

Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. Part V.¹ Crystal and Molecular Structure of the Amino-acid L-Arginine Dihydrate

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L-Arginine dihydrate, $C_6H_{14}N_4O_2 \cdot 2H_2O$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 5.638(6)$, $b = 11.85(1)$, $c = 15.68(1)$ Å, and $Z = 4$. The structure has been refined to $R 0.034$ (1364 reflections) by neutron diffraction techniques, and all hydrogen atoms located precisely. The arginine molecule is a zwitterion, with the positive charge residing in the guanidinium group. The neutral α -amino-group is not involved in the network of nine distinct N-H...O, N-H...N, and O-H...O hydrogen bonds present in the crystal structure. The barrier for internal rotation of the α -NH₂ group is estimated to be significantly less than the corresponding barrier for the hydrogen-bonded NH₃⁺ group in L-asparagine monohydrate. The N-H lengths in the guanidinium group are ca. 0.02 Å less than those found for comparably hydrogen-bonded ammonium groups in other amino-acids.

THE molecular structures of a series of protein and nucleic acid components are being determined by neutron diffraction in order to obtain a precise description of their atomic positions and thermal motion parameters. This will extend our knowledge of hydrogen-bonded systems and give us a better understanding of the factors influencing molecular conformation in these materials. We now report the structure of L-arginine dihydrate. An X-ray study of this crystal structure has been reported by Karle and Karle.²

EXPERIMENTAL

Large colourless crystals of L-arginine dihydrate were grown by slow cooling of aqueous solutions from 80 °C to room temperature. When removed from the liquid, the crystals tended to lose water, turning into a white powder.

A single crystal with 12 boundary planes, having a volume of 37.1 mm³ was used for the data collection. The sample was sealed under a quartz cap to prevent loss of water.

Crystal Data.—(NH₂)₂⁺CHN(CH₂)₃CH(NH₂)COO⁻·2H₂O, $M = 210.8$. Orthorhombic, $a = 5.638(6)$, $b = 11.85(1)$, $c = 15.68(1)$ Å, $U = 1046.8$ Å³, $D_m = 1.320$ g. cm⁻³, $Z = 4$, $D_c = 1.338$ g cm⁻³. Space group $P2_12_12_1$. Neutron wavelength $\lambda = 1.013(1)$ Å, $\mu = 2.74$ cm⁻¹.

Data Collection.—No. of reflections: 3093 (hkl and $\bar{h}\bar{k}\bar{l}$ forms); 1627 independent reflections; d^*_{\max} 1.4 Å⁻¹. Agreement between symmetry-related reflections: R [= $\sum |F_o^2 - \bar{F}_o^2| / \sum |F_o^2|$] 0.042, where \bar{F}_o^2 is the mean value of symmetry-related reflections.

X-Ray diffraction photographs indicated that the crystal was mounted with the b axis nearly parallel to the goniometer head spindle axis and that the space group is $P2_12_12_1$ as determined in the earlier study.²

Neutron-diffraction data were collected on an automatic four-circle diffractometer at the Brookhaven high-flux beam reactor, under the multiple spectrometer control system.³ The cell dimensions and orientation matrix were refined by a least-squares program, using as observations the setting angles of 29 automatically centred reflections well distributed in reciprocal space. Our cell parameters are significant

cantly smaller than the less precise X-ray values: $a = 5.68(1)$, $b = 11.87(2)$, and $c = 15.74(2)$ Å.²

Intensities were measured by the θ — 2θ step-scan technique. The scan length was varied as a function of the Bragg angle according to the formula $\Delta(2\theta) = 1.0^\circ (1 + 8 \tan \theta)$, and the step-size was chosen so that there were ca. 40 points in each scan.

Background corrections were made using a method⁴ which divides the peak and the background so that $\sigma(I)/I$ is minimized, where I is the integrated intensity and $\sigma(I)$ is the estimated standard deviation based on counting statistics. Squared structure amplitudes were calculated as $F_o^2 = I \sin 2\theta$. An absorption correction was calculated by numerical integration, using a 360-point Gaussian grid. The linear absorption coefficient was calculated assuming the incoherent scattering cross-section for hydrogen to be 40 barns, and using the values of (μ/ρ) for carbon, nitrogen, and oxygen in ref. 5. Finally, the corrected F_o^2 were averaged over symmetry-equivalent reflections.

