the agreement with experiment is not so good that it precludes the possibility of occasional incomplete tetrahedra or occasional isolated aluminum atoms. It would be of considerable interest to study more dilute alloys to see whether the tetrahedral arrangement found here persists even when the concentration is so low that each aluminum atom has the chance to isolate itself completely from like second and third nearest neighbors. It is clear that the experimental techniques for measurements of the sort described here are now sufficiently refined that meaningful results for alloys considerably more dilute may be obtained.

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An Application of the Symbolic Addition Method to the Structure of L-Arginine Dihydrate

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The crystal structure of L-arginine dihydrate was determined directly by means of the symbolic addition phase determination procedure, using the complete three-dimensional data obtained from Cu radiation. The space group is $P2_12_12_1$ and the cell dimensions are:

$$a=5{\cdot}68,\ b=11{\cdot}87,\ \text{and}\ c=15{\cdot}74\ \text{Å}\ .$$

The arginine molecule is a zwitterion with the guanidyl group, rather than the amino group, accepting an extra proton. Two planes characterize the arginine molecule, one through the acid group, and the other through the extended side chain which contains the guanidyl group. The dihedral angle between these planes is 74°. The arginine molecules and the water molecules each make infinite chains perpendicular to each other by hydrogen bonding. All 18 hydrogen atoms have been located.

Introduction

L-Arginine, $^+(H_2N)_2CNH(CH_2)_3CH(NH_2)COO^-$, is one of the amino acids essential for animal growth. It is also the most basic of the amino acids since, in addition to the α-amino group, it also contains a terminal guanidyl group. This investigation afforded a good opportunity to study a biologically important amino acid structure and its associated hydrogen bonding. It also provided a valuable experience in the first application of the symbolic addition method for phase determination (Karle & Karle, to be published) to a non-centrosymmetric crystal.

Experimental

Purified L-arginine was obtained from the Central Research Laboratories of General Mills, Inc. Recrystallization from water at room temperature yielded crystals of the dihydrate which were colorless, transparent prisms. They were elongated along the *a* axis. Crystals kept in air lost their sharp edges and appeared to deliquesce, whereas those kept in a desiccator became opaque and cracked. The crystals kept in the X-ray beam however were fairly well preserved. Eventually they showed signs of disintegration in the region where the X-ray beam impinged upon them.

Complete intensity data for Cu $K\alpha$ radiation were collected along the a, b and c axes by the multiple-film equi-inclination Weissenberg technique. Precession photographs for the $0kl$, $h0l$ and $hk0$ layers were also taken. No correction for absorption was made.

The space group is $P2_12_12_1$ and the unit cell parameters are:

$$a = 5{\cdot}68 \pm 0{\cdot}01, \quad b = 11{\cdot}87 \pm 0{\cdot}02, \quad c = 15{\cdot}74 \pm 0{\cdot}02 \text{ Å}.$$

The computed density is 1·314 g.cm^{-3} and the measured density by flotation in mixed solvents was found to be 1·320 g.cm^{-3}.

Phase determination

The normalized structure factor $E_{\mathbf{h}}$ is defined by

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2 / \varepsilon \sum_{j=1}^{N} f_{j\mathbf{h}}^2 \qquad (1)$$

where $\varepsilon = 2$ when $\mathbf{h}$ is $h00$, $0k0$ or 001, $\varepsilon = 1$ otherwise for space group $P2_12_12_1$, and f_j is the atomic scattering factor for the jth atom in the unit cell containing N atoms. Phases corresponding to 400 of the largest $|E_{\mathbf{h}}|$ were determined by means of the symbolic addition procedure for non-centrosymmetric space groups. The procedure is an extension of the symbolic addition method applied to centrosymmetric crystals (Karle & Karle, 1963; Karle, Britts & Gum, 1964).

The formula for starting the phase determination is (Karle & Karle, to be published),

$$\varphi_{\mathbf{h}} \approx \langle \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_r}, \qquad (2)$$

where the $\varphi_{\mathbf{h}}$ are the phases associated with the $|E_{\mathbf{h}}|$ and $\mathbf{k}_r$ implies that the average is taken only over those $\mathbf{k}$ corresponding to the larger $|E|$ values. Formula (2) is implemented by specifying appropriate phases (Hauptman & Karle, 1956) in order to fix the origin, and by assigning additional symbols to represent the phases associated with certain appropriately chosen reflections.

