

STRUCTURE OF THE DIPOTASSIUM GLUCOSE 1-PHOSPHATE DIHYDRATE
 $C_6H_{11}O_9P^{2-} \cdot 2K^+ \cdot 2H_2O$

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ABSTRACT

Glucose 1-phosphate dihydrate ($G1PK_2 \cdot 2H_2O$) crystallizes in the monoclinic space group $P2_1$ with unit cell dimensions $a = 10.447(1)$, $b = 9.019(1)$, $c = 7.523(1) \text{ \AA}$, $\beta = 110.44(1)^\circ$ with a single molecule in the asymmetric unit. Final R for 1434 observed reflections is 0.075. The endocyclic C–O bonds in the glucose ring are nearly equal, with $C(5)–O(5) = 1.458(7)$ and $C(1)–O(5) = 1.432(8) \text{ \AA}$. The pyranose sugar ring adopts a 4C_1 chair conformation. The conformation about the exocyclic $C(5)–C(6)$ bond is *gauche-trans*, in contrast to *gauche-gauche* observed in the structure of disodium glucose 1-phosphate. The phosphate ester bond, $P–O(1)$ ($1.630(5) \text{ \AA}$), is comparable in length to the ‘high-energy’ $P \sim O$ bond in monopotassium phosphoenolpyruvate [$1.612(6) \text{ \AA}$]. $K(1)$ is six coordinated and $K(2)$ has eight nearest ligands.

INTRODUCTION

WE wish to report here the molecular structure of dipotassium glucose 1-phosphate dihydrate (figure 1) obtained from x-ray diffraction studies. G1P is an intermediary molecule in glycolysis. It is classified as a ‘low-energy’ phosphate as its free energy of hydrolysis is small, $-20.9 \text{ kJ mol}^{-1}$, compared to that of ‘high-energy’ phosphates such as phosphoenolpyru-

vate ($-58.5 \text{ kJ mol}^{-1}$)¹. This investigation follows our earlier studies on $G1PNa_2$ ² and $G6PBa$ ³ and forms part of our current systematic studies on low-energy phosphates. During the course of this work it was found that the structure of $G1PK_2$ ⁴ was previously studied using visual estimation of intensities, with $R = 17.2\%$. The present analysis was, however, continued to obtain accurate bond distances and angles so that $G1PK_2$ can be compared with $G1PNa_2$ ² and as well as with some high and low-energy phosphate structures which had earlier been solved.

MATERIALS AND METHODS

Crystals of $G1PK_2$ were grown by diffusion of acetone into aqueous solutions of the compound. The density of the crystal was measured by floatation method using acetone and bromoform mixtures. $CuK\alpha$ intensity data upto $\sin \theta/\lambda = 0.63 \text{ \AA}^{-1}$ were collected on a CAD-4 diffractometer. Lorentz and polarization corrections were applied to 1434 unique reflections. The structure was solved by Patterson and SHELX-76⁵. All the H atoms except for hydroxyl and water hydrogens were located from difference Fourier synthesis. Full-matrix least squares refinement⁵ with anisotropic temperature factors for non-H and including H atoms converged at $R = 0.075$.

Positional parameters for the atoms are given in table 1. Bond lengths are listed in table 2. The ortep diagram of the molecule and the numbering scheme are shown in figure 1. The packing arrangement is shown in figure 2. The potassium co-ordination is shown in figure 3.

