Acta Cryst. (1971). B27, 11

The Crystal Structure of L-Arginine Phosphate Monohydrate

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(*Received* 16 *February* 1970)

The crystal structure of L-arginine phosphate monohydrate $C_6H_{14}N_4O_2.H_3PO_4.H_2O$, has been determined. The space group is $P2_1$ with unit-cell dimensions $a=10{\cdot}85$, $b=7{\cdot}91$, $c=7{\cdot}32$ Å, $\beta=98{\cdot}0°$, and the cell contains two formula units. Refinement by the full-matrix least-squares method gave an R value of 0·095 for 1229 observed reflexions. The locations of 17 out of 19 hydrogen atoms in the asymmetric unit have been determined. The arginine molecule exists as a zwitterion and both the amino and guanidyl groups are protonated. The phosphate group has two un-ionized OH groups. The rotation angles about the C^{γ}–C^{δ} and C^{δ}–N^{ε} bonds are both found to be staggered, which results in a rather unusual folded conformation of the side chain of the arginine molecule. The γ-carbon atom is found to be at the *trans* position to the amino group. The crystal structure consists of alternate layers of phosphate groups and arginine molecules stacked along the a axis and held together by hydrogen bonds.

Introduction

L-Arginine is one of the essential amino acids widely distributed in biological substances. It occurs mostly as a constituent of proteins especially in protamine, but in some materials such as in seeds it occurs as a free amino acid.

The functions and role of arginine molecules and residues in living matter are characterized by the strong basicity of the guanidyl group. The crystal structures of various compounds containing arginine molecules have been reported. These include L-arginine dihydrate (Karle & Karle, 1964), hydrochloride (Mazumdar & Srinivasan, 1968), hydrochloride monohydrate (Vankatesan, Mazumdar, Mez & Donohue, 1968), hydrobromide monohydrate (Mazumdar & Srinivasan, 1964). The present study of the crystal structure of L-arginine phosphate monohydrate,

$^{+}(H_2N)_2CNH(CH_2)_3CH(NH_3)^{+}COO^{-}.H_2PO_4^{-}.H_2O$,

was undertaken because a similar type of binding between the guanidyl and phosphate group is quite commonly found in nature and it seemed to be of particular importance to elucidate the conformation of the arginine molecule and its binding relation to the phosphate group, which possesses a rather complex charge distribution compared with that of the chloride or bromide anion.

Experimental

L-Arginine phosphate was prepared by adding an aqueous solution of phosphoric acid to that of L-arginine and purified by repeated recrystallization. The crystals for X-ray analysis were grown from the aqueous solution by slow cooling. The unit-cell dimensions and space group were determined from precession photographs taken with Cu $K\alpha$ radiation.

Crystal data

L-Arginine phosphate monohydrate,
$C_6H_{14}N_4O_2.H_3PO_4.H_2O$
F.W. 290·1
Monoclinic
$a=10{\cdot}85\pm0{\cdot}02$, $b=7{\cdot}91\pm0{\cdot}01$, $c=7{\cdot}32\pm0{\cdot}02$ Å,
$\beta=98{\cdot}0\pm0{\cdot}10°$
$U=621{\cdot}9$ Å^3
$D_m=1{\cdot}531$, $D_x=1{\cdot}544$ g.cm^{-3}
$F(000)=270$

Absent spectra, $0k0$ when k is odd
Space group, $P2_1$; $Z=2$

The density was measured by flotation in a mixture of carbon tetrachloride and chloroform. Three-dimensional intensity data were collected by use of the multiple-film equi-inclination Weissenberg technique for the b axis up to the fifth layer and for the c axis up to the fourth layer. The relative intensities were measured with the aid of a Narumi microdensitometer and were corrected for Lorentz and polarization factors in the usual way. No correction for absorption was made. Sets of structure factors for various layers were placed on a common scale by correlating those of the equivalent reflexions. A total of 1231 independent observed structure factors were obtained which corresponds to 88% of the possible reflexions within the limiting sphere of Cu $K\alpha$ radiation. These structure factors were put on an absolute scale by Wilson's method which gave an overall temperature factor of 1·75 Å^2.

Determination and refinement of the structure

A sharpened three-dimensional Patterson synthesis was computed and the approximate x and z coordinates of the phosphorus atom were determined on the Harker section. The y parameter was arbitrarily chosen to be 0·75. The pseudo-mirror plane through the phosphorus atom was eliminated by assuming a tetrahedral arrangement of phosphate oxygen atoms. A Fourier synthesis phased on the phosphate group showed all twelve atoms of the arginine molecule and one water oxygen atom together with several other ghost peaks.

The atomic parameters of all eighteen atoms were then refined by six cycles of the block-matrix followed

Table 1. *Final atomic parameters and standard deviations*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(1)	−0·0117 (2)	0·7500 (0)	0·1764 (3)	0·0051 (2)	0·0036 (2)	0·0077 (3)	0·0001 (2)	−0·0004 (2)	0·0001 (3)
O(1)	0·0155 (8)	0·8405 (12)	0·0076 (11)	0·0090 (7)	0·0135 (15)	0·0103 (13)	−0·0002 (9)	0·0038 (8)	0·0009 (11)
O(2)	0·0130 (7)	0·8537 (10)	0·3513 (10)	0·0072 (6)	0·0065 (10)	0·0140 (15)	−0·0003 (7)	−0·0005 (8)	−0·0003 (10)
O(3)	−0·1546 (6)	0·6965 (10)	0·1355 (10)	0·0053 (6)	0·0107 (12)	0·0128 (14)	−0·0003 (7)	−0·0018 (7)	0·0005 (11)
O(4)	0·0640 (7)	0·5824 (10)	0·2089 (11)	0·0071 (7)	0·0065 (11)	0·0190 (17)	0·0005 (7)	−0·0025 (8)	−0·0002 (12)
O(5)	0·3614 (7)	0·8351 (10)	0·9206 (11)	0·0078 (7)	0·0087 (12)	0·0184 (18)	−0·0004 (8)	−0·0058 (9)	−0·0000 (12)
O(6)	0·2374 (6)	0·9497 (9)	0·6859 (10)	0·0066 (6)	0·0049 (9)	0·0122 (13)	0·0002 (6)	−0·0007 (7)	−0·0001 (9)
O(W)	0·4750 (8)	0·5851 (11)	0·1527 (10)	0·0102 (9)	0·0102 (13)	0·0112 (15)	0·0006 (8)	−0·0009 (9)	0·0006 (11)
N(1)	0·0762 (7)	0·6832 (10)	0·6837 (10)	0·0057 (6)	0·0056 (10)	0·0082 (14)	0·0000 (7)	−0·0015 (7)	−0·0001 (10)
N(2)	0·3703 (8)	0·2243 (11)	0·4938 (11)	0·0074 (7)	0·0062 (13)	0·0102 (14)	−0·0001 (7)	0·0012 (8)	0·0006 (11)
N(3)	0·2316 (9)	0·0633 (14)	0·3070 (14)	0·0067 (8)	0·0110 (15)	0·0197 (22)	−0·0007 (9)	0·0011 (10)	0·0001 (16)
N(4)	0·3184 (8)	0·2953 (13)	0·1866 (12)	0·0062 (7)	0·0139 (18)	0·0119 (16)	−0·0012 (9)	0·0003 (8)	0·0012 (13)
C(1)	0·2740 (8)	0·8280 (12)	0·7924 (13)	0·0041 (6)	0·0070 (14)	0·0111 (17)	0·0000 (8)	0·0009 (8)	−0·0005 (13)
C(2)	0·2119 (8)	0·6546 (12)	0·7538 (15)	0·0037 (7)	0·0062 (14)	0·0170 (21)	0·0006 (8)	0·0002 (9)	0·0008 (14)
C(3)	0·2692 (9)	0·5572 (13)	0·6074 (13)	0·0050 (7)	0·0077 (13)	0·0108 (18)	0·0001 (8)	0·0016 (9)	−0·0004 (14)
C(4)	0·3944 (9)	0·4790 (13)	0·6847 (14)	0·0047 (8)	0·0091 (16)	0·0124 (18)	−0·0001 (9)	0·0008 (9)	−0·0003 (14)
C(5)	0·4487 (8)	0·3700 (14)	0·5472 (13)	0·0041 (7)	0·0098 (14)	0·0103 (17)	−0·0005 (8)	−0·0003 (8)	−0·0001 (14)
C(6)	0·3056 (8)	0·1956 (14)	0·3291 (14)	0·0037 (6)	0·0112 (16)	0·0141 (20)	0·0007 (8)	0·0010 (9)	−0·0002 (15)

Atom	Bonded to	x	y	z	B
H(1)	C(2)	0·204 (16)	0·560 (29)	0·863 (22)	3·2 (3·8) Å^2
H(2)	N(1)	0·050 (11)	0·691 (17)	0·822 (15)	1·3 (2·3)
H(3)	N(1)	0·023 (12)	0·574 (20)	0·651 (17)	1·0 (2·5)
H(4)	N(1)	0·075 (9)	0·756 (17)	0·569 (13)	0·3 (1·8)
H(5)	C(3)	0·283 (11)	0·590 (18)	0·497 (15)	0·0 (2·3)
H(6)	C(3)	0·227 (9)	0·453 (16)	0·558 (15)	1·3 (1·9)
H(7)	C(4)	0·453 (11)	0·564 (18)	0·718 (15)	0·4 (2·2)
H(8)	C(4)	0·395 (15)	0·424 (25)	0·840 (22)	4·4 (3·6)
H(9)	C(5)	0·458 (10)	0·432 (16)	0·457 (16)	0·3 (2·0)
H(10)	C(5)	0·541 (13)	0·376 (22)	0·554 (18)	1·9 (3·1)
H(11)	N(2)	0·377 (13)	0·122 (23)	0·570 (18)	1·9 (3·1)
H(12)	N(3)	0·239 (15)	−0·002 (24)	0·405 (22)	1·6 (3·4)
H(14)	N(4)	0·359 (10)	0·424 (15)	0·174 (15)	0·0 (1·9)
H(15)	N(4)	0·315	0·270	0·072	3·0
H(16)	O(W)	0·518 (12)	0·515 (19)	0·126 (18)	1·0 (2·8)
H(17)	O(W)	0·457 (17)	0·584 (31)	0·031 (24)	4·7 (4·5)
H(18)	O(3)	−0·171	0·690	0·265	3·0

To represent the L-arginine molecule the coordinates should refer to the right-handed coordinate system.

The temperature factors for the heavier atoms are of the form,

$$T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right],$$

and those for the hydrogen atoms are,

$$T=\exp\left[-B(\sin\theta/\lambda)^2\right].$$

The hydrogen atoms H(15) and H(18) were found on the final difference electron density map and their atomic parameters were not refined. Two hydrogen atoms bonded to N(3) and O(4) were not clearly found on the difference map.

by three cycles of the full-matrix least-squares calculations in which the anisotropic thermal parameters were allowed for. The weighting system was:

$$\sqrt{w}=80/F_o^2\,,\ \text{when}\ F_o\geq 20\,,$$
$$\sqrt{w}=\ 4/F_o\,,\ \text{when}\ 20>F_o>4\,,$$
$$\sqrt{w}=\ F_o/4\,,\ \text{when}\ F_o\leq 4\,.$$

The R value was 0·106 for 1231 observed reflexions.