Structure Determination and Refinement.—The hydrogen atoms were located from three successive difference-Fourier syntheses, the first of which was phased with the heavy-atom co-ordinates taken from the X-ray structure.²

The least-squares refinement was carried out by alternating cycles on two overlapping full-matrix blocks. The function minimized was $R = \sum w |F_o^2 - |F_c|^2|^2$, and the weights were $w = 1/\sigma^2(F_o^2)$ with $\sigma^2(F_o^2) = \sigma_{\text{count}}^2(F_o^2) + (0.04 F_o^2)^2$ where $\sigma_{\text{count}}(F_o^2)$ is based on counting statistics. The scattering lengths used were: $b_O = 0.575$, $b_N = 0.940$, $b_C = 0.6626$, and $b_H = -0.372$ (all $\times 10^{-12}$ cm). Reflections with $F_o^2 < 3\sigma_{\text{count}}(F_o^2)$ were not included; 1364 reflections were used in the refinement. The refinement included anisotropic temperature factors for all the atoms, and an extinction parameter g . The extinction factor E which multiplies the calculated structure factor is given by: $E = [1 + 2\bar{T}|F_c|^2 g \lambda^3 \cdot 10^4 / U^2 \sin 2\theta]^{-1/2}$, where \bar{T} is the average beam path-length in the crystal for the reflection, 2θ is twice the Bragg angle, U is the unit-cell volume, λ is the wavelength, and F_c is the calculated structure factor on an absolute scale. The value of g was 0.41(3) and the smallest extinction factor E^2 was 0.79.

The refinement was continued until the shifts in all parameters were $< 0.1\sigma$. Agreement factors were as

¹ Part IV, M. S. Lehmann, T. F. Koetzle, and W. C. Hamilton, *Internat. J. Peptide Protein Res.*, in the press.

² I. L. Karle and J. Karle, *Acta Cryst.*, 1964, **17**, 835.

³ D. R. Beaucage, M. A. Kelley, D. Ophir, S. Rankowitz, R. J. Spinrad, and R. van Norton, *Nuclear Instruments and Methods*, 1966, **40**, 26.

⁴ M. S. Lehmann, F. K. Larsen, and W. C. Hamilton, Abstracts Amer. Cryst. Assoc. Meeting, Albuquerque, New Mexico, 1972.

⁵ International Tables for X-Ray Crystallography, vol. III, Kynoch Press, Birmingham, 1962, p. 197.

⁶ W. H. Zachariasen, *Acta Cryst.*, 1967, **23**, 558.

TABLE I
Fractional co-ordinates ($\times 10^5$) and temperature parameters ($\times 10^4$) *