In space group $P2_12_12_1$, it is convenient to fix the origin by assigning the phases of two-dimensional data. The phases were assigned as follows:

$\mathbf{h}$	$\varphi_{\mathbf{h}}$	$\lvert E_{\mathbf{h}}\rvert$
3,0,10	0	3·46
3,3, 0	$-\pi/2$	2·17
3,0, 1	$+\pi/2$	2·77

With these assignments, it is immediately possible to obtain contributors to (2) for particular $\varphi_{\mathbf{h}}$. For example, the largest *guu* is $|E_{631}| = 2{\cdot}06$. We note that if $\mathbf{k} = 301$ and $\mathbf{h} - \mathbf{k} = 330$, $\mathbf{h} = 631$. Since $\varphi_{330} = -\pi/2$ and $\varphi_{301} = +\pi/2$, this pair contributes the value zero toward the average in (2) for φ_{631}. Similarly, since $\varphi_{\bar{3},0,10} = \pi$ and the value zero may be used for φ_{631} at this stage, this pair contributes the value of π to the average in (2) for $\varphi_{3,3,11}$. $|E_{3,3,11}| = 2{\cdot}05$, the second largest *uuu*. Two pairs of contributors are now available for φ_{0310} ($|E_{0310}| = 1{\cdot}85$) as follows:

$\mathbf{h}$	$\varphi_{\mathbf{h}}$	$\mathbf{h}$	$\varphi_{\mathbf{h}}$
$\bar{3}$,0, $\bar{1}$	$-\pi/2$	3,3, 0	$-\pi/2$
3,3,11	π	$\bar{3}$,0,10	π
0,3,10	$+\pi/2$	0,3,10	$+\pi/2$

Further contributors to new phases and also to φ_{631}, φ_{3311} and φ_{0310} were developed by continuing the process of forming pairs as required by (2). In order to facilitate this, it was necessary to assign symbols to other phases. The assignments were,

$\mathbf{h}$	$\varphi_{\mathbf{h}}$	$\lvert E_{\mathbf{h}}\rvert$
2,12, 0	p	3·21
2,10, 0	s	2·31
4, 0,14	m	2·56
3, 8, 3	a	2·31

These reflections were chosen because they entered into many of the combinations for the average in (2) and they were associated with relatively large $|E|$ values.* The symbols p, s, m must be either 0 or π, but a can be anywhere in the range $-\pi < a \leq \pi$. In forming the contributors to (2), maximum use was made of the three-dimensional reflections ($hkl \neq 0$). Too much reliance on two-dimensional reflections may lead to misleading phase indications.

In the course of application of the procedure, it soon became apparent that $m = \pi$. It was also apparent that a was near 0 or π. It was chosen to be zero, which, in effect, specified the enantiomorph. The specification of the enantiomorph for space group $P2_12_12_1$ is discussed in detail by Karle & Hauptman (1956).

By means of hand computation, 137 phases were determined in terms of $0, \pi, \pm\pi/2, p$, and s. Relatively few inconsistencies were found for pairs involving three-dimensional reflections or a three-dimensional and a two-dimensional reflection. However, there were a number of inconsistencies for pairs composed solely of two-dimensional data.

Since p and s have to be 0 or π, most phases in this first approximation were on the cardinal points, $0, \pi$ or $\pm\pi/2$. Some, however, were found to have intermediate values. For example, an approximately equal number of contributors to (2) might consist of the types $-\pi/2 + s$ and $p + s$. The average, $\frac{1}{2}[(-\pi/2 + s) + (p + s)]$, would then have the possible values, $\pi/4$, $-\pi/4$, $3\pi/4$ or $-3\pi/4$, depending upon the values of p and s.

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* A procedure based on the multiplication of symbols, rather than addition, can be used if the symbols represent $\exp(i\varphi)$ rather than φ.