A difference Fourier synthesis was computed at this stage to locate hydrogen atoms. In this calculation, two reflexions having the largest calculated structure factors were excluded, since they are obviously strongly affected by the secondary extinction effect. Of a total of nineteen hydrogen atoms in the asymmetric unit,

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	|F(CAL)|
2	0	-8	6.04	5.94
3	0	-8	8.14	6.87
4	0	-8	10.76	8.66
3	0	-7	17.30	16.97
4	0	-7	3.61	5.21
1	0	-6	19.75	17.28
2	0	-6	22.81	22.43
3	0	-6	29.20	28.25
4	0	-6	10.94	12.31
5	0	-6	7.79	7.92
6	0	-6	13.52	13.73
7	0	-6	10.26	11.35
8	0	-6	5.51	6.41
10	0	-6	9.18	8.08
1	0	-5	15.77	17.98
2	0	-5	28.69	29.27
3	0	-5	19.20	20.86
4	0	-5	26.90	24.96
6	0	-5	17.78	18.13
7	0	-5	10.06	11.45
8	0	-5	7.79	10.63
10	0	-5	4.04	4.05
1	0	-4	4.42	6.01
2	0	-4	8.22	5.71
3	0	-4	8.51	9.31
4	0	-4	5.36	6.30
5	0	-4	13.36	13.42
6	0	-4	14.56	13.42
8	0	-4	8.16	9.21
9	0	-4	7.81	8.48
10	0	-4	7.09	7.11
11	0	-4	3.22	5.91
12	0	-4	2.71	4.54
1	0	-3	5.91	5.87
2	0	-3	12.55	13.42
3	0	-3	2.69	2.65
4	0	-3	3.46	3.32
5	0	-3	12.79	13.14
6	0	-3	15.94	16.56
7	0	-3	8.13	7.20
10	0	-3	5.16	5.57
1	0	-2	28.58	33.48
2	0	-2	9.67	8.15
3	0	-2	8.07	7.18
4	0	-2	22.99	24.55
5	0	-2	23.77	22.34
7	0	-2	4.97	5.80
8	0	-2	9.67	10.36
9	0	-2	10.87	10.18
10	0	-2	15.18	15.75
12	0	-2	7.66	8.94
13	0	-2	3.94	6.09
1	0	-1	4.31	6.63
2	0	-1	15.18	12.08
3	0	-1	9.18	7.94
4	0	-1	19.97	19.57
6	0	-1	14.39	15.48
7	0	-1	21.96	19.03
8	0	-1	6.73	6.68
9	0	-1	5.69	6.82
1	0	0	26.88	25.54
2	0	0	21.23	18.87
3	0	0	48.97	57.09
4	0	0	53.93	49.71
5	0	0	29.04	24.95
6	0	0	14.89	13.31
7	0	0	6.02	5.20
8	0	0	16.25	15.46
9	0	0	7.54	7.27
10	0	0	2.19	2.97
11	0	0	7.13	7.49
12	0	0	1.71	2.48
13	0	0	11.72	11.25
0	0	1	2.01	0.04
1	0	1	53.41	56.51
2	0	1	41.90	37.8[illegible]
3	0	1	5.38	5.20
4	0	1	18.31	18.14
5	0	1	6.54	5.79
6	0	1	38.10	37.98
7	0	1	7.76	8.06
8	0	1	15.24	14.08
9	0	1	9.45	8.88
12	0	1	11.17	10.73
13	0	1	1.90	0.32
1	0	2	29.83	31.08
2	0	2	22.35	23.51
3	0	2	7.94	7.94
4	0	2	28.50	25.46
5	0	2	21.06	17.89
6	0	2	14.96	15.94
7	0	2	9.03	9.31
8	0	2	14.06	15.03
9	0	2	6.54	7.42
11	0	2	9.78	10.62
13	0	2	3.70	3.32
0	0	3	13.38	13.44
1	0	3	24.04	23.40
2	0	3	22.52	24.32
3	0	3	12.09	13.05
4	0	3	14.04	11.22
5	0	3	6.17	4.80
6	0	3	22.99	22.07
7	0	3	4.99	6.27
8	0	3	2.51	1.62
11	0	3	12.58	12.74
0	0	4	8.05	7.83
1	0	4	5.99	4.95
2	0	4	11.26	10.03
3	0	4	17.39	16.45
5	0	4	1.46	4.11
6	0	4	1.60	4.16
7	0	4	16.34	16.52
9	0	4	1.66	3.82
8	0	4	14.81	17.68
10	0	4	7.48	7.98
11	0	4	7.46	7.46
1	0	5	21.17	21.34
3	0	5	10.70	11.52
4	0	5	15.02	16.19
7	0	5	13.34	17.35
8	0	5	7.00	8.79
0	0	6	29.83	30.98
1	0	6	9.91	10.61
2	0	6	10.67	11.39
3	0	6	5.21	5.63
4	0	6	11.31	13.93
5	0	6	7.17	8.27
6	0	6	6.36	7.98
7	0	6	4.37	5.46
8	0	6	5.29	7.12
9	0	6	3.68	6.62
0	0	8	12.73	10.83
1	1	-9	3.08	3.38
2	1	-9	3.81	4.13
3	1	-9	6.34	6.49
4	1	-9	5.27	4.96
5	1	-9	5.64	5.65
1	1	-8	5.88	5.14
3	1	-8	9.12	8.01
7	1	-8	6.06	4.14
1	1	-7	9.73	9.85
2	1	-7	14.63	16.57
3	1	-7	5.27	4.96
4	1	-7	10.28	11.07
5	1	-7	16.86	13.32
6	1	-7	3.91	4.81
7	1	-7	7.54	6.20
8	1	-7	10.06	9.65
9	1	-7	6.36	5.63
10	1	-7	2.82	2.05
1	1	-6	21.24	20.98
2	1	-6	6.14	6.30
3	1	-6	9.12	9.47
4	1	-6	9.77	8.60
6	1	-6	4.99	4.79
7	1	-6	4.15	2.68
8	1	-6	5.86	6.06
9	1	-6	4.61	5.00
10	1	-6	8.16	6.84
11	1	-6	5.49	3.92
1	1	-5	15.68	15.75
2	1	-5	9.01	9.03
3	1	-5	20.06	20.60
4	1	-5	7.81	6.49
5	1	-5	12.62	13.72
6	1	-5	9.45	9.64
7	1	-5	3.28	3.54
8	1	-5	14.08	14.51
9	1	-5	6.28	6.24
11	1	-5	5.38	4.43
1	1	-4	18.65	17.53
2	1	-4	34.68	37.40
3	1	-4	10.26	8.74
4	1	-4	8.88	8.80
5	1	-4	11.31	11.35
6	1	-4	4.39	5.37
7	1	-4	5.77	6.80
8	1	-4	8.62	10.28
9	1	-4	8.00	8.56
10	1	-4	9.38	9.52
11	1	-4	4.00	5.37
13	1	-4	7.02	6.69
1	1	-3	13.82	13.66
2	1	-3	11.92	12.20
3	1	-3	34.14	36.03
4	1	-3	11.15	10.83
5	1	-3	21.06	22.23
6	1	-3	15.70	17.14
7	1	-3	5.55	5.65
8	1	-3	11.42	12.47
9	1	-3	9.80	10.66
10	1	-3	11.20	11.42
12	1	-3	8.22	7.62
1	1	-2	35.62	39.04
2	1	-2	20.18	20.13
3	1	-2	33.28	36.51
4	1	-2	17.06	17.82
5	1	-2	15.94	15.74
6	1	-2	13.27	13.92
7	1	-2	7.89	7.59
8	1	-2	6.87	5.24
9	1	-2	6.74	8.10
10	1	-2	5.66	6.95
11	1	-2	5.38	6.24
12	1	-2	5.47	3.98
1	1	-1	24.91	25.35
3	1	-1	15.79	15.31
4	1	-1	15.73	14.38
5	1	-1	35.06	34.76
6	1	-1	17.85	16.78
7	1	-1	23.73	21.94
8	1	-1	23.77	21.03
9	1	-1	3.72	2.82
10	1	-1	9.07	10.69
11	1	-1	4.42	4.27
12	1	-1	5.55	6.80
13	1	-1	6.93	7.21
1	1	0	10.72	7.25
2	1	0	22.94	24.36
3	1	0	37.72	36.64
4	1	0	11.94	10.69
5	1	0	31.56	30.54
6	1	0	14.91	14.36
7	1	0	14.17	12.97
8	1	0	10.50	9.75
9	1	0	9.14	9.12
10	1	0	13.04	12.73
11	1	0	3.59	3.32
12	1	0	0.79	1.86
13	1	0	4.05	4.78
0	1	1	6.98	6.39
1	1	1	43.10	44.61
2	1	1	39.41	32.99
3	1	1	20.03	17.13
4	1	1	10.10	8.40
5	1	1	26.18	26.44
6	1	1	31.23	27.84
7	1	1	18.61	16.31
8	1	1	9.45	8.46
9	1	1	7.52	7.50
10	1	1	4.85	4.71
11	1	1	7.33	6.64
12	1	1	8.11	6.42
13	1	1	2.63	2.37
0	1	2	51.39	62.75
1	1	2	24.71	22.58
2	1	2	17.28	15.41
3	1	2	30.95	27.06
4	1	2	21.34	21.08
5	1	2	10.61	8.77
6	1	2	8.29	8.07
7	1	2	15.77	16.23
8	1	2	11.22	10.87
9	1	2	1.71	3.23
10	1	2	12.07	12.00
11	1	2	4.24	4.12
12	1	2	6.84	6.29
13	1	2	9.30	11.62
0	1	3	13.43	12.50
1	1	3	26.29	27.25
2	1	3	2.89	3.53
3	1	3	3.43	4.02
4	1	3	18.41	18.18
5	1	3	11.28	11.00
6	1	3	11.07	11.20
7	1	3	16.31	17.28
8	1	3	9.05	9.70
9	1	3	11.72	11.59
10	1	3	6.60	6.96
11	1	3	0.99	1.90
12	1	3	4.44	4.30
0	1	4	31.27	30.49
1	1	4	9.51	9.03
2	1	4	7.09	6.98
3	1	4	12.64	11.59
4	1	4	8.11	7.36
5	1	4	6.98	7.56
6	1	4	7.09	7.18
7	1	4	5.45	4.76
8	1	4	0.74	1.93
9	1	4	8.75	8.29
10	1	4	1.60	3.15
11	1	4	4.33	4.56
0	1	5	14.96	14.52
1	1	5	20.64	19.65
2	1	5	9.08	9.72
3	1	5	8.63	8.86
4	1	5	10.15	10.74
5	1	5	12.53	14.11
6	1	5	13.04	15.81
7	1	5	7.26	8.07
8	1	5	8.70	7.91
9	1	5	2.89	2.88
10	1	5	7.19	7.05
2	1	6	13.86	16.80
3	1	6	12.11	13.78
5	1	6	13.54	12.73
6	1	6	16.80	7.06
