guanidinium carboxylate interactions reported so far, the carboxylate anion is bound to the terminal NH_2 groups (Salunke & Vijayan, 1981).

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* A figure illustrating this has been deposited. See deposition footnote.

* See deposition footnote.

Such a hydrogen-bonding scheme is compatible with a specific interaction between arginine and guanine in DNA, with O(6) and N(7) of guanine replacing the waters bound to the terminal NH_2 groups. Helene (1977) has proposed such a scheme for the specific recognition of a G.C base pair by arginylglutamic acid.

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Structure of DL-α-Methyl-*m*-tyrosine (MMT), $C_{10}H_{13}NO_3$

By Kenneth A. Satyshur and S. T. Rao

Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706, *USA*

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Abstract. $M_r = 195{\cdot}21$, monoclinic, $P2_1/c$, $a = 5{\cdot}933\,(1)$, $b = 9{\cdot}925\,(1)$, $c = 16{\cdot}679\,(2)$ Å, $\beta = 90{\cdot}71\,(1)°$, $V = 982{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}32$, $D_m = 1{\cdot}31$ Mg m^{-3}, $\mu = 6{\cdot}22$ mm^{-1}, $\lambda = 1{\cdot}5418$ Å, Cu $K\alpha$, $T = 291$ K, $F(000) = 416$, $R = 0{\cdot}048$ for 1438 unique reflections. The zwitterion forms an extended structure with torsional angles O—C′—C$^\alpha$—N [O(1)—C(1)—C(2)—N] $\psi = 5{\cdot}2\,(2)$, N—C$^\alpha$—C$^\beta$—C$^\gamma$ [N—C(2)—C(4)—C(5)] $\chi^1 = 301{\cdot}9\,(2)$, and C$^\alpha$—C$^\beta$—C$^\gamma$—C$^\delta$ [C(2)—C(4)—C(5)—C(6)] $\chi^2 = -93{\cdot}4\,(2)°$. The structure is stabilized by hydrogen bonding.

Introduction. The modified amino acid α-methyl-*m*-tyrosine (MMT) was one of the first analogues of tyrosine to be discovered as a precursor of a false neurochemical transmitter for sympathetic nerves. MMT acts as a substrate for the enzymes of norepinephrine biosynthesis, leading to the norepinephrine analogue metraminol (Kopin, 1971). This product accumulates in nerve endings in the same manner as normal transmitters of nerve impluses. However, their release upon stimulation leads to diminished nerve response and thus have been found useful as drugs for the relief of hypertension in man (Horita, 1971). It is of interest to understand the role of α-methylation on the conformation of this amino acid.

Experimental. Source, Sigma Chemical Co.; D_m by flotation in heptane–chloroform; plates, $0{\cdot}12 \times 0{\cdot}28 \times 0{\cdot}28$ mm; Picker FACS-I diffractometer; lattice parameters from 12 general reflections with $40° \le 2\theta \le 60°$; systematic absences, $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$; no absorption correction; $2\theta_{\max} = 128°$; range, $+h$, $+k$, $\pm l$; standard reflections, $14\bar{1}$, 152, 034 with standard deviation of 1·6%; 1818 measured, 1438 unique, 1018 observed at $3{\cdot}0\sigma(F)$ and $F \le 12{\cdot}0$; $R_{\rm sym} = \sum\sum\big||F_i| - |\bar{F}_i|\big|/\sum\sum|\bar{F}_i| = 0{\cdot}01$; solved by direct methods (Long, 1965); based on F; H atoms located from difference Fourier, not refined; positional and anisotropic thermal parameters for nonhydrogen atoms refined; final R for unique = 0·048, weighted $R = 0{\cdot}048$, $S = 1{\cdot}11$; weight evaluated from an analysis of $|\Delta F|$ *vs* F_o; $(\Delta/\sigma)_{\max} = 0{\cdot}16$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}02$; min. height $\Delta F = -0{\cdot}06$, max. $= 0{\cdot}15$ e Å^{-3}; atomic scattering factors: nonhydrogen Cromer & Waber (1965), H Stewart, Davidson & Simpson (1965); computer programs in-house.

Discussion. The molecule is shown in Fig. 1 and the positional parameters are given in Table 1.* The bond lengths (Table 2) show no noticeable changes from those of L-tyrosine (Mostad, Nissen & Rømming, 1972)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38765 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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