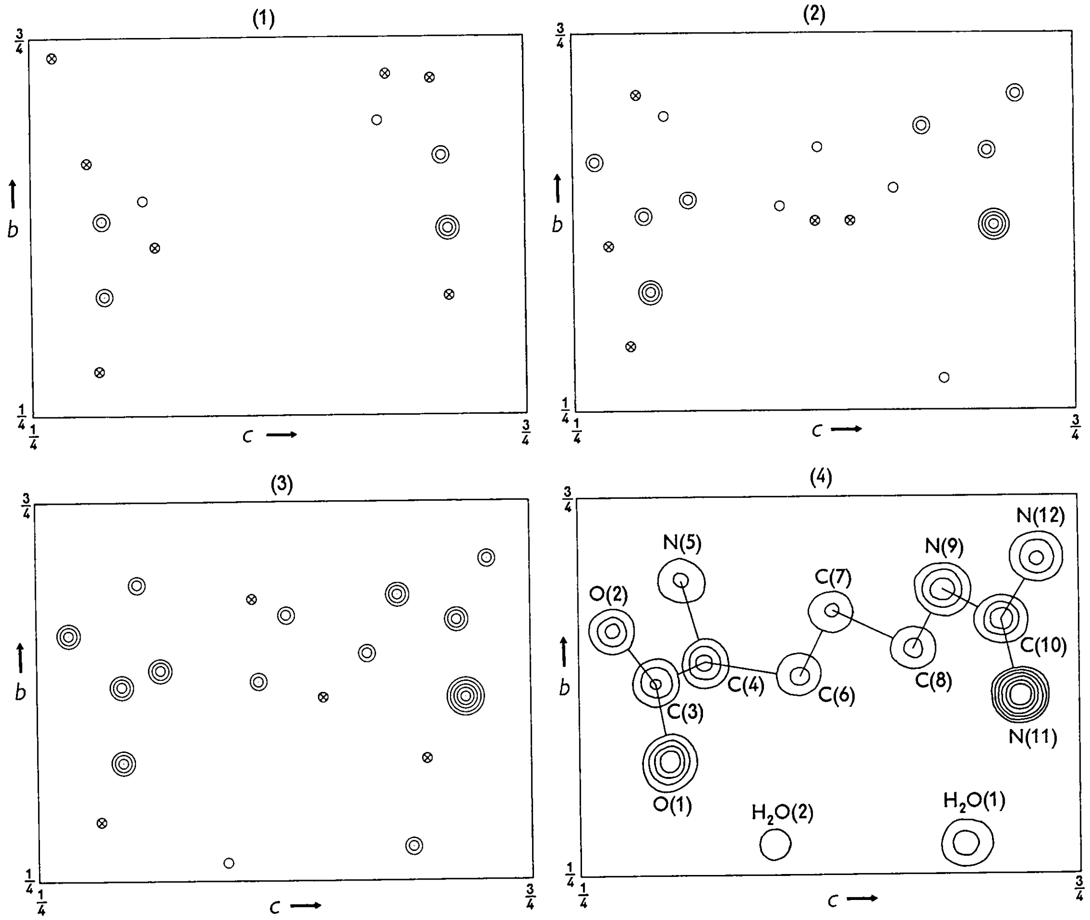

Fig. 1. Three-dimensional E-maps for arginine, viewed along the a axis, which were computed with normalized structure factors, E, as coefficients. The phases were obtained from the symbolic addition procedure. (1) 137 data with $|E|_{\min}=1\cdot50$, (2) 200 data with $|E|_{\min}=1\cdot40$, (3) 300 data with $|E|_{\min}=1\cdot15$, and (4) 400 data with $|E|_{\min}=1\cdot00$. The peaks marked with crosses are extraneous. The contours are at equal intervals on an arbitrary scale.

The following four combinations of values for p and s,

p	s
0	π
π	0
0	0
π	π

were substituted into the set of 137 phases defined in terms of these symbols. Each of the four sets of phases so obtained was used as a basic set for the application of the tangent formula (Karle & Hauptman, 1956)

$$\tan \varphi_{\mathbf{h}} \approx \frac{\sum\limits_{\mathbf{k}_r} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \sin(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})}{\sum\limits_{\mathbf{k}_r} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \cos(\varphi_{\mathbf{k}}+\varphi_{\mathbf{h}-\mathbf{k}})}\,, \tag{3}$$

where $\mathbf{k}_r$ ranges over 137 values of $\mathbf{k}$. This formula is used to reiterate the determination of values for the initial set of phases and to obtain additional ones. Since the numerator of (3) is proportional to $|E_{\mathbf{h}}|\sin\varphi_{\mathbf{h}}$ and the denominator of (3) is proportional to $|E_{\mathbf{h}}|\cos\varphi_{\mathbf{h}}$, the sum of the squares would be proportional to $|E_{\mathbf{h}}|^2$. If this formula is calculated for many $\mathbf{h}$ values, the proportionality constant may be obtained from a comparison with the experimental values for $|E_{\mathbf{h}}|^2_{\text{obs}}$ over the same range of $\mathbf{h}$. The adjustment is made by setting the average of the calculated $|E_{\mathbf{h}}|^2_{\text{calc}}$ equal to the average of the observed $|E_{\mathbf{h}}|^2_{\text{obs}}$. In the course of the calculation those reflections were eliminated whose $|E_{\mathbf{h}}|_{\text{calc}}$ were very small. An arbitrary level of 0·3 was chosen. Reflections whose phases changed greatly from reiteration cycle to reiteration cycle were also eliminated. Usually, the tangent formula (3) converges in one or two iterations if no new data are introduced.