7	1	6	6.25	6.11
8	1	6	4.59	5.17
0	1	7	7.22	6.10
0	1	8	5.79	7.33
0	1	9	2.54	3.90
1	2	-9	6.34	4.79
2	2	-9	5.25	4.56
3	2	-9	4.13	3.56
4	2	-9	3.54	4.04
1	2	-8	14.43	11.71
2	2	-8	10.69	7.41
3	2	-8	12.05	9.31
4	2	-8	8.68	6.55
5	2	-8	4.75	3.34
6	2	-8	7.37	6.15
7	2	-8	9.08	7.68
1	2	-7	12.16	11.19
3	2	-7	7.70	8.10
4	2	-7	7.61	5.53
5	2	-7	6.71	6.21
7	2	-7	4.90	0.84
8	2	-7	5.40	4.37
9	2	-7	3.72	3.75
10	2	-7	2.60	0.53
1	2	-6	18.02	18.06
2	2	-6	15.53	14.71
3	2	-6	16.66	15.81
4	2	-6	7.17	7.05
5	2	-6	12.42	11.63
6	2	-6	7.09	6.91
7	2	-6	11.74	12.16
9	2	-6	7.90	5.75
10	2	-6	8.13	6.70
1	2	-5	6.85	6.32
2	2	-5	13.95	12.41
3	2	-5	15.33	14.09
4	2	-5	15.51	15.39
5	2	-5	12.93	12.28
6	2	-5	8.88	8.78
7	2	-5	11.96	12.23
8	2	-5	11.05	9.75
9	2	-5	12.07	13.06
10	2	-5	7.33	7.09
12	2	-5	5.38	6.07
1	2	-4	14.78	14.78
2	2	-4	13.54	12.85
3	2	-4	13.60	11.05
4	2	-4	7.04	8.09
5	2	-4	10.10	10.11
6	2	-4	1.82	1.38
7	2	-4	12.99	13.72
8	2	-4	11.81	12.65
9	2	-4	5.29	4.40
10	2	-4	6.69	7.03
11	2	-4	9.29	8.43
13	2	-4	1.97	1.67
1	2	-3	17.71	17.86
2	2	-3	36.37	38.36
3	2	-3	20.03	20.12
4	2	-3	17.32	16.03
5	2	-3	23.27	24.19
6	2	-3	11.15	10.16
7	2	-3	10.35	10.37
8	2	-3	20.78	23.36
9	2	-3	5.34	4.82
11	2	-3	5.64	2.34
1	2	-2	38.69	43.06
2	2	-2	25.17	25.58
3	2	-2	25.02	23.57
4	2	-2	14.13	13.33
5	2	-2	5.97	4.81
6	2	-2	15.16	14.74
7	2	-2	18.96	18.21
8	2	-2	10.21	10.10
9	2	-2	13.89	14.61
10	2	-2	9.18	8.96
11	2	-2	7.33	7.67
12	2	-2	8.75	8.44
13	2	-2	3.81	4.07
1	2	-1	17.34	18.28
2	2	-1	38.73	41.27
3	2	-1	37.00	36.37
4	2	-1	16.99	16.92
5	2	-1	12.62	11.77
6	2	-1	5.10	4.54
7	2	-1	5.23	4.68
8	2	-1	10.08	9.84
9	2	-1	7.50	6.95
10	2	-1	6.73	6.61
12	2	-1	5.12	2.50
0	2	0	51.42	40.88
1	2	0	40.59	39.29
2	2	0	31.25	26.69
3	2	0	58.79	59.32
4	2	0	12.16	10.63
5	2	0	23.27	20.61
6	2	0	38.18	37.21
7	2	0	24.86	22.34
8	2	0	12.99	10.67
9	2	0	12.47	11.76
10	2	0	8.48	7.84
11	2	0	10.78	9.69
12	2	0	2.17	2.77
13	2	0	5.45	4.78
0	2	1	24.74	25.67
1	2	1	24.74	21.75
2	2	1	41.09	40.48
3	2	1	40.37	37.31
4	2	1	18.68	16.22
5	2	1	25.91	23.15
6	2	1	16.34	13.79
7	2	1	22.59	20.32
8	2	1	10.63	9.45
9	2	1	11.98	10.70
12	2	1	10.50	8.41
13	2	1	3.10	2.97
0	2	2	29.46	30.49
1	2	2	10.96	9.91
2	2	2	16.14	16.66
3	2	2	11.88	11.10
4	2	2	23.58	21.33
5	2	2	16.99	14.76
6	2	2	9.18	8.40
7	2	2	12.88	13.02
8	2	2	18.24	16.55
9	2	2	9.56	9.34
10	2	2	11.22	10.08
11	2	2	1.81	2.32
12	2	2	3.24	2.23
0	2	3	33.48	35.62
1	2	3	14.68	14.67
2	2	3	12.27	10.29
3	2	3	11.31	11.75
4	2	3	12.27	12.71
5	2	3	31.01	31.10
6	2	3	15.27	15.31
7	2	3	9.42	9.67
8	2	3	15.72	16.30
9	2	3	1.82	4.23
10	2	3	3.68	2.02
11	2	3	1.93	3.40
12	2	3	6.08	6.03
0	2	4	6.61	5.30
1	2	4	16.27	16.77
2	2	4	11.29	9.80
3	2	4	20.97	20.44
4	2	4	4.07	3.49
5	2	4	20.86	21.67
6	2	4	10.15	10.70
7	2	4	8.75	8.91
8	2	4	6.54	7.34
9	2	4	7.43	6.85
10	2	4	4.48	4.32
11	2	4	4.22	4.96
0	2	5	13.06	10.92
1	2	5	13.08	12.88
3	2	5	10.37	9.84
4	2	5	18.52	18.82
5	2	5	9.27	10.48
6	2	5	6.25	5.55
7	2	5	7.09	7.37
8	2	5	4.55	3.56
9	2	5	4.88	4.42
10	2	5	3.54	4.62
0	2	6	13.84	13.94
1	2	6	15.62	15.02
2	2	6	9.86	9.17
3	2	6	16.69	16.87
4	2	6	13.08	13.72
5	2	6	7.50	7.36
6	2	6	15.81	14.14
7	2	6	8.62	7.34
8	2	6	3.48	4.96
0	2	7	6.98	4.91
1	2	7	8.60	8.75
2	2	7	9.29	8.80
3	2	7	5.31	3.31
4	2	7	7.89	6.41
5	2	7	11.11	7.92
6	2	7	5.75	5.65
7	2	7	5.25	5.26
0	2	8	6.15	4.73
1	2	8	6.78	6.40
2	2	8	9.38	8.72
3	2	8	7.43	6.72
4	2	8	8.48	6.76
0	2	9	5.67	5.58
1	2	9	4.94	4.67
1	3	-8	9.65	7.68
2	3	-8	4.77	3.98
3	3	-8	8.00	6.84
1	3	-7	9.88	10.39
2	3	-7	6.98	8.29
3	3	-7	4.13	3.62
4	3	-7	5.44	6.18
5	3	-7	9.75	10.03
7	3	-7	5.49	4.41
8	3	-7	7.09	7.28
9	3	-7	6.74	6.34
1	3	-6	6.50	5.04
2	3	-6	7.59	6.28
3	3	-6	7.35	6.77
4	3	-6	5.18	4.99
5	3	-6	7.52	8.13
6	3	-6	6.30	5.12
7	3	-6	9.29	10.54
8	3	-6	4.48	4.38
9	3	-6	5.44	5.24
10	3	-6	5.67	5.41
1	3	-5	14.30	10.79
2	3	-5	12.44	11.89
3	3	-5	6.50	5.33
4	3	-5	6.61	6.06
5	3	-5	10.10	10.20
7	3	-5	4.37	2.93
8	3	-5	4.99	2.73
9	3	-5	3.94	3.01
10	3	-5	4.40	3.63
11	3	-5	3.33	1.80
1	3	-4	28.96	28.42
2	3	-4	17.78	17.44
3	3	-4	12.03	12.95
4	3	-4	5.91	5.25
5	3	-4	17.91	19.76
6	3	-4	6.56	6.13
7	3	-4	18.52	18.99
8	3	-4	10.02	10.84
9	3	-4	5.69	4.96
10	3	-4	8.57	10.23
11	3	-4	7.54	6.07
12	3	-4	3.24	3.98
1	3	-3	4.51	4.29
2	3	-3	23.62	24.60
3	3	-3	12.64	12.21
4	3	-3	12.09	11.69
5	3	-3	9.08	8.43
6	3	-3	10.87	10.93
7	3	-3	6.95	6.35
8	3	-3	7.11	7.47
9	3	-3	11.20	12.39
10	3	-3	5.86	5.77
11	3	-3	6.39	6.66
1	3	-2	27.07	28.10
2	3	-2	12.12	10.41
3	3	-2	13.03	14.29
4	3	-2	11.29	10.81
5	3	-2	5.86	6.02
6	3	-2	27.67	28.92
7	3	-2	4.51	4.25
8	3	-2	9.86	10.82
9	3	-2	6.50	5.93
11	3	-2	4.57	3.94
13	3	-2	4.15	3.31
1	3	-1	22.15	23.29
2	3	-1	11.09	10.27
3	3	-1	15.22	14.76
4	3	-1	24.15	24.25
5	3	-1	31.67	31.79
6	3	-1	4.74	4.85
7	3	-1	21.87	22.30
8	3	-1	15.70	15.72
9	3	-1	11.28	11.34
10	3	-1	6.36	6.25
11	3	-1	5.25	4.90
13	3	-1	4.42	4.78
1	3	0	31.43	32.90
2	3	0	20.14	18.01
3	3	0	14.26	11.87
4	3	0	21.39	18.06
5	3	0	21.72	18.62
6	3	0	5.56	4.78
7	3	0	12.42	13.25
8	3	0	19.64	20.49
9	3	0	13.98	13.22
10	3	0	4.88	5.54
11	3	0	6.23	6.70
12	3	0	5.51	4.79
13	3	0	4.96	4.55
0	3	1	6.14	6.62
1	3	1	35.73	35.97
2	3	1	37.88	34.23
3	3	1	14.11	11.34
4	3	1	29.44	26.86
5	3	1	20.12	18.40
6	3	1	9.43	7.96
7	3	1	5.84	4.82
8	3	1	17.37	18.29
9	3	1	15.94	15.49
10	3	1	2.30	3.06
11	3	1	5.62	5.59
12	3	1	5.36	4.20
0	3	2	33.22	34.00
1	3	2	24.03	25.80
2	3	2	26.83	28.74
3	3	2	23.01	22.01
4	3	2	6.82	6.62
5	3	2	28.25	28.39
6	3	2	14.33	14.80
7	3	2	22.99	24.59
8	3	2	8.60	8.79
9	3	2	6.93	6.10
10	3	2	13.43	11.84
11	3	2	6.54	6.17
12	3	2	4.27	3.47
0	3	3	7.72	7.57
1	3	3	14.13	15.06
2	3	3	4.77	3.92
3	3	3	19.99	18.84
4	3	3	12.49	12.02
5	3	3	7.52	6.99
6	3	3	6.36	5.01
7	3	3	15.42	17.59
8	3	3	1.36	1.87
9	3	3	1.49	2.42
10	3	3	7.72	6.96
11	3	3	7.72	7.50
0	3	4	11.11	10.14
1	3	4	13.17	14.90
2	3	4	15.22	14.55
3	3	4	20.23	20.40
4	3	4	15.99	16.54