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	66556(48)	41768(18)	71694(16)	535(14)	321(9)	600(12)	32(10)	307(12)	25(10)
O(2)	69760(50)	59516(19)	67657(17)	624(15)	318(10)	727(14)	127(10)	350(14)	64(10)
C	76794(32)	49473(14)	67820(10)	359(8)	289(7)	352(7)	-11(7)	103(7)	-12(6)
C(α)	99152(28)	46981(12)	62726(9)	267(6)	257(7)	276(6)	-29(6)	10(6)	-37(5)
N	108578(23)	35704(10)	64790(9)	306(6)	306(6)	479(7)	14(5)	-61(5)	-58(5)
C(β)	93833(32)	48034(15)	53190(10)	387(8)	391(9)	262(7)	-95(8)	-10(7)	-3(6)
C(γ)	74512(42)	40166(16)	49920(10)	644(13)	422(10)	370(8)	-187(10)	-223(9)	75(7)
C(δ)	61666(36)	45139(15)	42508(11)	386(9)	380(9)	435(9)	-53(8)	-129(8)	97(8)
N(ε)	44528(22)	37309(10)	38861(7)	361(6)	310(6)	370(5)	27(5)	-106(5)	10(5)
C(ζ)	27052(29)	40518(13)	33654(9)	304(7)	285(7)	253(6)	15(6)	-37(6)	16(5)
N(η1)	21953(25)	51352(11)	32434(8)	381(6)	312(6)	372(5)	12(5)	-65(5)	56(5)
N(η2)	13807(29)	32674(11)	29859(9)	463(7)	326(7)	476(7)	1(5)	-167(7)	-12(5)
H(α)	111930(68)	53587(30)	64425(22)	423(16)	424(18)	509(17)	-94(15)	-22(16)	-85(15)
H(1)	107508(116)	34467(39)	71143(33)	912(36)	621(25)	570(23)	122(28)	-193(28)	-35(20)
H(2)	125787(69)	35624(38)	63480(44)	326(20)	505(22)	1514(52)	62(19)	58(27)	32(30)
H(β1)	89526(108)	56832(33)	51960(25)	943(34)	439(21)	559(20)	-169(23)	-210(26)	109(17)
H(β2)	110212(97)	46552(54)	49854(26)	589(25)	1169(44)	503(20)	-208(29)	229(21)	-152(25)
H(γ1)	82239(142)	32286(46)	47961(52)	1388(61)	517(28)	1720(69)	153(32)	-1159(59)	-140(34)
H(γ2)	62451(132)	37984(71)	54708(31)	1263(51)	1778(69)	518(22)	-1162(55)	-236(31)	318(35)
H(δ1)	52251(109)	52373(41)	44901(52)	820(38)	476(24)	1750(60)	87(24)	-682(44)	-280(31)
H(δ2)	73284(125)	48410(64)	37885(30)	966(38)	1503(57)	548(23)	-693(42)	-189(28)	359(31)
H(ε)	48948(70)	28939(30)	38570(23)	507(18)	396(18)	510(18)	59(16)	-105(16)	40(15)
H(η11)	31426(73)	57700(32)	35041(24)	548(20)	367(17)	557(18)	-9(16)	-120(19)	62(15)
H(η12)	7933(74)	53454(28)	28627(24)	487(19)	410(17)	514(17)	32(16)	-103(18)	56(15)
H(η21)	18110(82)	24443(32)	30086(25)	599(23)	396(19)	569(20)	-2(17)	-88(19)	-15(16)
H(η22)	1482(84)	35188(33)	25555(25)	542(21)	439(19)	546(18)	-5(18)	-178(19)	-21(15)
O(W1)	44922(60)	72020(21)	37678(25)	574(16)	299(12)	1117(24)	-29(13)	-146(18)	31(14)
H(W11)	37277(89)	78840(38)	35565(31)	682(26)	417(20)	822(26)	14(21)	-171(25)	-26(21)
H(W12)	60798(98)	74175(46)	38763(42)	571(27)	640(29)	1053(38)	-74(25)	-19(30)	29(28)
O(W2)	37823(80)	71111(48)	56418(32)	663(22)	1257(37)	893(27)	294(26)	170(23)	144(30)
H(W21)	49243(147)	67289(59)	59397(45)	863(44)	1003(44)	901(41)	113(38)	46(37)	105(35)
H(W22)	40400(150)	71333(62)	50698(51)	918(45)	971(48)	1057(40)	180(42)	158(44)	199(45)

* The form of the anisotropic thermal ellipsoid is $\exp\{-2\pi^2[U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}ha^*kb^* + 2U_{13}ha^*lc^* + 2U_{23}hb^*lc^*]\}$.

follows: R^2 0.052, R' 0.081, and R 0.034. The refined atomic parameters are listed in Table I, and F_o , $\sigma(F_o)$, and $|F_c|$ (all $\times 100$) are tabulated in Supplementary Publication No. SUP 20494 (3 pp., 1 microfiche).* The extinction correction has been applied to F_o , so that F_o should be on correct relative scale.

DISCUSSION

The Molecular Structure.—Bond distances and angles within the L-arginine molecule (Figure 1) and the two independent water molecules are listed in Tables 2 and 3. For bonds between non-hydrogen atoms, our neutron bond lengths are generally shorter than the reported X-ray values,² but the difference is at most 3σ (X-ray), and part of this discrepancy may be explained by the fact that we have used a slightly smaller unit-cell. Our standard deviations are slightly underestimated, because of the partially blocked matrix approach used in the least-squares refinement. Selected torsion angles are presented in Table 4.