The correct answer was found to correspond to the combination $p=s=\pi$. The other three combinations did not produce E-maps which were crystallographically meaningful. E-maps are Fourier maps employing the $E_{\mathbf{h}}$ as coefficients (Karle, Hauptman, Karle & Wing, 1958). Fig. 1 shows E-maps calculated for (1) 137 data (minimum $|E|=1\cdot50$), (2) 200 data (minimum $|E|=1\cdot40$), (3) 300 data (minimum $|E|=1\cdot15$), (4) 400 data (minimum $|E|=1\cdot00$). It is seen that calculation (3) of Fig. 1 reveals the molecular structure quite well. This map includes about one fifth of the total data collected. The peaks marked with crosses are extraneous. In calculation (4) of Fig. 1, there were no extraneous peaks as strong as the fourteen peaks which corresponded to the structure.

It is of interest to note that phase-determining formulas obtained in the past, which define phases in terms of structure factor magnitudes, could have been used to determine the correct values of p and s directly. One type of formula which could have been used is the Σ_1 formula for space group $P2_12_12_1$ (Karle & Hauptman, 1956). The two forms of interest are

$$SE_{2h2k0} \sim S\sum_{l}(-1)^{l+h}(|E_{hkl}|^2-1), \tag{4}$$

and

$$SE_{02k2l} \sim S\sum_{h}(-1)^{h+k}(|E_{hkl}|^2-1)\,, \tag{5}$$

where S means 'sign of'. Table 1 shows the results of the application of (4) and (5). There were nineteen terms in the sum for (4) and seven in the sum for (5). The probability that the sign be positive for the $E_{2\mathbf{h}}$ in question, $P_+(E_{2\mathbf{h}})$, is given by

$$P_+(E_{2\mathbf{h}}) = \tfrac{1}{2}+\tfrac{1}{2}\tanh \sigma_3|E_{2\mathbf{h}}|\Sigma_1/2\sigma_2^{3/2} \tag{6}$$

where Σ_1 is the sum contained in (4) or (5), and $\sigma_n=\sum_{j=1}^{N} Z_j^n$, Z_j being the atomic number of the jth atom in a unit cell containing N Atoms. It is seen from Table 1 that three determinations indicate that p has a value of π with probabilities 0·86, 0·72, and 0·73, and s has a value of π with probabilities 0·85 and 0·72. The over-all probability from the three determinations that p is equal to π is about 0·97 and that for s from the two determinations is about 0·94, assuming that the determinations are independent.

Table 1. *An application of the* Σ_1 *formula*

2h	symbol	Σ_1	$P_+(E_{2\mathbf{h}})$
2,12, 0	p	−	0·14
2,10, 0	s	−	0·15
4, 8, 0	$\pi+p$	+	0·72
0,12, 8	p	−	0·27
0,10,14	s	−	0·28

Another type of phase-determining formula which could have been used for determining the value of p and s is $B_{3,0}$ (Karle & Hauptman, 1958). With this formula there were several indications that the values of p and s were π. The value of m was also found to be π. It is interesting to note that when the data were extended by use of a Patterson map, improved by the application of a positivity criterion (Karle & Hauptman, 1964), the results of formula $B_{3,0}$ were more definitive.

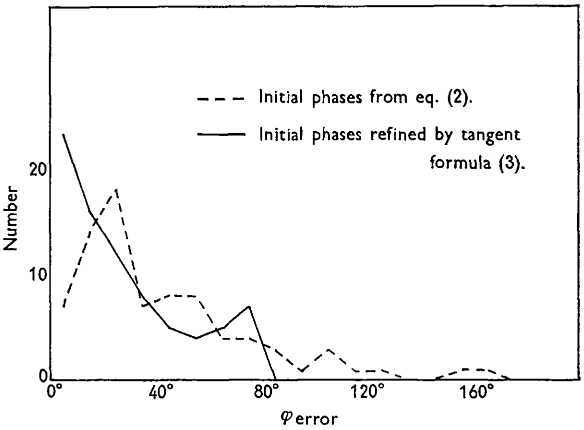

Fig. 2. The magnitude of the difference between the initial values of phases for three-dimensional reflections and the final values calculated from the refined structure.