Table 2 (*cont.*)

5	3	4	8.49	9.34	4	4	1	17.08	14.41	7	5	-2	5.95	5.64	4	6	-1	6.34	5.92	6	7	3	4.74	4.39
6	3	4	16.73	19.19	5	4	1	17.12	16.36	8	5	-2	8.51	9.82	5	6	-1	7.87	8.13	7	7	3	5.16	5.64
7	3	4	10.02	9.08	6	4	1	15.06	15.18	9	5	-2	7.87	8.35	6	6	-1	5.48	7.32	8	7	3	6.04	7.03
8	3	4	4.86	5.28	7	4	1	17.45	17.46	10	5	-2	3.54	3.76	7	6	-1	12.34	9.48	0	7	4	8.20	9.41
10	3	4	7.76	7.18	8	4	1	10.52	9.99	11	5	-2	2.78	2.92	0	6	0	12.12	13.41	1	7	4	6.96	7.96
11	3	4	3.81	4.46	9	4	1	13.14	13.86	1	5	-1	13.86	14.74	1	6	0	8.11	8.37	2	7	4	10.24	12.02
0	3	5	8.70	7.88	10	4	1	3.56	4.71	2	5	-1	15.31	15.94	2	6	0	14.02	15.69	3	7	4	7.44	7.94
1	3	5	13.80	14.16	11	4	1	7.79	7.07	3	5	-1	9.71	8.75	3	6	0	3.46	3.05	4	7	4	5.24	7.17
2	3	5	9.36	10.27	12	4	1	7.81	7.90	4	5	-1	5.18	4.44	4	6	0	14.43	13.78	5	7	4	6.23	6.28
3	3	5	16.71	17.73	0	4	2	9.42	10.39	5	5	-1	11.28	10.75	5	6	0	4.39	3.79	6	7	4	6.04	6.09
4	3	5	11.11	11.10	1	4	2	11.05	9.76	6	5	-1	11.07	11.31	6	6	0	6.14	5.30	7	7	4	9.60	10.97
5	3	5	19.42	22.31	2	4	2	6.67	6.42	7	5	-1	8.94	9.22	7	6	0	6.41	5.79	1	8	-4	4.59	4.08
6	3	5	5.34	4.78	3	4	2	6.26	5.26	8	5	-1	5.56	5.85	8	6	0	6.34	5.80	2	8	-4	2.25	2.12
7	3	5	8.46	9.69	4	4	2	9.82	9.29	9	5	-1	5.07	5.84	9	6	0	5.69	4.89	3	8	-4	2.75	3.13
8	3	5	8.83	7.39	5	4	2	10.91	10.13	10	5	-1	11.72	10.85	10	6	0	4.39	2.91	4	8	-4	1.71	0.40
9	3	5	2.84	3.44	6	4	2	16.58	16.95	11	5	-1	4.68	4.88	11	6	0	5.69	4.88	5	8	-4	2.76	2.26
0	3	6	4.39	3.86	7	4	2	10.85	11.92	12	5	-1	4.26	4.36	0	6	1	8.20	7.15	6	8	-4	5.56	5.48
1	3	6	9.21	8.77	8	4	2	5.01	4.87	1	5	0	15.75	14.46	1	6	1	4.97	4.39	1	8	-3	5.20	6.62
2	3	6	8.75	9.33	9	4	2	4.92	5.26	2	5	0	5.40	4.64	2	6	1	10.98	10.96	2	8	-3	4.29	5.25
4	3	6	5.93	5.92	10	4	2	2.23	3.14	3	5	0	10.80	9.69	3	6	1	5.73	5.04	3	8	-3	9.75	9.72
5	3	6	6.41	6.51	0	4	3	17.12	17.93	4	5	0	8.97	8.70	4	6	1	10.91	10.22	4	8	-3	9.01	9.25
6	3	6	5.42	5.15	1	4	3	33.40	33.36	5	5	0	4.35	3.69	5	6	1	2.93	3.26	5	8	-3	9.08	9.39
7	3	6	3.46	4.34	2	4	3	12.95	11.88	6	5	0	19.27	19.79	6	6	1	6.76	5.73	1	8	-2	6.02	6.81
8	3	6	6.45	6.56	3	4	3	28.48	30.62	7	5	0	7.28	7.14	7	6	1	11.72	9.48	2	8	-2	12.73	11.11
0	3	7	5.25	5.38	4	4	3	12.84	12.94	8	5	0	6.71	6.25	8	6	1	10.23	6.51	3	8	-2	8.60	7.46
1	3	7	14.46	12.49	5	4	3	24.34	24.79	9	5	0	10.47	8.50	9	6	1	11.13	7.74	4	8	-2	9.73	10.23
2	3	7	8.11	7.89	6	4	3	22.87	25.42	10	5	0	9.18	8.09	10	6	1	15.38	12.72	5	8	-2	16.42	16.62
3	3	7	8.90	7.83	7	4	3	9.64	9.95	11	5	0	10.35	9.31	0	6	2	12.66	11.73	6	8	-2	12.11	12.01
4	3	7	12.47	11.82	8	4	3	8.51	9.88	12	5	0	4.39	5.44	1	6	2	17.04	17.77	7	8	-2	7.78	7.72
5	3	7	12.49	10.44	9	4	3	9.71	10.25	0	5	1	13.65	13.15	2	6	2	11.92	11.37	1	8	-1	10.34	8.57
6	3	7	7.76	8.07	10	4	3	5.12	5.84	1	5	1	4.90	4.02	3	6	2	4.92	5.81	2	8	-1	8.68	7.45
0	3	8	7.66	6.98	11	4	3	3.67	3.98	2	5	1	32.24	30.39	4	6	2	9.10	8.39	4	8	-1	6.95	5.80
1	3	8	5.66	4.25	0	4	4	5.44	4.80	3	5	1	16.21	15.08	5	6	2	4.96	4.80	5	8	-1	3.68	2.07
2	3	8	3.72	4.05	1	4	4	8.88	7.81	4	5	1	4.94	3.99	6	6	2	2.62	2.82	6	8	-1	4.77	4.38
3	3	8	5.71	5.37	2	4	4	10.37	7.99	5	5	1	4.04	3.30	8	6	2	3.32	3.72	7	8	-1	8.53	6.10
4	3	8	5.95	6.08	3	4	4	6.89	6.85	6	5	1	9.86	9.48	9	6	2	8.25	6.95	8	8	0	16.97	17.52
1	-8	8	10.76	10.30	4	4	4	13.12	12.79	7	5	1	9.25	7.94	10	6	2	6.65	6.58	1	8	0	5.38	6.46
2	-8	8	7.57	4.17	5	4	4	11.22	12.27	8	5	1	3.50	3.17	0	6	3	21.67	23.59	2	8	0	16.79	20.50
3	-8	8	7.26	7.67	6	4	4	4.88	4.75	9	5	1	3.53	4.43	1	6	3	14.78	16.31	3	8	0	11.48	11.39
4	-8	8	6.74	7.19	7	4	4	13.78	16.43	10	5	1	6.10	5.53	2	6	3	18.42	20.48	4	8	0	5.23	4.72
5	-8	8	8.53	8.05	8	4	4	4.51	3.83	11	5	1	4.90	4.29	3	6	3	18.02	21.89	5	8	0	16.90	14.92
6	-8	8	4.90	5.81	9	4	4	7.22	6.69	0	5	2	32.02	34.38	4	6	3	7.26	6.86	6	8	0	13.43	11.26
1	-7	8	4.05	3.09	10	4	4	2.98	2.80	1	5	2	13.08	13.02	5	6	3	4.31	3.66	7	8	0	8.94	8.19
5	-7	8	7.04	6.87	0	4	5	18.65	19.14	2	5	2	14.96	13.41	6	6	3	10.24	9.36	8	8	0	7.31	7.59
6	4	-7	7.72	7.47	1	4	5	10.15	10.62	3	5	2	13.12	11.48	7	6	3	6.47	5.82	0	8	1	1.77	1.67
7	4	-7	4.77	3.96	2	4	5	8.29	7.43	4	5	2	20.47	20.99	8	6	3	6.45	5.11	1	8	1	6.25	5.76
8	4	-7	2.78	3.25	3	4	5	10.69	10.88	5	5	2	17.78	18.08	9	6	3	9.10	8.22	2	8	1	4.94	4.74
1	4	-6	6.02	6.83	4	4	5	8.73	9.53	6	5	2	6.12	5.46	0	6	4	4.94	5.15	3	8	1	11.76	9.00
2	4	-6	5.31	3.58	5	4	5	5.53	5.69	7	5	2	9.91	10.20	1	6	4	12.03	13.89	4	8	1	11.44	8.77
3	4	-6	5.99	5.30	6	4	5	5.55	5.94	8	5	2	15.05	14.01	2	6	4	6.02	6.99	5	8	1	8.73	6.65
4	4	-6	8.62	9.55	7	4	5	3.74	2.88	9	5	2	6.43	6.52	3	6	4	5.31	6.60	6	8	1	4.24	2.98
5	4	-6	5.12	4.85	0	4	6	11.87	12.26	10	5	2	4.50	3.55	4	6	4	9.51	11.69	7	8	1	10.69	9.57
6	4	-6	7.22	7.38	1	4	6	9.97	9.01	11	5	2	8.92	9.63	5	6	4	2.45	2.37	8	8	1	5.56	4.55
7	4	-6	5.80	6.71	2	4	6	12.88	7.89	0	5	3	12.64	12.16	6	6	4	8.59	8.36	0	8	2	3.17	3.47
10	4	-6	4.29	4.55	3	4	6	15.07	14.46	1	5	3	11.35	11.15	7	6	4	5.69	4.71	1	8	2	5.45	5.16
1	4	-5	12.79	12.75	4	4	6	4.83	4.65	2	5	3	10.19	10.93	8	6	4	3.17	2.83	2	8	2	5.77	5.88
2	4	-5	5.23	4.39	5	4	6	14.36	12.63	3	5	3	14.13	15.04	1	7	-4	5.49	6.89	3	8	2	4.46	4.67
3	4	-5	7.98	8.77	6	4	6	5.44	5.99	4	5	3	10.56	10.71	2	7	-4	11.58	13.08	4	8	2	3.59	3.38
4	4	-5	7.78	7.10	7	4	6	5.12	5.60	5	5	3	5.10	5.25	3	7	-4	6.65	8.59	6	8	2	5.79	5.57
5	4	-5	7.55	8.47	1	4	7	10.35	9.77	6	5	3	3.96	3.90	4	7	-4	10.37	11.85	7	8	2	3.19	3.65
6	4	-5	8.51	9.67	4	4	7	3.19	2.15	7	5	3	8.22	7.88	5	7	-4	10.54	10.54	0	8	3	11.83	11.49
7	4	-5	8.05	9.12	5	4	7	4.81	5.23	8	5	3	5.77	6.22	6	7	-4	8.51	8.26	1	8	3	12.71	12.41
9	4	-5	13.04	12.96	0	4	8	5.44	6.47	9	5	3	5.67	5.35	7	7	-4	8.49	8.93	2	8	3	6.47	6.37
10	4	-5	5.10	4.75	1	4	8	6.06	5.92	10	5	3	9.75	8.37	8	7	-4	5.88	5.69	3	8	3	10.04	9.95
11	4	-5	5.60	6.39	2	4	8	7.55	7.87	0	5	4	15.64	16.03	1	7	-3	6.36	7.36	4	8	3	12.07	11.99
1	4	-4	16.84	17.84	3	4	8	4.00	4.99	1	5	4	24.39	25.31	2	7	-3	5.82	7.24	5	8	3	5.67	5.33
2	4	-4	10.06	9.09	1	5	-8	5.34	5.54	2	5	4	10.30	9.03	3	7	-3	6.26	7.08	6	8	3	6.95	6.39
3	4	-4	7.76	8.07	2	5	-8	6.30	6.40	3	5	4	6.56	6.04	4	7	-3	5.16	5.89	0	8	4	1.60	0.96
4	4	-4	6.60	6.12	3	5	-8	3.96	3.95	4	5	4	16.77	19.18	5	7	-3	2.97	2.98	1	8	4	5.44	5.67
5	4	-4	8.38	9.42	1	5	-7	6.01	5.22	5	5	4	9.77	11.52	6	7	-3	2.23	2.54	2	8	4	7.63	7.16
6	4	-4	6.17	6.59	2	5	-7	13.38	11.46	6	5	4	5.75	5.60	7	7	-3	4.51	3.94	3	8	4	11.79	12.24
7	4	-4	4.97	5.59	3	5	-7	8.05	8.31	7	5	4	5.99	5.18	8	7	-3	6.21	6.41	4	8	4	6.52	7.31
8	4	-4	5.55	4.61	4	5	-7	4.59	5.14	8	5	4	8.70	8.44	1	7	-2	4.51	5.02	5	8	4	6.95	7.94
11	4	-4	3.02	4.07	5	5	-7	2.86	2.71	9	5	4	5.51	5.92	2	7	-2	8.59	9.17	1	9	-4	3.26	3.83
12	4	-4	3.35	4.11	6	5	-7	5.77	5.30	0	5	5	4.16	4.09	3	7	-2	15.09	14.99	2	9	-4	3.25	3.44
1	4	-3	24.69	26.07	7	5	-7	7.13	8.30	1	5	5	5.18	5.26	4	7	-2	6.69	5.79	3	9	-4	3.22	4.78
2	4	-3	23.03	24.47	1	5	-6	2.73	3.45	2	5	5	14.65	16.40	5	7	-2	7.65	8.09	3	9	-3	2.75	1.90
3	4	-3	15.42	17.15	2	5	-6	2.23	2.44	5	5	5	11.48	12.21	6	7	-2	7.31	7.52	4	9	-3	5.53	5.76
4	4	-3	12.11	12.75	3	5	-6	6.32	6.74	6	5	5	3.98	4.65	7	7	-2	4.33	4.62	5	9	-3	5.09	6.55
5	4	-3	20.30	20.96	4	5	-6	10.15	9.36	7	5	5	10.43	10.28	8	7	-2	4.80	5.57	1	9	-2	6.54	6.76
6	4	-3	17.08	17.85	5	5	-6	6.56	6.29	8	5	5	3.63	4.49	1	7	-1	9.73	10.08	2	9	-2	2.14	2.59
7	4	-3	11.94	13.23	6	5	-6	4.26	3.71	0	5	6	4.29	5.56	2	7	-1	13.84	13.77	3	9	-2	5.80	6.27
8	4	-3	15.90	17.21	7	5	-6	4.55	3.76	1	5	6	4.50	3.48	3	7	-1	12.38	13.55	5	9	-2	1.75	2.64
9	4	-3	7.00	7.26	8	5	-6	7.19	7.22	2	5	6	3.00	1.88	4	7	-1	19.18	20.03	1	9	-1	7.15	6.60
10	4	-3	5.87	6.71	9	5	-6	6.68	7.05	3	5	6	7.94	7.60	5	7	-1	4.42	4.93	2	9	-1	10.74	10.19
11	4	-3	6.34	6.80	1	5	-5	6.74	7.25	4	5	6	3.00	3.43	6	7	-1	5.49	5.44	3	9	-1	13.54	12.86
1	4	-2	7.19	6.57	2	5	-5	10.48	12.30	5	5	6	2.56	1.90	7	7	-1	6.26	4.69	4	9	-1	10.69	9.56
2	4	-2	18.68	20.28	3	5	-5	6.45	7.17	6	5	6	6.28	5.24	8	7	-1	8.55	7.20	5	9	-1	9.29	9.24
3	4	-2	17.26	16.35	4	5	-5	4.62	4.84	0	5	7	6.41	6.18	1	7	0	9.07	8.46	6	9	-1	7.04	7.15
4	4	-2	8.53	7.44	5	5	-5	4.83	5.96	1	5	7	9.56	10.50	3	7	0	6.14	5.95	1	9	0	3.52	3.07
5	4	-2	14.43	14.68	6	5	-5	3.32	4.01	2	5	7	5.88	6.06	4	7	0	12.95	13.54	2	9	0	1.82	2.15
6	4	-2	14.68	14.51	7	5	-5	2.78	4.29	3	5	7	7.57	7.98	5	7	0	10.86	10.86	3	9	0	11.11	10.19
7	4	-2	21.38	22.87	8	5	-5	2.73	2.90	4	5	7	9.75	8.60	6	7	0	11.33	8.38	4	9	0	3.61	3.99
8	4	-2	8.25	8.38	9	5	-5	2.87	3.09	0	5	8	2.36	2.04	7	7	0	6.02	4.88	5	9	0	9.58	7.97
9	4	-2	8.81	9.86	10	5	-5	4.96	4.54	1	6	-4	4.13	4.23	8	7	0	3.92	3.11	6	9	0	3.06	2.51
11	4	-2	4.31	3.88	1	5	-4	11.22	12.38	2	6	-4	2.01	2.46	9	7	0	7.72	7.07	0	9	1	11.40	9.51
12	4	-2	5.69	5.64	2	5	-4	7.89	7.76	3	6	-4	4.31	4.85	10	7	0	2.86	3.44	1	9	1	12.46	10.43
1	4	-1	17.63	15.77	3	5	-4	14.21	14.74	4	6	-4	8.71	9.26	0	7	1	23.62	27.41	2	9	1	8.24	7.38
2	4	-1	26.68	27.79	4	5	-4	22.83	24.83	5	6	-4	5.12	5.26	1	7	1	15.64	15.12	3	9	1	16.79	14.56
3	4	-1	27.38	24.97	5	5	-4	11.46	11.81	6	6	-4	5.55	5.92	2	7	1	7.89	7.49	4	9	1	7.66	8.06
4	4	-1	10.87	9.83	6	5	-4	7.70	8.20	7	6	-4	3.89	4.14	3	7	1	11.18	12.16	5	9	1	4.66	4.19
5	4	-1	12.81	12.26	7	5	-4	11.39	12.05	8	6	-4	1.90	0.83	4	7	1	12.75	12.89	0	9	2	3.57	3.60
6	4	-1	13.52	12.66	8	5	-4	8.88	10.41	1	6	-3	16.14	18.72	5	7	1	6.67	5.16	1	9	2	4.57	4.16
7	4	-1	10.58	9.22	9	5	-4	6.37	6.45	2	6	-3	28.37	32.81	6	7	1	7.85	5.53	2	9	2	5.88	5.48
8	4	-1	12.58	12.89	10	5	-4	6.87	6.59	3	6	-3	15.85	18.29	8	7	1	5.69	5.24	3	9	2	12.20	12.31
12	4	-1	8.68	8.92	1	5	-3	11.28	12.70	4	6	-3	13.71	15.32	9	7	1	4.97	4.21	4	9	2	10.72	10.03
0	4	0	17.74	15.73	2	5	-3	2.14	0.95	5	6	-3	18.13	19.83	0	7	2	7.90	8.03	5	9	2	7.04	8.07
1	4	0	7.41	6.78	3	5	-3	13.51	14.30	6	6	-3	11.70	13.46	1	7	2	5.77	5.28	1	9	3	3.19	3.84
2	4	0	17.34	15.41	4	5	-3	9.49	10.37	7	6	-3	3.63	3.98	2	7	2	18.09	19.63	2	9	3	1.82	2.18
3	4	0	25.17	23.03	5	5	-3	2.71	2.77	8	6	-3	7.98	7.96	3	7	2	11.81	14.13	3	9	3	1.88	0.88
4	4	0	22.77	20.01	6	5	-3	4.77	4.46	1	6	-2	16.05	16.75	4	7	2	7.61	8.40	4	9	3	2.87	3.60
5	4	0	10.82	10.95	7	5	-3	5.07	4.90	2	6	-2	18.87	19.21	5	7	2	17.45	16.15	0	9	4	1.66	2.70
6	4	0	9.27	7.96	8	5	-3	2.58	2.51	3	6	-2	10.94	11.08	6	7	2	12.14	14.53	1	9	4	3.63	4.85
7	4	0	9.53	8.43	9	5	-3	5.09	6.28	4	6	-2	9.80	9.54	7	7	2	5.67	4.81	0	10	0	12.14	12.84
8	4	0	10.74	10.40	10	5	-3	6.52	6.12	5	6	-2	11.74	11.46	8	7	2	8.59	8.29	1	10	-1	3.11	2.46
10	4	0	3.61	4.38	11	5	-3	5.62	5.68	6	6	-2	12.01	13.38	9	7	2	4.62	4.94	2	10	-1	5.18	5.19
11	4	0	5.23	5.04	1	5	-2	10.63	10.93	7	6	-2	4.82	4.16	0	7	3	5.82	5.44	1	10	0	8.59	9.65
12	4	0	5.66	5.11	2	5	-2	16.99	18.35	8	6	-2	7.61	8.41	1	7	3	7.63	9.44	2	10	0	5.36	5.65
0	4	1	21.54	19.79	3	5	-2	20.76	20.24	9	6	-2	4.46	4.82	2	7	3	7.70	7.95	0	10	1	2.14	2.36
1	4	1	30.03	29.19	4	5	-2	25.00	28.10	1	6	-1	18.38	18.81	3	7	3	2.06	1.33	1	10	1	8.64	8.19
2	4	1	22.83	20.44	5	5	-2	7.59	6.45	2	6	-1	14.45	14.18	4	7	3	2.80	3.76	2	10	1	2.87	3.14
3	4	1	14.85	11.53	6	5	-2	10.65	10.54	3	6	-1	15.05	13.85	5	7	3	3.11	3.89					