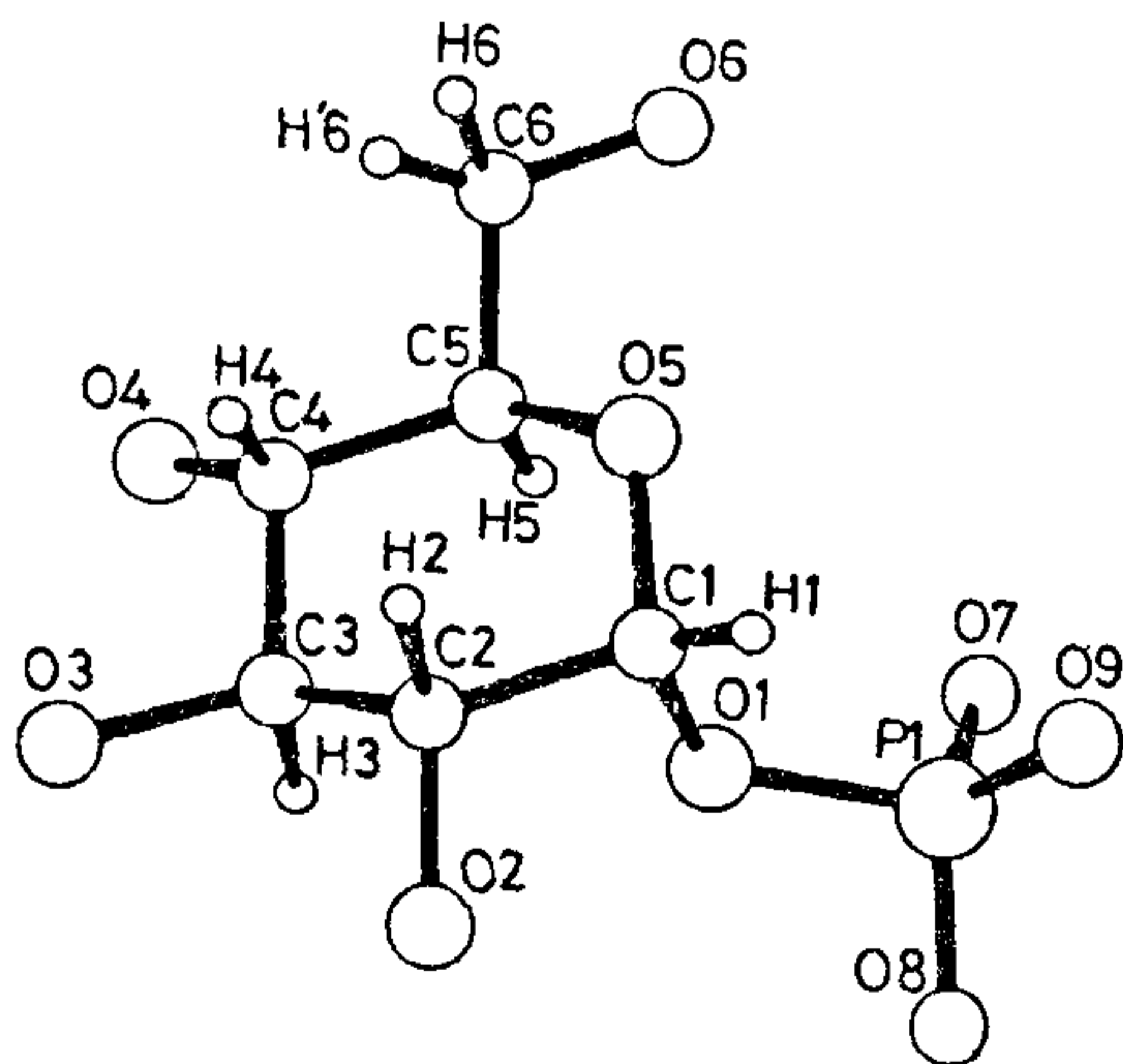


Figure 1. The ortep diagram of the G1P dianion, showing the numbering of the atoms. Further H atoms (not located in the analysis) are linked to O(2), O(3), O(4) and O(6).

Table 1 Final positional parameters ($\times 10^4$; for H $\times 10^3$) and equivalent isotropic temperature factors ($\times 10^2$) with e.s.d.'s in

$$\text{parentheses. } V_{\text{eq}} = \frac{1}{3} \sum_i \sum_j V_{ij} \bar{a}_i \cdot \bar{a}_j$$

ATOM	X	Y	Z	U
P	2033(1)	5100(0)	9861(2)	1.21(.04)
O(7)	866(5)	6079(7)	9899(7)	2.53(.14)
O(8)	3309(5)	5971(7)	10029(8)	2.78(.14)
O(9)	1629(5)	4019(6)	8220(7)	2.28(.13)
O(1)	2399(5)	4159(6)	11826(7)	1.75(.12)
C(1)	2611(6)	2624(8)	11916(9)	1.44(.14)
C(2)	2232(6)	1963(8)	13523(9)	1.53(.15)
C(3)	3130(6)	2566(7)	15420(8)	1.24(.14)
C(4)	4614(6)	2283(8)	15698(9)	1.38(.15)
C(5)	4980(6)	2811(7)	14006(9)	1.31(.14)
O(5)	4008(5)	2272(6)	12215(6)	1.66(.12)
O(2)	830(5)	2235(7)	13295(7)	2.47(.14)
O(3)	2817(5)	1883(6)	16937(7)	2.05(.13)
O(4)	5490(5)	3010(7)	17353(7)	2.47(.14)
C(6)	6363(7)	2264(9)	14112(10)	2.03(.16)
O(6)	6851(5)	2931(7)	12750(8)	2.60(.14)
K(1)	5784(1)	5047(3)	10112(2)	2.29(.04)
K(2)	-540(2)	4565(3)	14379(2)	2.86(.05)
OW(1)	8532(5)	4355(8)	10250(8)	3.09(.15)
OW(2)	9542(6)	2071(8)	6891(8)	3.25(.15)
H(1)	224(4)	225(4)	1078(4)	1.96(.16)
H(2)	240(4)	79(4)	1336(4)	1.89(.16)
H(3)	296(4)	369(4)	1563(4)	1.92(.16)
H(4)	452(4)	125(4)	1567(4)	1.88(.16)
H(5)	505(4)	404(4)	1406(4)	1.91(.16)
H(6)	643(4)	115(4)	1403(4)	1.86(.16)
H'(6)	703(4)	243(4)	1542(4)	1.89(.16)