In the initial set of 137 phases obtained from formula (2), the phases of the three-dimensional reflections had errors which were distributed as indicated by the dashed curve in Fig. 2. The symbol φ_{error} is defined as the magnitude of the difference between a phase calculated for the refined structure and one calculated from (2) or (3). It is seen from the solid curve that application of (3) to the initial phases improved their values considerably. The average error for the three-dimensional phases decreased from 43° to 27° by the use of the tangent formula.

Refinement

The preliminary coordinates of the fourteen atoms, other than hydrogen, which were obtained from the fourth E-map in Fig. 1, were subjected to a three-dimensional least-squares refinement (Busing, Martin & Levy, 1962) using all the 1406 data. After two cycles, employing isotropic temperature factors, the R index was 14·8%. Next, two cycles with anisotropic temperature factors reduced the R index to 11·6%. All the terms were evenly weighted with the value of one. At this point, a difference Fourier synthesis was computed in order to find the hydrogen atoms. All 18 hydrogen atoms were located. One more refinement was performed which included all the 32 atoms. Then another difference map was computed, which used the ΔF from the heavier atoms alone while the phase angles included the calculated contributions from the hydrogen atoms as well. The final R index was 10·3%.*

The difference map showing the location of the 18 hydrogen atoms is illustrated in Fig. 3. It is a composite drawing projected along the a axis. Although the coordinates of the hydrogen atoms have not been extensively refined, there is no doubt about the approximate location of each hydrogen and the configuration about the heavy atom to which it is bonded. A final electron density map computed with F values

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* A microfilm containing the observed F and the computed F, A and B has been deposited with the Library of Congress, Washington, D.C., U.S.A. The reel number is 8496.

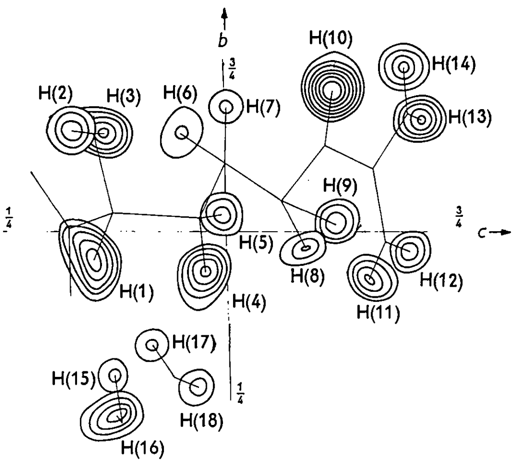

Fig. 3. A projection along the a axis of sections of a difference map for the location of hydrogen atoms. Contours are at intervals of 0·05 e.Å^{-3}, starting with the 0·15 e.Å^{-3} contour.

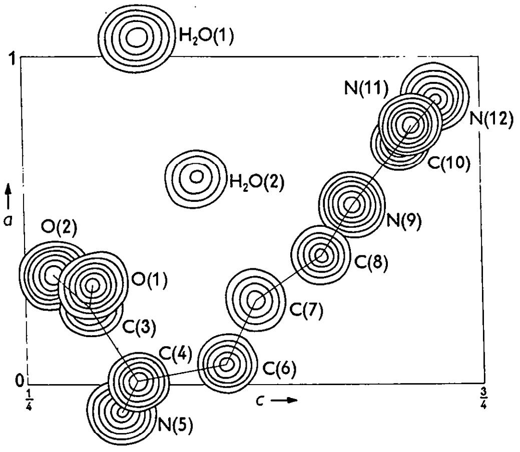

Fig. 4. A projection along the b axis of sections of the final electron density map. Only one arginine molecule is shown. Contours are at intervals of 1 e.Å^{-3}, starting with the 1·5 e.Å^{3} contour.

Table 3. *The approximate coordinates for the hydrogen atoms as determined from the second difference map*

Atom	Bonded to	x	y	z
H(1)	C(4)	0·908	0·458	0·350
H(2)	N(5)	0·847	0·650	0·328
H(3)	N(5)	0·938	0·645	0·362
H(4)	C(6)	0·076	0·442	0·475
H(5)	C(6)	0·933	0·525	0·495
H(6)	C(7)	0·366	0·645	0·450
H(7)	C(7)	0·208	0·682	0·502
H(8)	C(8)	0·388	0·478	0·589
H(9)	C(8)	0·253	0·512	0·623
H(10)	N(9)	0·525	0·703	0·617
H(11)	N(11)	0·722	0·433	0·660
H(12)	N(11)	0·862	0·472	0·705
H(13)	N(12)	0·933	0·663	0·719
H(14)	N(12)	0·822	0·741	0·700
H(15)	$W(1)$	0·533	0·207	0·629
H(16)	$W(1)$	0·459	0·267	0·628
H(17)	$W(2)$	0·558	0·335	0·412
H(18)	$W(2)$	0·558	0·275	0·463

is shown in Fig. 4. This composite drawing is viewed along the b axis.