fifteen atoms were actually located unambiguously. The heights of these hydrogen peaks were distributed over the range 0·4–0·9 e.Å^{-3} which seems to be significantly larger than the background level since the estimated standard deviation in the electron density is 0·12 e.Å^{-3}.

The missing hydrogen atoms were the two of the phosphate group and two of the guanidyl group. Three more cycles of full-matrix least-squares calculations using the *ORFLS* computer program (Busing, Martin & Levy, 1962) completed the refinement, in which the fifteen hydrogen atoms were included and treated as isotropic along with the eighteen heavier atoms for which the anisotropic thermal vibrations were allowed for. The final R value was 0·095 for 1229 observed structure factors. The refined atomic parameters are

given in Table 1 together with their standard deviations. A list of observed and calculated structure factors is presented in Table 2. The atomic scattering factors used in the present structure determination were: for hydrogen atoms those cited as Q-1 in *International Tables for X-ray Crystallography* (1962), for carbon SX-6, for nitrogen SX-7, for oxygen SX-8 and for phosphorus SX-70.

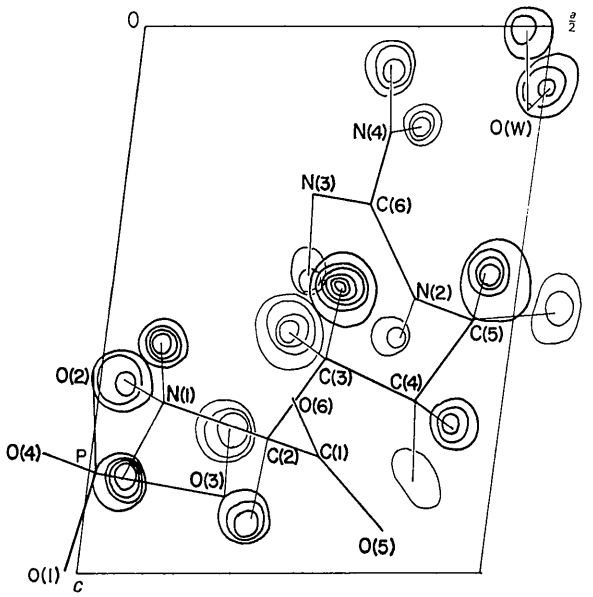
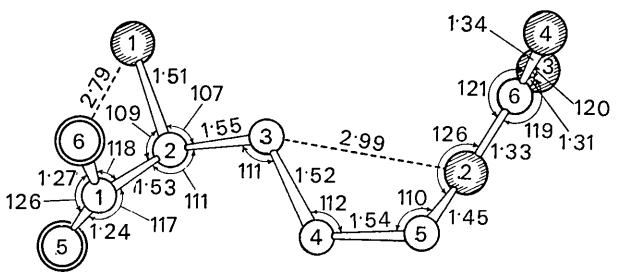
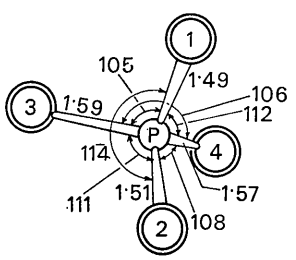


Fig. 1. Composite drawing of the difference electron density map viewed along the *b* axis showing the locations of seventeen of the nineteen hydrogen atoms. Contours are drawn at intervals of 0·1 e.Å^{-3} starting at 0·4 e.Å^{-3}.



(*a*)



(*b*)

Fig. 2. Perspective drawing of (*a*) L-arginine molecule and (*b*) the phosphate group, found in the present crystal showing the bond lengths, angles and conformations.