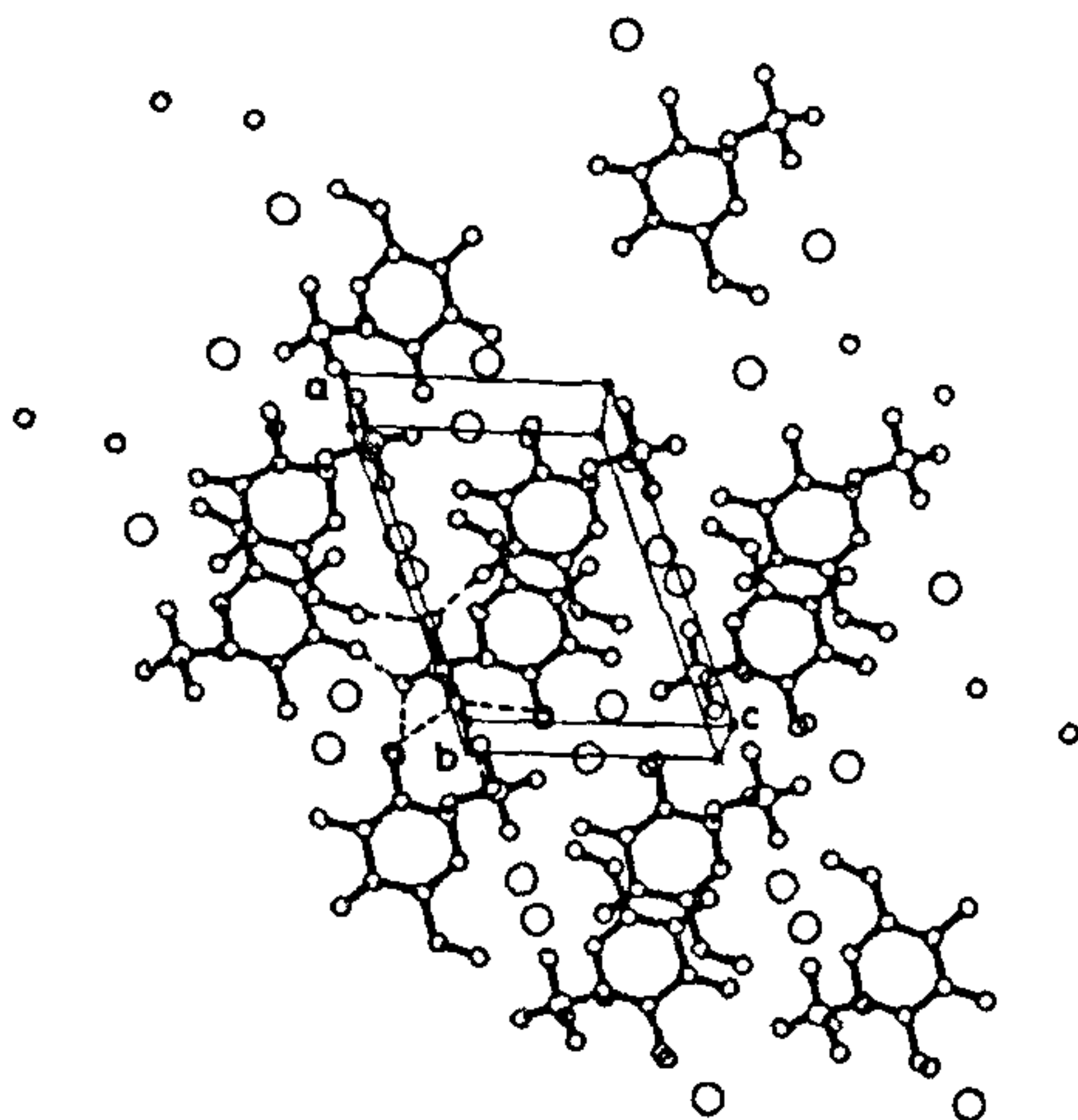
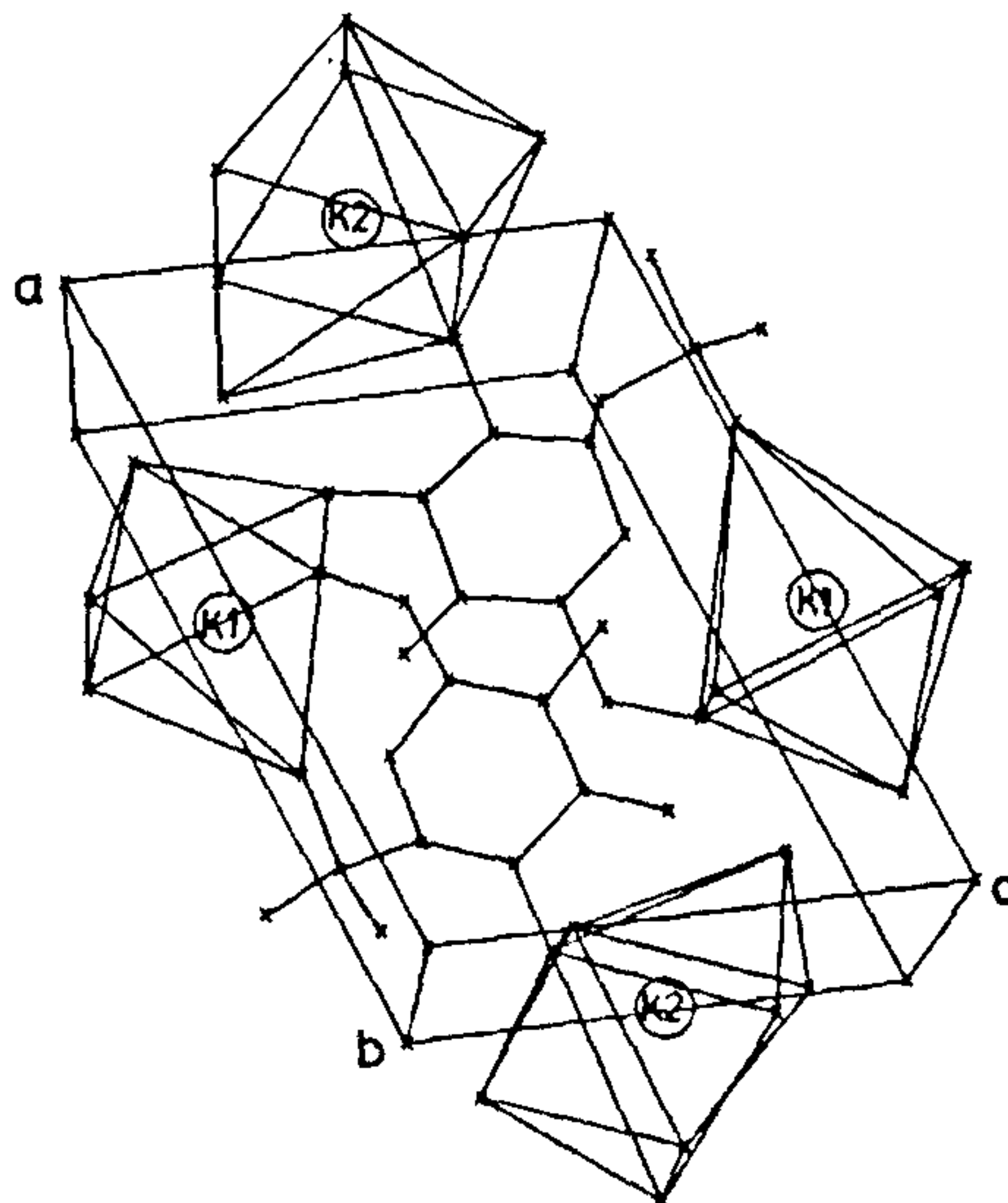
Table 2 Bond lengths (Å) not involving H atoms with e.s.d.'s in parentheses.