The final coordinates and anisotropic temperature factors for the heavier atoms are listed in Table 2. The approximate coordinates for the hydrogen atoms are given in Table 3.

Geometry of the molecule

The arginine molecule is characterized by two planes, one through the carboxyl group and the other through the side chain which terminates with the guanidyl group. The molecule is a zwitterion with the guanidyl group, rather than the amino group, accepting a proton from the acid group. The bond lengths and angles are listed in Table 4 and shown in Fig. 5.

The dimensions of the amino acid group are quite similar to those reported for glycine (Marsh, 1958) and L-lysine (Wright & Marsh, 1962). The equation

Table 2. *The final parameters and their standard deviations*

The thermal parameters are of the form $T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$. For the oxygen atoms of the water molecules, the alternate symbols $W(1)$ and $W(2)$ are used in the succeeding Tables. The standard deviations are multiplied by 10^4

	x	σ_x	y	σ_y	z	σ_z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
O(1)	0·3022	(11)	0·4036	(4)	0·3231	(4)	244	44	42	23	68	4
O(2)	0·3340	(11)	0·5832	(4)	0·2830	(4)	219	45	31	6	53	2
C(3)	0·2353	(14)	0·5047	(6)	0·3220	(4)	162	41	17	−2	16	3
C(4)	0·0072	(11)	0·5293	(5)	0·3724	(4)	95	35	14	−4	6	−3
N(5)	−0·0839	(11)	0·6432	(6)	0·3524	(4)	136	44	23	7	0	−2
C(6)	0·0622	(13)	0·5186	(7)	0·4680	(4)	149	56	12	−31	1	1
C(7)	0·2546	(17)	0·5995	(7)	0·5002	(5)	288	59	19	−45	−52	11
C(8)	0·3822	(14)	0·5478	(7)	0·5753	(5)	148	52	22	−14	−39	11
N(9)	0·5532	(11)	0·6274	(5)	0·6118	(3)	127	37	14	−3	−24	1
C(10)	0·7315	(12)	0·5955	(6)	0·6633	(4)	110	46	10	−12	8	−2
N(11)	0·7796	(12)	0·4862	(5)	0·6760	(4)	161	36	16	9	−6	6
N(12)	0·8579	(13)	0·6739	(6)	0·7016	(4)	191	41	24	−1	−52	1
$H_2O(1)$, $W(1)$	0·5506	(13)	0·2790	(6)	0·6214	(5)	252	45	66	17	25	6
$H_2O(2)$, $W(2)$	0·6222	(17)	0·2871	(12)	0·4356	(5)	323	195	50	89	42	28

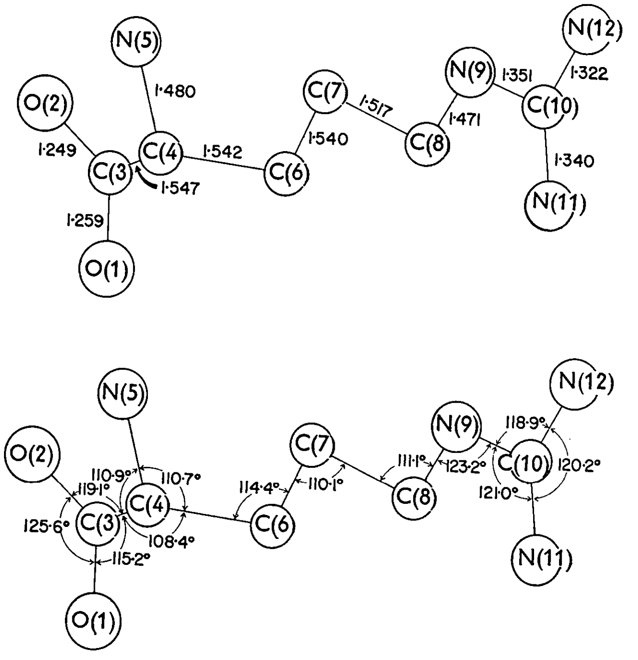

Fig. 5. Bond distances and angles.