Finally, a difference Fourier synthesis was computed in order to locate the four missing hydrogen atoms, in which the contributions of all the hydrogen atoms were not included in the F_c values. Two well defined positive regions of peak height 0·64 and 0·67 e.Å^{-3} were found at the positions expected for the hydrogen atoms attached to N(4) of the guanidyl group and O(3) of the phosphate group. The difference electron density map showing the location of the seventeen hydrogen atoms is illustrated in Fig. 1.

Discussion of the structure

Arginine molecule

The bond lengths, angles and the internal rotation angles of the L-arginine molecule are listed in Table 3. In this Table, the values are compared with those of the L-arginine molecules found in the dihydrate, hydrochloride, hydrochloride monohydrate and hydrobromide monohydrate; they are in overall agreement with each other. The bond lengths and some bond angles in volving the hydrogen atoms are listed in Table 4. Fig. 2 is a perspective drawing of the L-arginine molecule and the phosphate group showing the bond lengths, angles and conformations. It is clear that the carboxyl group is in the ionized form and is strictly planar within the limit of experimental error. The equation of the plane and the distances of the atoms from the plane are shown in Table 5.

The amino nitrogen atom N(1) lies 0·76 Å off the plane, the angle of twist of the C–N bond out of the carboxyl plane being 33·7°. This angle is rather large compared with those found in various amino acids reported to date (Lakshminarayanan, Sasisekharan & Ramachandran, 1967). As shown in Table 8, the amino nitrogen atom accepts an extra proton to form a tetrahedral $-NH_3^+$ group as in other salts of arginine.

The guanidyl group is attached to the carbon chain through a C–N bond of length 1·452 Å which is significantly shorter than the usual C–N single-bond length such as found in spermine and spermidine (Huse & Iitaka, 1969) and is even the shortest among the corresponding bond lengths in the arginine molecules shown in Table 3. The guanidyl group is protonated and exists as a guanidinium ion. The three C–N bonds in this group are nearly equal in length with an average value of 1·326 Å. The three N–C–N angles are very close to 120° and the guanidyl group is strictly planar. The equation of the plane and the distances of the atoms from the plane are shown in Table 5. Like other arginine molecules listed in Table 5, the carbon atom C(5) is only slightly displaced from the plane of the guanidyl group.

Table 3. *Comparison of arginine molecules in different compounds*

Compound	Arg.H_3PO_4.H_2O	Arg.$2H_2O$	Arg.HCl		Arg.HCl.H_2O		Arg.HBr.H_2O	
Space group	$P2_1$	$P2_12_12_1$	$P2_1$		$P2_1$		$P2_1$	
No. of molecules in the cell	2	4	4		4		4	
			Mol. I	Mol. II	Mol. I	Mol. II	Mol. I	Mol. II
Bond lengths (Å) (e.s.d.'s)	(±0·017)	(±0·012)	(±0·015)	(±0·015)	(±0·03)	(±0·03)	(±0·03)	(±0·03)
C(1)–C(2)	1·529	1·547	1·535	1·585	1·52	1·52	1·57	1·55
C(2)–C(3)	1·549	1·542	1·528	1·526	1·59	1·58	1·53	1·57
C(3)–C(4)	1·523	1·540	1·561	1·487	1·57	1·56	1·58	1·61
C(4)–C(5)	1·537	1·517	1·539	1·524	1·58	1·58	1·55	1·52
C(1)–O(5)	1·244	1·259	1·250	1·253	1·29	1·23	1·28	1·20
C(1)–O(6)	1·266	1·249	1·268	1·248	1·29	1·31	1·27	1·27
C(2)–N(1)	1·510	1·480	1·484	1·493	1·52	1·51	1·49	1·45
C(5)–N(2)	1·452	1·471	1·489	1·471	1·51	1·49	1·46	1·49
C(6)–N(2)	1·325	1·351	1·348	1·325	1·33	1·25	1·30	1·31
C(6)–N(3)	1·313	1·322	1·354	1·357	1·34	1·37	1·39	1·34
C(6)–N(4)	1·340	1·340	1·301	1·314	1·33	1·38	1·40	1·42
Bond angles (°) (e.s.d.'s)	(±1·0)	(±0·9)	(±0·9)	(±0·9)	(±1·8)	(±1·8)	(±1·8)	(±1·8)
C(2)–C(1)–O(5)	116·8	115·2	118·8	116·2	115	117	113	119
C(2)–C(1)–O(6)	117·7	119·1	115·5	118·1	119	119	119	118
O(5)–C(1)–O(6)	125·5	125·6	125·5	125·7	126	124	128	123
C(1)–C(2)–N(1)	109·1	110·9	109·7	108·3	108	109	109	110
C(1)–C(2)–C(3)	110·5	108·4	111·6	111·1	109	107	110	107
N(1)–C(2)–C(3)	107·1	110·7	109·7	109·2	112	113	110	113
C(2)–C(3)–C(4)	110·6	114·4	113·5	113·6	109	109	111	109
C(3)–C(4)–C(5)	111·9	110·1	110·0	110·4	104	106	106	107
C(4)–C(5)–N(2)	110·2	111·1	106·5	108·6	110	110	110	110
C(5)–N(2)–C(6)	126·4	123·2	121·5	123·6	123	125	124	127
N(2)–C(6)–N(3)	119·3	118·9	116·0	116·7	117	122	120	124
N(2)–C(6)–N(4)	120·6	121·1	122·5	122·8	123	123	125	119
N(3)–C(6)–N(4)	120·1	120·2	121·5	120·4	120	115	116	117

Table 3 (*cont.*)

Compound	$Arg.H_3PO_4.H_2O$	$Arg.2H_2O$	Arg.HCl		$Arg.HCl.H_2O$		$Arg.HBr.H_2O$	
Space group	$P2_1$	$P2_12_12_1$	$P2_1$		$P2_1$		$P2_1$	
No. of molecules in the cell	2	4	4		4		4	
Internal rotation angles (°)*								
O(5)–C(1)–C(2)–N(1)	148	168	135	138	178	157	177	156
O(5)–C(1)–C(2)–C(3)	−94	−70	−104	−102	−60	−80	−61	−80
O(6)–C(1)–C(2)–N(1)	−34	−11	−51	−41	−6	−26	−6	−29
O(6)–C(1)–C(2)–C(3)	84	111	71	79	116	97	115	95
N(1)–C(2)–C(3)–C(4)	−164	62	171	168	−63	−54	−61	−55
C(1)–C(2)–C(3)–C(4)	78	−60	49	49	178	−175	178	−177
C(2)–C(3)–C(4)–C(5)	175	151	−173	166	−166	172	−163	168
C(3)–C(4)–C(5)–N(2)	−64	175	172	175	−179	−175	−180	−174
C(4)–C(5)–N(2)–C(6)	113	162	−172	170	−81	100	−86	101
C(5)–N(2)–C(6)–N(3)	−176	172	175	−179	−169	165	−167	165
C(5)–N(2)–C(6)–N(4)	5	−8	−7	6	13	−19	9	−18
Mean C–C bond length (Å)	1·535	1·537	1·541	1·531	1·57	1·56	1·56	1·56
Mean C–N bond length in guanidyl group (Å)	1·326	1·338	1·334	1·332	1·33	1·33	1·36	1·36
Mean C–C–C angle (°)	111·0	111·0	111·7	111·7	107	107	109	108
Deviation of N(1) from the carboxyl plane (Å)	0·763	0·280	1·024	0·946	0·08	0·57	0·10	0·59
State of protonation								
Carboxyl group	—†	−	—	−	−	−	−	−
Amino group	+‡	0§	+	+	+	+	+	+
Guanidyl group	+**	+	+	+	+	+	+	+
Reference	Present study	Karle & Karle (1964)	Mazumdar & Srinivasan (1968)		Vankatesan, Mazumdar, Mez & Donohue (1968)		Mazumdar & Srinivasan (1964)	

* Definition of the internal rotation angle is given by Mitsui, Tsuboi & Iitaka (1969).
† Deprotonated, $-COO^-$.
‡ Protonated, $-NH_3^+$.
§ Not protonated, $-NH_2$.
** Protonated, $-NHC(NH_2)_2^+$.

Table 4. *Bond lengths and some bond angles involving hydrogen atoms*

Bond	Length	Bond	Angle
C(2)—H(1)	1·1 ± 0·2 Å	C(2)–N(1)–H(2)	93 ± 6°
N(1)—H(2)	1·1 ± 0·1	C(2)–N(1)–H(3)	116 ± 7
N(1)—H(3)	1·1 ± 0·2	C(2)–N(1)–H(4)	105 ± 6
N(1)—H(4)	1·0 ± 0·1	C(5)–N(2)–H(11)	121 ± 9
C(3)—H(5)	0·9 ± 0·1	C(6)–N(2)–H(11)	103 ± 9
C(3)—H(6)	1·0 ± 0·1	C(6)–N(3)–H(12)	112 ± 11
C(4)—H(7)	0·9 ± 0·1	C(6)–N(4)–H(14)	134 ± 6
C(4)—H(8)	1·2 ± 0·2	P(1)–O(3)–H(18)	97
C(5)—H(9)	0·8 ± 0·1		
C(5)—H(10)	1·0 ± 0·1		
N(2)—H(11)	1·0 ± 0·2		
N(3)—H(12)	0·9 ± 0·2		
N(4)—H(14)	1·1 ± 0·1		
N(4)—H(15)	0·9		
O(*W*)–H(16)	0·8 ± 0·2		
O(*W*)–H(17)	0·9 ± 0·2		
O(3)—H(18)	1·0 ± 0·2		

Table 5. *Least-squares planes through the three planar groups and dihedral angles between them*

			Arg.HCl		Arg.HCl.H_2O		Arg.HBr.H_2O	
Compound	Arg.H_3PO_4.H_2O	Arg.$2H_2O$	Mol. I	Mol. II	Mol. I	Mol. II	Mol. I	Mol. II
(1) Plane through the carboxyl group								
O(5)	−0·007 Å	−0·003 Å	0·011 Å	0·002 Å	−0·008 Å	−0·006 Å	−0·007 Å	−0·010 Å
O(6)	−0·007	−0·003	0·011	0·002	−0·008	−0·006	−0·007	−0·009
C(1)	0·020	0·008	0·008	0·001	0·023	0·017	0·020	0·025
C(2)	−0·005	−0·002	−0·030	−0·005	−0·006	−0·005	−0·005	−0·007
N(1)†	0·785	−0·280	−1·024	0·946	0·076	0·572	0·098	0·590
C(3)†	−1·418	1·368	1·380	−1·390	−1·334	−1·506	−1·294	−1·502
A	−0·6591	0·5490	−0·0780	0·0398	0·7460	0·8452	0·7646	0·8708
B	0·2396	0·1941	−0·3462	0·4982	0·6106	0·4408	0·5789	0·3690
C	0·7129	0·8130	0·9349	0·8662	0·2659	0·3022	0·2833	0·3249
D	−4·665	6·010	−1·566	12·755	9·032	7·451	9·095	7·202
(2) Plane through the side chain								
C(2)	−0·028	0·181	−0·047	0·086	0·094	−0·054	0·110	−0·075
C(3)	0·027	−0·207	0·047	−0·091	−0·102	0·058	−0·120	0·079
C(4)	0·029	−0·141	0·042	−0·079	−0·082	0·050	−0·094	0·072
C(5)	−0·028	0·168	−0·045	0·084	0·091	−0·053	0·104	−0·076
N(1)†	−0·425	−0·754	−0·257	−0·220	−1·045	−1·245	−0·971	−1·254
C(1)†	1·338	1·631	−1·186	−0·900	0·130	−0·167	0·137	−0·138
N(2)†	−1·270	0·123	−0·235	−0·035	0·112	−0·187	0·131	−0·247
A	0·4717	0·7257	0·6919	−0·4455	−0·0059	−0·3362	0·0363	−0·3160
B	0·8138	−0·5185	−0·6885	0·8657	0·9952	0·9357	0·9970	0·9407
C	−0·3395	−0·4522	−0·2173	−0·2280	−0·0979	−0·1066	−0·0688	−0·1231
D	9·111	−6·059	−0·110	3·463	4·197	3·507	4·616	3·627
(3) Plane through the guanidyl group								
N(2)	−0·004	−0·001	0·004	0·007	0·003	0·007	−0·065	0·005
C(6)	0·012	0·002	−0·011	−0·021	−0·010	−0·018	0·018	−0·015
N(3)	−0·004	−0·001	0·003	0·007	0·003	0·006	−0·005	0·005
N(4)	−0·004	−0·001	0·004	0·007	0·003	0·006	−0·006	0·005
C(5)†	0·112	−0·180	−0·120	−0·048	−0·247	0·993	−0·256	−0·316
C(4)†	1·408	0·291	−0·278	−0·244	1·079	−0·328	1·073	0·963
A	−0·7497	0·6296	0·6055	0·6014	0·7133	0·6952	0·7299	0·7000
B	0·5681	0·0148	−0·7954	−0·7987	−0·3001	0·3535	−0·2743	0·3515
C	0·3393	−0·7767	−0·0274	0·0226	0·6334	0·6259	0·6262	0·6217
D	−9·485	−5·391	0·070	−3·610	4·777	4·414	4·941	4·431
Dihedral angles between the planes								
(1) and (2)	111°	94°	91°	77°	57°	84°	54°	89°
(2) and (3)	90	37	13	165	111	88	106	87

† The atoms marked † were not included in the least-squares calculations.