The molecule is a zwitterion, with the α -amino-group remaining neutral and the extra proton residing in the guanidinium group. This can be explained by the higher proton affinity of the guanidinium group; the pK_A value for the ammonium group is 9.04 while that for the guanidinium group is 12.48.⁷

The N(ϵ), C(ζ), N(η 1), N(η 2), H(η 11), H(η 12), H(η 21), and H(η 22) atoms, constituting the guanidinium group,

* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 3 pp. are sent as full size copies).

are coplanar within 0.05(1) Å. The distances of H(ϵ) and C(δ) from this plane are 0.14 and 0.18 Å respectively, and

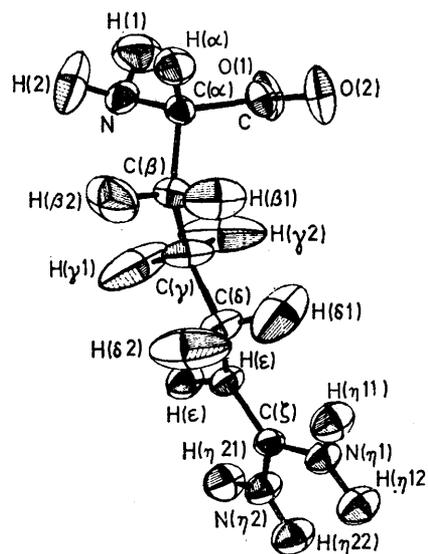


FIGURE 1 Drawing of the molecule with 50% probability vibrational ellipsoids

in the case of H(ϵ) this deviation from planarity facilitates hydrogen bond formation. The planarity of the guanidinium group causes some very short non-bonded intra-

⁷ A. White, P. Handler, and E. L. Smith, 'Principles of Biochemistry,' McGraw-Hill, New York, 1964, p. 108.

molecular contacts between hydrogen atoms. The distances $H(\eta_{11}) \cdots H(\delta_{11})$, $H(\eta_{22}) \cdots H(\eta_{12})$, and $H(\eta_{21}) \cdots H(\epsilon)$ are 2.041(7), 2.246(5), and 2.253(5) Å respectively, showing that the van der Waals radius of 1.2 Å for hydrogen does not apply in this case, and that perhaps a value of 1.0 Å⁸ would be more reasonable.

TABLE 2
Molecular bond distances (Å)

	Neutron	Cor- rected for rigid- body motion	Min. cor- rec- tion ^a	X-Ray ^b
C-O(1)	1.239(3)	1.251		1.249
C-O(2)	1.254(3)	1.264		1.259
C-C(α)	1.521(2)	1.539		1.547
C(α)-N	1.474(2)	1.485		1.480
C(α)-H(α)	1.096(4)		1.100	
N-H(1)	1.008(6)	1.047	1.019	
N-H(2)	0.992(4)	1.027	1.007	
C(α)-C(β)	1.530(2)	1.542		1.542
C(β)-H(β1)	1.087(5)	1.109	1.095	
C(β)-H(β2)	1.076(5)	1.097	1.090	
C(β)-C(γ)	1.523(2)			1.540
C(γ)-H(γ1)	1.075(7)	1.134	1.105	
C(γ)-H(γ2)	1.045(6)	1.099	1.075	
C(γ)-C(δ)	1.490(2)	1.508		1.517
C(δ)-H(δ1)	1.075(7)	1.120	1.099	
C(δ)-H(δ2)	1.051(6)	1.094	1.076	
C(δ)-N(ε)	1.456(2)	1.469		1.471
N(ε)-H(ε)	1.023(4)		1.025	
N(ε)-C(ζ)	1.335(2)	1.351		1.351
C(ζ)-N(η1)	1.329(2)	1.344		1.340
N(η1)-H(η11)	1.009(4)	1.012	1.011	
N(η1)-H(η12)	1.021(4)	1.025	1.022	
C(ζ)-N(η2)	1.332(2)	1.345		1.322
N(η2)-H(η21)	1.005(4)	1.011	1.006	
N(η2)-H(η22)	1.013(4)	1.018	1.014	
O(W1)-H(W11)	0.974(6)	0.981		
O(W1)-H(W12)	0.946(7)	0.953		
O(W2)-H(W21)	0.915(11)	0.921		
O(W2)-H(W22)	0.909(11)	0.915		

^a From ref. 20. ^b σ 0.008 Å; from ref. 2.