for the least-squares plane through the atoms O(1)O(2)C(3)C(4) is

$$3{\cdot}1187x + 2{\cdot}3040y + 12{\cdot}795z = 6{\cdot}0093 \qquad (7)$$

and the deviations of the individual atoms from the plane are:

$$\mathrm{O}(1) - 0{\cdot}003,\ \mathrm{O}(2) - 0{\cdot}003,\ \mathrm{C}(3) + 0{\cdot}008, \text{ and } \mathrm{C}(4) - 0{\cdot}002 \text{ Å}.$$

Table 4. *Bond lengths and angles*

Bond		Angle	
C(3)–O(1)	1·259 Å	O(1)–C(3)–O(2)	125·6°
C(3)–O(2)	1·249	O(1)–C(3)–C(4)	115·2
		O(2)–C(3)–C(4)	119·1
C(4)–N(5)	1·480	C(3)–C(4)–N(5)	110·9
		C(6)–C(4)–N(5)	110·7
C(8)–N(9)	1·471	C(8)–N(9)–C(10)	123·2
C(10)–N(9)	1·351	N(9)–C(10)–N(11)	121·0
C(10–N(11)	1·340	N(9)–C(10)–N(12)	118·9
C(10)–N(12)	1·322	N(11)–C(10)–N(12)	120·2
C(3)–C(4)	1·547	C(3)–C(4)–C(6)	108·4
C(4)–C(6)	1·542	C(4)–C(6)–C(7)	114·4
C(6)–C(7)	1·540	C(6)–C(7)–C(8)	110·1
C(7)–C(8)	1·517	C(7)–C(8)–N(9)	111·1

The standard deviation for the bond lengths is 0·008 to 0·012 Å and for the angles 0·9°.

The nitrogen atom N(5) lies 0·280 Å out of the plane; the values found in glycine and lysine were near 0·44 Å. Although the amino group does not accept an extra proton to form C–NH_3^+ as was the case, for example, in glycine and lysine, the nitrogen in the amino group does assume a tetrahedral configuration with C(4), H(2) and H(3), and the fourth position on N(5) is occupied by a hydrogen bond from N(9′).

The guanidyl group is attached to the carbon chain by a C–N bond of 1·471 Å, whereas the three C–N bonds in the guanidyl group are nearly equal and average 1·338 Å. The C–N bonds in urea were found to be 1·336 Å (see, *e.g.* Sklar, Senko, & Post, 1961), 1·34 Å in nitroguanidine (Bryden, Burkardt, Hughes & Donohue, 1956), and 1·34 Å in guanidinium bromate (Drenth, Drenth, Vos & Wiebenga, 1953). The N–C–N angles are nearly 120° and the guanidyl group is planar. The equation of the least-squares plane through the atoms N(9)C(10)N(11)N(12) is

$$3{\cdot}5764x + 0{\cdot}1756y - 12{\cdot}226z = -5{\cdot}3907 \qquad (8)$$

and the deviations of the individual atoms from this plane are:

$$\mathrm{N}(9) - 0{\cdot}0005,\ \mathrm{C}(10) + 0{\cdot}0015,\ \mathrm{N}(11) - 0{\cdot}0005 \text{ and } \mathrm{N}(12) - 0{\cdot}0005 \text{ Å}.$$

The five hydrogen atoms, H(10) to H(14), of the guanidyl group, $-NHC(NH_2)_2^+$, are also very nearly in the plane of the NCNN, thus making the whole guanidyl group planar.

The average of the four C–C bond lengths in this molecule is 1·537 Å and the average of the four C–C–C angles is 111·0°. However, the angle C(4)–C(6)–C(7) at 114·4° is somewhat larger than the other three. A similar widening of the C–C–C angle adjacent to the amino group has been observed in other amino acids and peptides. The side chain including the guanidyl group is fully extended and lies approximately in a plane. The equation for the least-squares plane through these atoms is

$$3{\cdot}6684x - 0{\cdot}5873y - 11{\cdot}992z = -5{\cdot}6305 \qquad (9)$$

and the dihedral angle between this plane and the one through the acid group is 74°.