The equation of each plane is defined by $AX+BY+CZ=D$, where X, Y and Z are the orthogonal coordinates measured in Å units along the crystallographic a^*, b and c axes, respectively.

The conformation of the arginine molecule may be characterized by the three planar groups:

(1) the carboxyl group;
(2) the side chain carbon atoms consisting of α, β, γ and δ-carbon [C(2), C(3), C(4) and C(5)];
(3) the guanidyl group including δ-carbon atom [N(2), C(6), N(3), N(4) and C(5)].

The planarity and the dihedral angles between the above planes are calculated for the molecules in various crystals and are shown in Table 5.

Lakshminarayanan, Sasisekharan & Ramachandran (1967) reviewed the conformation of the arginine molecule in various crystals and showed that the γ-carbon atom is found to occur at all the three possible staggered conformations in which the internal rotation angles, N–C$^{\alpha}$–C$^{\beta}$–C$^{\gamma}$, are found to be about 60, 180 and 300°, corresponding to the *gauche* position to both the amino and carboxyl groups, *trans* to the amino and *trans* to the carboxyl group, respectively (Fig. 3). In the present crystal, the γ-carbon atom is at the *trans* position to the amino group as found in arginine hydrochloride. In all the arginine molecules shown in Table 3, the side chain carbon atoms are arranged approximately in *trans* planar form, while the guanidyl group is attached to this carbon chain either in a completely extended or in a slightly folded form. The former conformation is found in the dihydrate or in the hydrochloride in which most of the side chain atoms C(2), C(3), C(4), C(5), N(2), C(6) and N(3) are in a nearly *trans* planar arrangement. The latter conformation is found in the hydrochloride monohydrate or in the hydrobromide monohydrate in which the side chain is slightly folded at C(5). Each of the latter two compounds contains two crystallographically independent molecules I and II, and the internal rotation angles, C(4)–C(5)–N(2)–C(6) are found to be about −85 and 100° respectively for molecules I and II, indicating that the conformation of the N(2)–C(6) bond with respect to C(5)–C(4) is staggered. A similar conformation is also found in the present structure, but in this case, the C(5)–N(2) bond also adopts the staggered conformation with respect to C(3)–C(4). As a result of the two successive staggered conformations, the side chain of the present molecule is strongly folded, which has never previously been found in arginine molecules. The folding of the molecule may be caused by the intermolecular hydrogen bonds which will be discussed later.

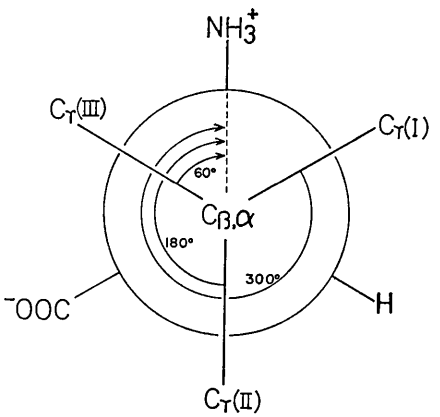


Fig. 3. The internal rotation angles about the C$^{\alpha}$–C$^{\beta}$ bond showing the three possible staggered positions of the C$^{\gamma}$ atom.

Phosphate group

In Table 6, bond lengths and angles of the phosphate group are listed and compared with those found in some other organic phosphate compounds. The values found in the present compound are in good agreement with those found in adenosine-5′-phosphate (AMP) and phosphoserine. In these compounds, two of the four P–O bonds have rather short lengths of about 1·50 Å,

Table 6. *Comparison of* P–O *lengths and* O–P–O *angles of the phosphate group*

	Arg.H_3PO_4.H_2O	Phosphoserine	Adenosine-5′-phosphate	β-Adenosine-2′-β-uridine-5′-phosphoric acid	Spermine phosphate
Bond lengths					
P–O(1)	1·490 ± 0·010 Å	1·497 Å	1·495 ± 0·008 Å	1·478 ± 0·006 Å	1·505 ± 0·006 Å
P–O(2)	1·513 ± 0·008	1·517	1·514	1·518	1·523
P–O(3)	1·594 ± 0·008*	1·608†	1·610†	1·593†	1·527
P–O(4)	1·570 ± 0·009*	1·560*	1·566*	1·586†	1·595*
Bond angles					
O(1)–P–O(2)	114·4 ± 0·5°		118·2 ± 0·4°	117·7 ± 0·5°	113·6 ± 0·3°
O(1)–P–O(3)	105·3 ± 0·5		105·7	112·7	109·5
O(1)–P–O(4)	111·6 ± 0·5		106·9	108·1	108·1
O(2)–P–O(3)	111·0 ± 0·4		108·7	104·8	112·3
O(2)–P–O(4)	107·9 ± 0·5		110·2	109·8	108·2
O(3)–P–O(4)	106·3 ± 0·4		106·5	102·8	104·7
Reference	Present study	McCallum, Robertson & Sim (1959)	Kraut & Jensen (1963)	Shefter, Barlow, Sparks & Trueblood (1969)	Huse & Iitaka (1969)

* P–OH bond.
† P–O bond where the oxygen atom is the ester oxygen bonded to carbon.

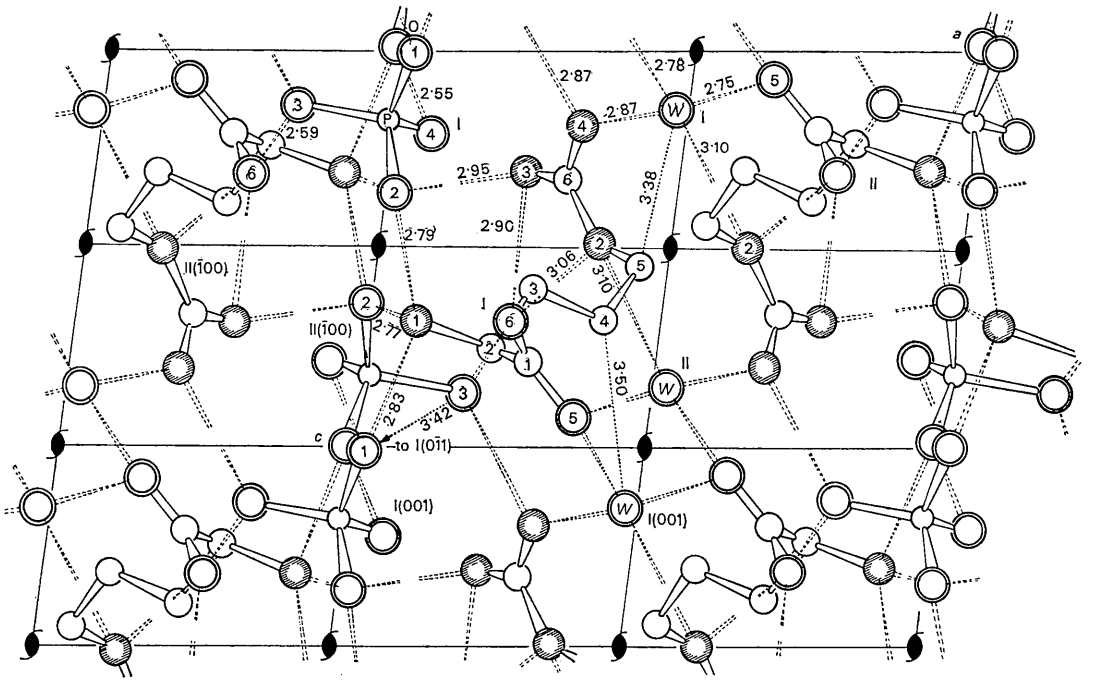


Fig. 4. Projection of the crystal structure along the *b* axis. Oxygen atoms are indicated by double circles, nitrogen by shaded circles and carbon by single circles. Hydrogen bonds are shown by double broken lines and the short interatomic distances less than 3·5 Å are shown by dotted lines.

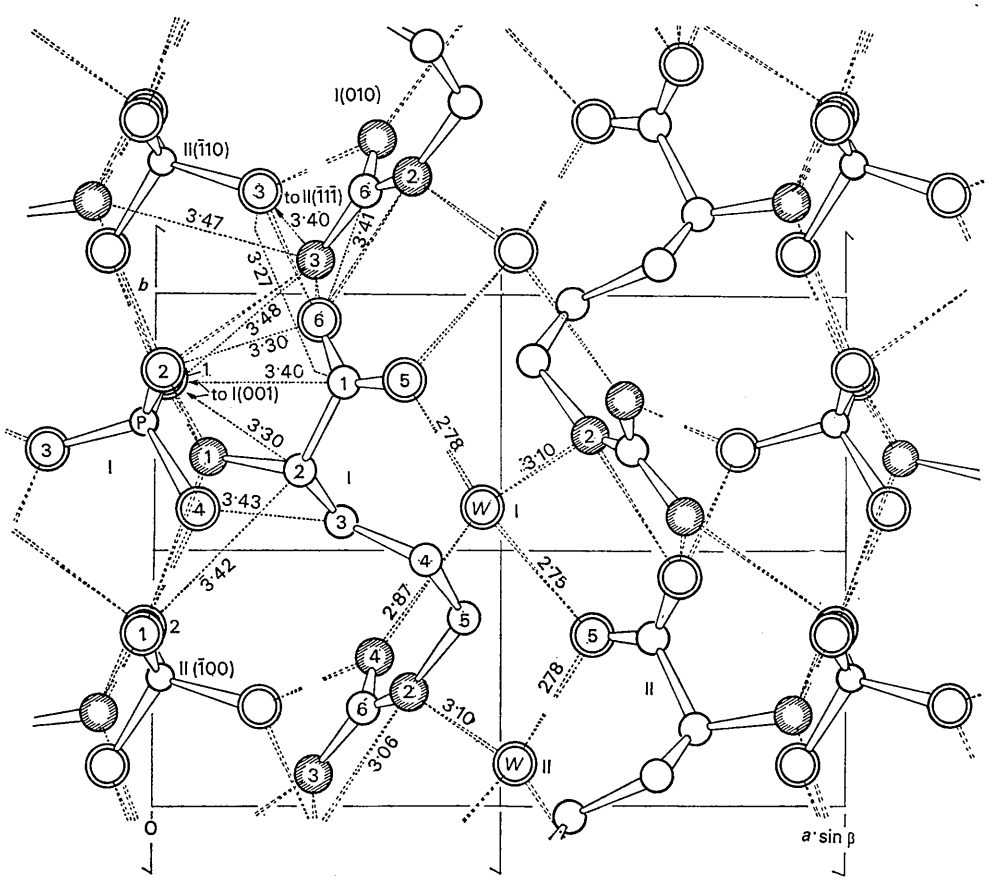
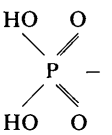


Fig. 5. Projection of the crystal structure along the *c* axis. Short interatomic distances less than 3·5 Å found between the arginine molecule and phosphate groups are shown by dotted lines.

while the remaining two have lengths ranging from 1·56 to 1·61 Å. As in the case of AMP and phosphoserine, the two shorter P–O bonds in the present crystal may have partial double-bond character while the longer bonds are associated with P–OH bonds. The phosphate group in the present crystal can then be written in the following ionized form,



This structure is also favoured by the hydrogen bond system which indicates that the oxygen atoms O(1) and O(2) accept hydrogen bonds and O(3) and O(4) donate their hydrogen atoms to O(6) and O(1) of the neighbouring molecules, respectively. The state of ionization of the phosphate group and the protonation of the arginine molecule indicate that the charge distribution of the present salt can be written as $^{+}(H_2N)_2CNH(CH_2)_3CH(NH_3)^{+}COO^{-}.H_2PO_4^{-}.H_2O$.