The three C-N distances in the guanidinium group are equal. We find the mean value of the C-N bond length to be 1.332(2) Å, in excellent agreement with the value of 1.34(1) Å obtained by averaging the N(ε)-C(ζ), C(ζ)-N(η1), and C(ζ)-N(η2) distances determined by X-ray diffraction in the following salts of arginine: H₃PO₄·H₂O,⁹ HCl,¹⁰ HCl·H₂O,¹¹ and HBr·H₂O.¹² In X-ray and neutron studies of the anti-leukemia drug methylglyoxal bisguanyldihydrazone (methyl GAG) dihydrochloride monohydrate,¹³ and in an X-ray study of the closely related compound dimethyl GAG dihydrochloride dihydrate,¹⁴ the terminal C-N bonds in the guanidinium groups have been found to be 0.03 Å shorter than the

⁸ W. H. Baur, *Acta Cryst.*, 1972, B, **28**, 1456.

⁹ K. Aoki, K. Nagano, and Y. Iitaka, *Acta Cryst.*, 1971, B, **27**, 11.

¹⁰ S. K. Mazumdar, K. Venkatesan, H-C. Mez, and J. Donohue, *Z. Krist.*, 1969, **130**, 328.

¹¹ J. Dow, L. H. Jensen, S. K. Mazumdar, R. Srinivasan, and G. N. Ramachandran, *Acta Cryst.*, 1970, B, **26**, 1662.

¹² S. K. Mazumdar and R. Srinivasan, *Current Sci.*, 1964, **33**, 573; *Z. Krist.*, 1969, **123**, 186.

TABLE 3
Molecular bond angles (deg.)

	Neutron	X-Ray ^a
O(1)-C-O(2)	124.1(2)	125.6
O(1)-C-C(α)	120.0(2)	119.1
O(2)-C-C(α)	115.8(2)	115.2
C-C(α)-H(α)	106.2(2)	
C-C(α)-C(β)	109.5(1)	108.4
C-C(α)-N	111.1(1)	110.9
H(α)-C(α)-C(β)	107.9(2)	
H(α)-C(α)-N	110.9(2)	
C(β)-C(α)-N	111.1(1)	110.7
C(α)-N-H(1)	109.1(3)	
C(α)-N-H(2)	108.4(3)	
H(1)-N-H(2)	105.2(5)	
C(α)-C(β)-H(β1)	107.2(2)	
C(α)-C(β)-H(β2)	107.1(3)	
C(α)-C(β)-C(γ)	114.8(1)	114.4
H(β1)-C(β)-H(β2)	105.2(4)	
H(β1)-C(β)-C(γ)	111.5(3)	
H(β2)-C(β)-C(γ)	110.5(3)	
C(β)-C(γ)-H(γ1)	109.7(4)	
C(β)-C(γ)-H(γ2)	112.0(3)	
C(β)-C(γ)-C(δ)	111.6(1)	110.1
H(γ1)-C(γ)-H(γ2)	104.7(7)	
H(γ1)-C(γ)-C(δ)	108.5(4)	
H(γ2)-C(γ)-C(δ)	110.0(4)	
C(γ)-C(δ)-H(δ1)	106.4(3)	
C(γ)-C(δ)-C(δ2)	112.4(3)	
C(γ)-C(δ)-N(ε)	112.1(1)	111.1
H(δ1)-C(δ)-H(δ2)	104.7(6)	
H(δ1)-C(δ)-N(ε)	108.5(3)	
H(δ2)-C(δ)-N(ε)	112.2(3)	
C(δ)-N(ε)-H(ε)	118.2(2)	
C(δ)-N(ε)-C(ζ)	123.3(1)	123.2
H(ε)-N(ε)-C(ζ)	115.4(2)	
N(ε)-C(ζ)-N(η1)	121.5(1)	121.0
N(ε)-C(ζ)-N(η2)	119.2(1)	118.9
N(η1)-C(ζ)-N(η2)	119.2(1)	120.1
C(ζ)-N(η1)-H(η11)	123.2(2)	
C(ζ)-N(η1)-H(η12)	119.1(2)	
H(η11)-N(η1)-H(η12)	117.7(3)	
C(ζ)-N(η2)-H(η21)	121.7(3)	
C(ζ)-N(η2)-H(η22)	118.5(3)	
H(η21)-N(η2)-H(η22)	118.3(3)	
H(W11)-O(W1)-H(W12)	104.8(5)	
H(W21)-O(W2)-H(W22)	113.9(7)	