Packing of the molecules

The packing of the arginine molecules is characterized by a three-dimensional network of hydrogen bonds. A drawing of the structure viewed along the *a* axis is shown in Fig. 6. The arginine molecules lie extended parallel to the *c* axis and they form infinite chains by means of the hydrogen bonding between two of the NH of the guanidyl group and the two O of the carboxyl group. The guanidyl and carboxyl groups involved in the hydrogen bonding are approximately coplanar. The deviations of the carboxyl atoms from the least-squares plane through the guanidyl group (equation 8) are

$$\mathrm{O}(1) - 0{\cdot}28,\ \mathrm{O}(2) + 0{\cdot}06, \text{ and } \mathrm{C}(3) - 0{\cdot}05 \text{ Å}.$$

Hydrogen bonding between arginine molecules also occurs parallel to the *b* axis in which O(2) from the carboxyl group is bonded to N(12′)H(14′) of the

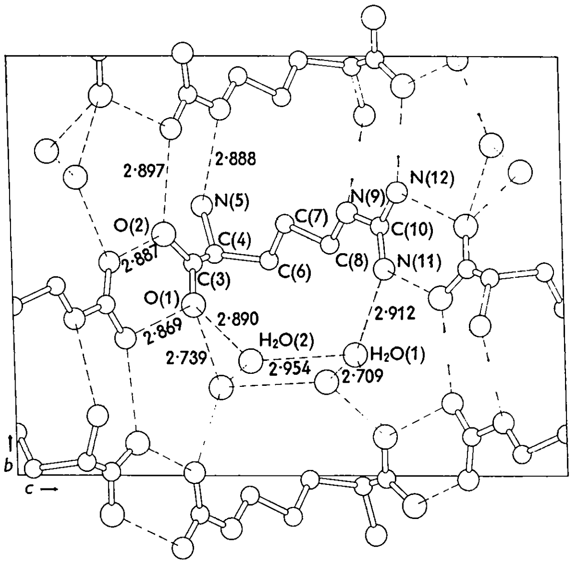

Fig. 6. A drawing of the structure of L-arginine dihydrate viewed along the *a* axis. The dashed lines indicate the hydrogen bonding.

guanidyl group and N(9′)H(10′) of the guanidyl group is bonded to N(5) of the amino group. The two hydrogen atoms, H(2) and H(3), in the amino group are not involved in hydrogen bond formation. This is a rather unusual occurrence. It is expected that molecules in a crystal usually arrange themselves to form a maximum number of hydrogen bonds (see, *e.g.*, Fuller, 1959).

The water molecules form infinite chains perpendicular to the arginine chains and parallel to the *a* axis by hydrogen bonding to each other. In addition, the water molecules form lateral hydrogen bonds to the arginine molecules. They are the donors of two hydrogen bonds and the acceptor for one.

The hydrogen bond lengths and angles are listed in Table 5. The values are consistent with those found in many other crystals (Fuller, 1959). The four hydrogen bonds around *W*(1), the oxygen atom in H_2O(1), are arranged in a roughly tetrahedral configuration, whereas the three hydrogen bonds around *W*(2) are approximately in a plane.

The closest intermolecular approaches between non-bonded atoms are those between N(5) and N(12′) (3·42 Å), and between N(5) and N(11″) (3·36 Å), where hydrogen bonds may have been expected to form, and 3·45 Å between two water molecules not hydrogen-bonded to each other.

Table 5. *Hydrogen-bonds lengths and angles*

Bond		Angle	
N(9)H(10) ··· N(5′)	2·888 Å	C(8)N(9) ··· N(5′)	112·7°
		C(10)N(9) ··· N(5′)	110·5
N(12)H(14) ··· O(2′)	2·897	C(10)N(12) ··· O(2′)	135·6
N(12)H(13) ··· O(1″)	2·869	C(10)N(12) ··· O(1″)	116·3
N(11)H(12) ··· O(2″)	2·887	C(10)N(11) ··· O(2″)	121·2
W(1)H(15) ··· O(1′)	2·739	N(11) ··· *W*(1) ··· *W*(2)	101·7
N(11)H(11) ··· *W*(1)	2·912	N(11) ··· *W*(1) ··· O(1′)	109·9
W(2)H(18) ··· *W*(1)	2·954	N(11) ··· *W*(1) ··· *W*(2′)	138·0
W(1)H(16) ··· *W*(2′)	2·709	*W*(2) ··· *W*(1) ··· O(1′)	105·6
W(2)H(17) ··· O(1)	2·890	*W*(2) ··· *W*(1) ··· *W*(2′)	78·8
		W(2′) ··· *W*(1) ··· O(1′)	110·2
		O(1) ··· *W*(2) ··· *W*(1)	122·4
		O(1) ··· *W*(2) ··· *W*(1′)	120·0
		W(1) ··· *W*(2) ··· *W*(1′)	116·2

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