P-O(7)	1.514(6)	P-O(8)	1.514(6)
P-O(9)	1.513(5)	P-O(1)	1.630(5)
C(1)-O(1)	1.400(9)	C(1)-C(2)	1.519(9)
C(1)-O(5)	1.432(9)	C(2)-C(3)	1.509(9)
C(2)-O(2)	1.435(9)	C(3)-C(4)	1.512(9)
C(3)-O(3)	1.432(8)	C(4)-C(5)	1.528(9)
C(4)-O(4)	1.422(8)	C(5)-O(5)	1.458(8)
C(5)-C(6)	1.502(10)	C(6)-O(6)	1.427(10)

DISCUSSION

Glucose ring

In the present structure the two endocyclic C-O bonds are nearly equal with C(5)-O(5) = 1.458(7) and C(1)-O(5) = 1.432(8) Å. Interestingly they are significantly different in the structure of G6PBa [1.463(23), 1.395(23) Å]³. These bonds are also found to be nearly equal in other glucose structures such as G1PNa₂², β-

**Figure 2.** The packing arrangement in the unit cell along *b*. The dotted lines indicate hydrogen bonds.**Figure 3.** Potassium co-ordination polyhedra viewed down *b*-axis. K(1) is six co-ordinated and K(2) is eight co-ordinated.

D-glucose⁶ and α -D-glucose⁷. The C(1)–O(1) distance (table 2) follows the usual trend of being shorter than the other exocyclic C–O(H) distances. The pyranose sugar ring has the ⁴C₁ chair conformation with C(4) and C(1) displaced from C(2)–C(3)–C(5)–O(5) plane by $-0.610(7)$ and $0.675(7)$ Å respectively. The Cremer-Pople⁸ puckering parameters are $Q = 0.551(3)$ Å, $\theta = 6.3(3)^\circ$ and $\phi = 95(3)^\circ$.

Conformation about exocyclic C(5)–C(6) bond

The torsion angles O(6)–C(6)–C(5)–O(5) and O(6)–C(6)–C(5)–C(4) are $67.9(7)$ and $-169.8(6)^\circ$ respectively. The conformation about C(5)–C(6) bond is therefore *gauche-trans*. It is significantly different from the *gauche-gauche* geometry ($-70.3, 48.6^\circ$) observed in G1PNa₂².

Phosphate group

The three terminal P–O bonds are nearly equal (table 2). Presumably the negative charges are distributed between O(7), O(8) and O(9) atoms. The phosphate ester bond ($1.630(5)$ Å) is comparable to the 'high-energy' P ~ O bond in monopotassium phosphoenolpyruvate [$1.612(6)$ Å]⁹.

There are significant differences between the molecular dimensions reported here, and those found in the photographic study of Beevers *et al*⁴. For example, in the present structure the two endocyclic C–O bonds are considerably shorter (C(5)–O(5) = 1.458 , C(1)–O(5) = 1.432 Å) than the corresponding C–O bonds obtained in the earlier studies (1.49 and 1.46 Å). Also the P–O(1) ester bond is $1.630(5)$ instead of 1.59 Å. The terminal P–O(9) bond is $1.513(5)$, which is nearly equal to P–O(7) and P–O(8) ($1.514, 1.514$ Å) and not 1.48 Å which is considerably shorter than P–O(7) and P–O(8) ($1.52, 1.53$ Å) as found in previous studies.

K⁺ co-ordination and hydrogen bonding

There are two crystallographically independent pot-

assium ions in the structure. K(1) is six co-ordinated and K(2) is eight co-ordinated within a distance of 3.2 Å as shown in figure 3. Only O(8) and O(9) involve in the direct interaction with the K⁺ ions and O(7) interacts through waters and O(2). There is no intramolecular hydrogen bonding similar to that found in G1PNa₂². The molecules related by the two-fold screw axis, are linked to each other through O(7) . . . O(2), O(8) . . . O(4) and O(8) . . . O(6) hydrogen bonds.

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1. Lehninger, A. L., *Bioenergetics*, W. A. Benjamin Inc., Menlo Park, California, 1973, p. 42.
2. Narendra, N., Seshadri, T. P. and Viswamitra, M. A., *Acta Crystallogr.*, 1984, (in press).
3. Katti, S. K., Seshadri, T. P. and Viswamitra, M. A., *Acta Crystallogr.*, 1982, **B38**, 1136.
4. Beevers, C. A. and Maconochie, G. H., *Acta Crystallogr.*, 1965, **18**, 232.
5. Sheldrick, G. M., SHELX-76, *Program for crystal structure determination*, Univ. of Cambridge, England, 1976.
6. Chu, S. S. C. and Jeffrey, G. A., *Acta Crystallogr.*, 1968, **B24**, 830.
7. Brown, G. M. and Levy, H. A., *Acta Crystallogr.*, 1979, **B35**, 656.
8. Cremer, D. and Pople, J. A., *J. Am. Chem. Soc.*, 1975, **97**, 1345.
9. Hosur, M. V., and Viswamitra, M. A., *Acta Crystallogr.*, 1981, **B37**, 839.