^a From ref. 2; σ 0.9°.

TABLE 4
Torsion angles (deg.)

IUPAC-IUB Designation *	Atoms involved	Angle
$\phi(1)$	H(1)-N-C(α)-C	-41.7(4)
$\phi(2)$	H(2)-N-C(α)-C	-155.9(4)
$\psi(1)$	O(1)-C-C(α)-N	-13.0(2)
$\psi(2)$	O(2)-C-C(α)-N	168.0(2)
$\chi(1)$	N-C(α)-C(β)-C(γ)	63.9(2)
$\chi(2)$	C(α)-C(β)-C(γ)-C(δ)	150.5(2)
$\chi(3)$	C(β)-C(γ)-C(δ)-N(ε)	175.1(2)
$\chi(4)$	C(γ)-C(δ)-N(ε)-C(ζ)	163.2(2)
$\chi(5,6,1)$	C(δ)-N(ε)-C(ζ)-N(η1)	-10.1(2)
$\chi(5,6,2)$	C(δ)-N(ε)-C(ζ)-N(η2)	172.6(2)

* IUPAC-IUB Commission on Biochemical Nomenclature, *J. Mol. Biol.*, 1970, **52**, 1.

¹³ W. C. Hamilton and S. J. La Placa, *Acta Cryst.*, 1968, B, **24**, 1147.

¹⁴ J. W. Edmonds and W. C. Hamilton, *Acta Cryst.*, 1972, B, **28**, 1362.

non-terminal C-N bond. This difference, which has not been found in arginine, may be associated with the interaction of the π clouds of the two guanidinium groups in the planar methyl GAG and dimethyl GAG ions. If we average the guanidinium C-N distances in methyl GAG and dimethyl GAG, in each case we obtain a value of 1.33(1) Å, which is in good agreement with the corresponding mean value in arginine given above.

We have determined the C(γ)-C(δ) distance in arginine to be 1.490(2) Å, which is shorter than expected for a single bond between sp^3 carbon atoms, possibly because of conjugation with the guanidinium π system. Mean values of the angles at the CH₂ carbon atoms are 109.5(7)° for C-C-H with individual angles ranging from 106.4 to 112.4°, 104.9(2)° for H-C-H, and 112.8(10)° for C-C-C or C-C-N.

Hydrogen Bonding.—Hydrogen bond distances and angles are listed in Table 5. The σ values were obtained

linked to the carboxy-group of a neighbouring arginine molecule *via* two N-H...O hydrogen bonds. The distances from O(1), O(2), and C to the plane of the guanidinium group are 0.06, -0.24, and -0.01 Å, respectively. The three hydrogen bonds around O(W2) are also coplanar within 0.04(1) Å. This plane is nearly perpendicular to that of the guanidinium group.

The N-H distances in the guanidinium group are *ca.* 0.02 Å shorter than would be predicted from a curve of N-H *vs.* H...O distances for ammonium group hydrogen bonds in thirteen amino-acids we have so far studied by neutron diffraction. This result is expected, since an sp^2 should form slightly shorter N-H bonds than an sp^3 nitrogen. It is also possible that the energetics of the guanidinium group N-H...O hydrogen bonds may differ from those of hydrogen bonds formed by NH₃⁺ groups.

The O(W1)-H(W12)...O(W2) bond lies along the

TABLE 5
Hydrogen bond distances (Å) and angles (deg.)