Crystal structure

Projections of the crystal structure of L-arginine phosphate monohydrate viewed along the *b*, *c* and *a* axes are shown in Figs. 4, 5 and 6 respectively. In these Figures, hydrogen bonds are indicated by broken lines and the positions of the molecules are denoted as following: I at x, y, z; II at $1-x, -\frac{1}{2}+y, 1-z$, with the x, y and z coordinates as given in Table 1. The translations along the three edges of the unit cell are indicated in parentheses.

As shown in Fig. 4, the crystal structure consists of alternate layers of phosphate groups and arginine molecules stacked along the *a*-axis and held together by hydrogen bonds. The lengths and the directions of the hydrogen bonds are summarized in Tables 7 and 8.

The structure of the phosphate layer is illustrated in Fig. 6. This Figure is a partial projection showing the linkage of the phosphate groups within the (100) plane and the binding relation of the phosphate anions to the arginine molecules. It will be seen that the phosphate groups are arranged about the twofold screw axis passing through the origin of the unit cell and are bound together through the hydrogen bonds O(4)–H···O(1)

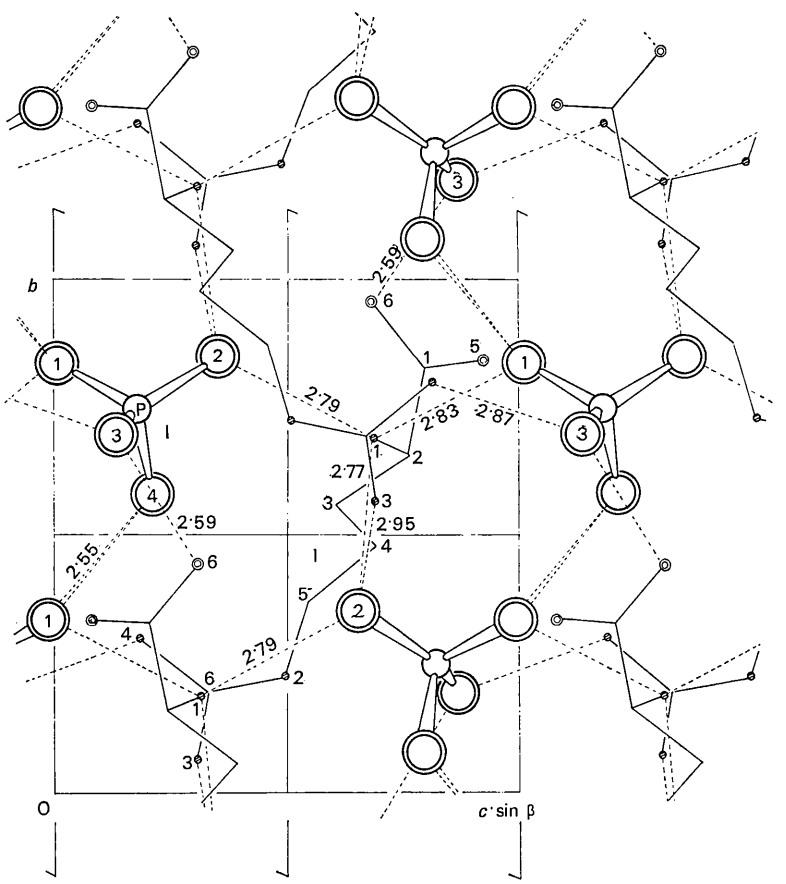


Fig. 6. Partial projection of the crystal structure along the *a* axis showing the linking of the phosphate groups. Hydrogen bonds are shown by broken lines.

to form a chain of phosphate groups. The length of this hydrogen bond connecting the phosphate groups is 2·55 Å which is appreciably shorter than the corresponding value found in spermine phosphate hexahydrate (2·65 Å, Iitaka & Huse, 1965) but nearly of the same order of magnitude as that found in spermidine phosphate trihydrate (2·58 Å, Huse & Iitaka, 1969). The phosphate chains in the present crystal are held

Table 7. *Hydrogen bond distances and angles*

The e.s.d.'s are not shown in case the values are identical with the preceding one.

Donor (*D*)	Acceptor (*A*)	Of molecule	Distance (*D*)···(*A*)	Distance H···(*A*)	Angle H–(*D*)···(*A*)
O(4)	O(1)	II ($\bar{1}0\bar{1}$)	2·554±0·014 Å	—*	—
O(3)	O(6)	II ($\bar{1}00$)	2·586	2·1±0·2 Å	50±6°
N(1)	O(1)	I (001)	2·827	1·9	23
N(1)	O(2)	II ($\bar{1}00$)	2·773	1·8	15
N(1)	O(2)	I (000)	2·787	1·8	14
N(2)	O(6)	I ($0\bar{1}0$)	3·058	2·3	32±9
N(2)	O(*W*)	II (000)	3·098	2·4	41
N(3)	O(2)	I ($0\bar{1}0$)	2·954	—*	—
N(3)	O(6)	I ($0\bar{1}0$)	2·900	2·1	18±11
N(4)	O(3)	II ($\bar{1}0\bar{1}$)	2·866	2·2	36±6
N(4)	O(*W*)	I (000)	2·874	1·8	13
O(*W*)	O(5)	II (000)	2·753	2·3	4±14
O(*W*)	O(5)	I ($00\bar{1}$)	2·779	2·0	51

* Hydrogen atoms are not located by the present analysis.

Table 8. *Hydrogen bond directions around each atom*

The e.s.d.'s are not shown in case the values are identical with the preceding one.

Hydrogen bond from	to: Atom	Symmetry operation	Translation	Code No.	Angles subtended at each atom*	
O(4)	O(1)	II	$\bar{1}0\bar{1}$	1	P——O(4) ····1	114·4±0·5°
O(3)	O(6)	II	$\bar{1}00$	2	P——O(3) ····2	120·1±0·4
N(1)	O(1)	I	001	3	C(2)–N(1)·····3	95·3±0·6
	O(2)	II	$\bar{1}00$	4	C(2)–N(1)·····4	101·9
	O(2)	I	000	5	C(2)–N(1)·····5	119·5
					3····N(1)·····4	111·9±0·4
					3····N(1)·····5	109·4
					4····N(1)·····5	117·4
N(2)	O(6)	I	$0\bar{1}0$	6	C(5)–N(2)·····6	138·4±0·7
	O(*W*)	II	000	7	C(5)–N(2)·····7	80·1
					C(6)–N(2)·····6	93·8
					C(6)–N(2)·····7	148·6
					C(5)–N(2)——C(6)	126·4±1·0
					6····N(2)·····7	66·4±0·4
N(3)	O(2)	I	$0\bar{1}0$	8	C(6)–N(3)·····8	157·6±0·9
	O(6)	I	$0\bar{1}0$	9	C(6)–N(3)·····9	101·5
					8····N(3)·····9	68·7±0·4
N(4)	O(3)	II	$\bar{1}0\bar{1}$	10	C(6)–N(4)····10	111·1±0·7
	O(*W*)	I	000	11	C(6)–N(4)····11	131·6
					10···N(4)····11	117·0±0·4
O(*W*)	O(5)	II	000	12	12···O(*W*) ··13	129·5
	O(5)	I	$00\bar{1}$	13	12···O(*W*) ··14	81·3
	N(4)	I	000	14	12···O(*W*) ··15	113·7
	N(2)	II	010	15	13···O(*W*) ··14	113·6
					13···O(*W*) ··15	97·2
					14···O(*W*) ··15	118·1

* Some of the atoms are designated by code No.

together in the **c** direction mainly through N–H···O hydrogen bonds between the amino nitrogen and phosphate oxygen atoms.

The arginine molecule is linked to the phosphate group by O–H···O hydrogen bonds from the phosphate to carboxyl oxygen atoms and N–H···O hydrogen bonds from the amino and guanidyl nitrogen atoms N(1), N(3) and N(4) to the phosphate oxygen atoms. As shown in Figs. 4 and 5 these hydrogen bonds bind the molecules on one side of the phosphate layer. The other side is attached to another arginine molecule. The layer of arginine which lies between the two phosphate layers is, therefore, made up of double layers of arginine molecules and chains of water molecules. The water molecules and the carboxyl oxygen atoms O(5) are arranged about the twofold screw axis ($\frac{1}{2}$, y, 0) to form a hydrogen-bonded chain. As shown in Table 8, the directions of the hydrogen bonds around the water oxygen atom are approximately tetrahedral.

The ε-nitrogen atom N(2) forms a bifurcated hydrogen bond to the water oxygen atom O(W) and the carboxyl oxygen atom O(6) of the neighbouring molecule translated by **b**.

The authors wish to express their thanks to Mr N. Nagashima of Ajinomoto Co. Ltd. for preparing the samples. This work was supported by a Research Grant from the Ministry of Education.

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Crystal Structure of n-Bromoacetamide, n-CH_3CO–NH–Br

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(*Received* 25 *August* 1969)

n–Bromoacetamide has been studied by X-ray diffraction. The crystals are orthorhombic, space group *Aba*2, $a=8{\cdot}74\pm0{\cdot}02$, $b=12{\cdot}58\pm0{\cdot}02$, $c=8{\cdot}80\pm0{\cdot}03$ Å, $Z=8$. Three-dimensional data collected by precession photography gave a final R index of 10·68%. The atom Br bonded to the amide N atom has a bond length of 1·82 Å.

Introduction

n-Bromoacetamide is of interest as it inhibits the enzyme action of rennin (G. C. Cheeseman, private communication), the structure of which is under investigation (Bunn, Camerman, T'sai, Moews & Baumber, 1970). The compound was synthesized by the method described by Oliveto & Gerald (1951). The crystal structure of orthorhombic acetamide has been described by Hamilton (1965).

Experimental

Crystallographic data

C_2H_4NOBr, $M=137{\cdot}9$, orthorhombic, *mm*2, space group *Aba*2 (C_{2v}^{17}), $a=8{\cdot}72\pm0{\cdot}02$, $b=12{\cdot}58\pm0{\cdot}02$, $c=8{\cdot}80\pm0{\cdot}03$ Å, $V=967{\cdot}5$ Å^3, $d_m=1{\cdot}95$, $d_c=1{\cdot}90$ g.cm^{-3}, $Z=8$, $F(000)=528$, ($\lambda=0{\cdot}71$ Å; Mo $K\alpha$).

Crystals suitable for X-ray diffraction measurements were obtained from a slightly supersaturated aqueous

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