A-H...B-C	A...B	H...B	<A-H...B	<H...B-C
N(η 1)H(η 11)O(W1)	2.889(3)	1.904(5)	164.4(3)	
N(η 1)H(η 12)O(1)C	2.865(3)	1.846(4)	176.1(3)	114.3(3)
N(η 2)H(η 21)O(1)C	2.910(3)	1.942(4)	160.5(4)	129.5(4)
N(η 2)H(η 22)O(2)C	2.845(3)	1.833(5)	176.6(4)	121.1(4)
N(ϵ)H(ϵ)NC(α)	2.896(2)	1.892(4)	166.0(3)	131.8(7)
O(W1)H(W11)O(2)C	2.738(4)	1.770(6)	172.1(5)	124.6(6)
O(W1)H(W12)O(W2)	2.715(5)	1.789(7)	164.9(7)	
O(W2)H(W21)O(2)C	2.869(6)	1.965(9)	169.1(7)	130.1(7)
O(W2)H(W22)O(W1)	2.967(7)	2.058(9)	177.8(7)	

from a special least-squares cycle varying all parameters associated with atoms involved in hydrogen bonds.

All nine hydrogen bonds are intermolecular and show some distortion from linearity, but none is severely bent. The complex three-dimensional hydrogen bonding framework is illustrated in Figure 2.

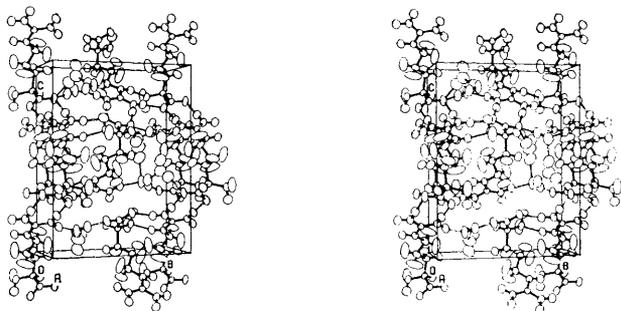


FIGURE 2 Stereoscopic view of molecular packing, showing the unit-cell outline. Molecular bonds are drawn thick, hydrogen bonds thin

The most striking feature of this framework is the near-planarity of the hydrogen-bond system involving the five guanidinium hydrogens and both hydrogens of the O(W1) water molecule, giving an infinite network of bonds in the *b* direction. The guanidinium group is

¹⁵ R. Chidambaram, A. Sequeira, and S. K. Sikka, *J. Chem. Phys.*, 1964, **41**, 3616.

bisector of the O(W2) lone-pairs. As a result, this molecule can be classified as type F according to ref. 15, whereas the O(W1) molecule is of type E with two hydrogen bonds along the lone-pairs. The high thermal motion of the water molecules prevents us from making any attempt to correlate their geometry with the type of hydrogen-bond acceptance. The water molecules form infinite chains parallel to the *a* axis.

The amino-group acts only as a hydrogen-bond acceptor. Neither H(1) nor H(2) are within hydrogen bonding range of any negative polar group. The shortest such distance is H(1)...O(1) (intramolecular): 2.467(6) Å; it can be seen from the ϕ (1) and ψ (1) torsion angles that the N-H(1) and C-O(1) bonds are far from being eclipsed.

Thermal Motion.—In the studies of the amino-acid L-asparagine monohydrate¹⁶ the barrier to rotation of the ammonium group was estimated to be 7 kcal mol⁻¹. The ammonium group in asparagine is hydrogen-bonded whereas this is not the case for the arginine amino-group. To obtain the barrier to rotation for the amino-group as well as the best molecular geometry, a series of calculations were carried out describing the motion of various parts of the arginine molecule as rigid-body motions using *T*, *L*, and *S* tensors.¹⁷

¹⁶ J. J. Verbist, M. S. Lehmann, T. F. Koetzle, and W. C. Hamilton, *Acta Cryst.*, in the press.

¹⁷ V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B**, **24**, 63.

An inspection of the thermal motions of the individual non-hydrogen atoms indicated that it is not likely that the whole framework behaves as a rigid body. Nevertheless, good results were obtained by dividing the molecule into two rigid groups: group (I) containing atoms O(1), O(2), N, C(α), and C(β) and group (II) containing atoms C(γ), C(δ), N(ϵ), C(ζ), N(η 1), and N(η 2). The r.m.s. differences between observed and calculated U_{ij} were 0.003 and 0.004 Å², for groups (I) and (II), respectively. The precision of the individual U_{ij} from the least-squares refinement is *ca.* 0.001 Å². The corrected interatomic distances obtained from the rigid-body calculations are given in Table 2.

Separate rigid-body calculations were carried out for the α -amino-group, the methylene groups, the guanidinium NH₂ groups, and the water molecules. For the α -amino-group the C(α) atom was included in the calculation; an orthogonal-co-ordinate system was used with one axis along the C(α)-N vector, and with the origin at the nitrogen atom. The motion of the group was described by the tensors T and L . The root-mean-square goodness-of-fit for the U_{ij} was 0.009 Å², and the maximum libration was found to be about an axis inclined 11.9° to the C(α)-N axis with a mean-square value of 299(53) deg². The mean-square values of libration about the two other principal axes of the L tensor were both $<2\sigma$; thus the principal motion of the group is a hindered rotation around the C(α)-N axis. The corrected N-H distances are given in Table 2. A three-fold hindered rotor with potential energy $V(\alpha) = (1/2)V_0(1 - \cos 3\alpha) \cong (1/4)V_0 3^2\alpha^2$, where α is the angle of rotation around the rotor axis, and with the same moment of inertia and mean-square amplitude of rotation as the amino-group would have a barrier $V_0 = 1.6(5)$ kcal mol⁻¹, if the potential in the bottom of the well were assumed to be harmonic. Although the amino-group does not possess three-fold symmetry, this qualitative estimate indicates that the barrier is much smaller than the corresponding value for the hydrogen-bonded group in L-asparagine monohydrate and the other amino-acids we have studied.

The calculations for the CH₂ groups, the guanidinium NH₂ groups and the water molecules were carried out using a modification of a procedure described in ref. 18 in a treatment of the rigid-body motions in Ice IX. The

origin for the group was chosen at the heavy atom, and the motion of the rigid group was described by a general translation and a libration about an axis orthogonal to the plane of the group, generally referred to as the rocking motion. Values of root-mean-square goodness-of-fit are in the range 0.007–0.016 for the CH₂ groups, 0.004 for the NH₂ groups, and 0.007 and 0.008 Å² for the water molecules. The thermal motion shown in Figure 1 is reflected in the amplitudes of the rocking motions. The mean-square librations are 207(35), 551(80), 425(69), 30(19), 44(12), 76(33), and 58(47) deg² for the groups containing C(β), C(γ), C(ζ), N(η 1), N(η 2), O(W1), and O(W2). The hydrogen-bonded NH₂ groups and water molecules exhibit considerably smaller librational motion than do the CH₂ groups, again reflecting the strength of hydrogen bonding.

The C-H distances obtained from the separate rigid-body calculations seem generally to be overcorrected; the mean corrected C-H distance is 1.109 Å as compared to a standard value of 1.096 Å.¹⁹ The riding motion correction²⁰ leads to an even larger average value of 1.143 Å. The minimum correction,²⁰ which sets a lower limit for the bond length, leads to a mean value of 1.090 Å, very close to the expected distance. A similar result is found for L-lysine monohydrochloride dihydrate,²¹ where the mean C-H distance obtained by use of the minimum correction is 1.100 Å. Although the minimum correction is based on the assumption that the motions of the two bonded atoms are in phase, this correction leads to rather reasonable results in amino-acids. The minimum corrections for the N-H and the C-H bond lengths are listed in Table 2 for comparison.

Calculations were performed on CDC 6600 computers using programs from the Brookhaven Crystallographic Computing Library which have been described in ref. 22.

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¹⁹ *Chem. Soc. Special Publ.*, No. 11, 1956; No. 18, 1965.

²⁰ W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

²¹ T. F. Koetzle, M. S. Lehmann, J. J. Verbist, and W. C. Hamilton, *Acta Cryst.*, in the press.

²² E. O. Schlemper, W. C. Hamilton, and S. J. La Placa, *J. Chem. Phys.*, 1971, **54**, 3990.