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THE CRYSTAL STRUCTURE OF D-GLUCOSE 6-(SODIUM HYDROGENPHOSPHATE)

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ABSTRACT

The title compound, when recrystallised from water, is monoclinic, space group $P2_1$, with $a = 5.774(4)$, $b = 7.189(5)$, $c = 12.69(1)$ Å, $\beta = 106.66(5)°$, and $Z = 2$. The crystal structure was determined from three-dimensional X-ray diffraction data taken on an automatic diffractometer with CuKα, and refined by least-squares techniques to $R = 0.034$ for 977 reflexions. The pyranose ring adopts the $^4C_1$ conformation. The conformation about the exocyclic C-5–C-6 bond is *gauche–trans* [the torsion angles O-6–C-6–C-5–O-5 and O-6–C-6–C-5–C-4 are 64.2(8) and −175.6(7)°, respectively], which is significantly different from the *gauche–gauche* geometry in D-glucose 6-(barium phosphate). The phosphate ester bond, P–O-6, is 1.584(3) Å. All of the oxygen-bonded hydrogen atoms are involved in intermolecular hydrogen-bonds.

INTRODUCTION

D-Glucose 6-(phosphoric acid) (G6P) occupies an important position in the metabolism of carbohydrates in plants. Depending on pH, the molecules of this acid may also exist as monoanion or dianion. Of these three forms, only the structure of the dianion (as the barium salt) is known[1]. Therefore, the structure of the monoanion in the crystalline state as the monosodium salt has been investigated. This study is a continuation of earlier studies of the crystal structures of β-glycerophosphates and related phosphates.

EXPERIMENTAL

Crystals of D-glucose 6-(sodium hydrogenphosphate) were obtained by slow concentration of an aqueous solution of the commercially available compound (Sigma Chemical Co.). Most of the crystals were needles, with the b axis along. They proved to be twinned and were stable in air.

Weissenberg and oscillation photographs showed the crystals to be monoclinic, and space group $P2_1$ was indicated by the systematic absence of reflexions 0k0 with k odd. A crystal fragment, having the approximate dimensions 0.05 ×

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TABLE I

CRYSTAL DATA FOR D-GLUCOSE 6-(SODIUM HYDROGENPHOSPHATE)

Stoichiometry $C_6H_{12}O_9P^- Na^+$; Z = 2; Space group $P2_1$
$a = 5.774(4)$ Å, $b = 7.189(5)$ Å
$c = 12.69(1)$ Å, $\beta = 106.66(5)°$
D (calculated) 1.86 g cm^{-3}, D (observed)[a] 1.83 g.cm^{-3}
μ(MoKα) 32.8 cm^{-1}

[a] The density was measured by flotation in a mixture of carbon tetrachloride and 1,2-dibromoethane.

TABLE II

THE FINAL ATOM COORDINATES AND ISOTROPIC THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	*x*	*y*	*z*	B_{eq} or B_{iso}
P	−0.1047(3)	0.64(fixed)	0.8995(1)	1.49(7)
Na	0.5153(4)	0.4721(4)	0.0343(2)	2.54(15)
O-1	0.3540(6)	1.3107(6)	0.8440(3)	2.19(26)
O-2	0.5620(7)	1.3598(6)	0.6666(3)	2.36(27)
O-3	0.5604(6)	1.0410(6)	0.5358(3)	2.30(25)
O-4	0.1469(6)	0.7988(6)	0.5165(3)	2.16(25)
O-5	0.2263(6)	1.0238(6)	0.7816(3)	1.83(23)
O-6	−0.1172(6)	0.7579(5)	0.7926(3)	2.06(24)
O-7	−0.0803(6)	0.4370(5)	0.8718(3)	1.85(24)
O-8	−0.3175(6)	0.6944(6)	0.9375(3)	2.07(25)
O-9	0.1443(6)	0.6931(6)	0.9873(3)	2.26(26)
C-1	0.2811(9)	1.2051(8)	0.7487(4)	1.58(31)
C-2	0.4827(9)	1.1842(7)	0.6936(4)	1.64(33)
C-3	0.3762(8)	1.0715(8)	0.5893(4)	1.61(31)
C-4	0.2805(8)	0.8848(7)	0.6160(4)	1.59(32)
C-5	0.1129(8)	0.9101(8)	0.6878(4)	1.67(32)
C-6	0.0567(9)	0.7249(8)	0.7326(4)	2.03(35)
H-11	0.227	1.364	0.864	4.0
H-22	0.707	1.407	0.735	4.0
H-33	0.495	0.992	0.469	4.0
H-44	0.227	0.682	0.500	4.0
H-9	0.136	0.783	1.042	4.0
H-1	0.141	1.269	0.693	2.5
H-2	0.628	1.122	0.744	2.5
H-3	0.237	1.142	0.540	2.5
H-4	0.424	0.807	0.655	2.5
H-5	−0.039	0.971	0.640	2.5
H-6	0.211	0.670	0.784	2.5
H-6′	−0.009	0.633	0.671	2.5

[a] For non-H atoms, $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$. The *y* coordinate of the P was not refined.

0.15 × 0.03 mm, was cut from a large twinned crystal. A Syntex $P2_1$ diffractometer, CuKα radiation (λ = 1.5418 Å), and a graphite monochromator were used for measurements of lattice parameters and intensities at T = 296 ±2 K. Measurements were made for 1099 symmetry-independent reflexions having $2\theta \leqslant 146°$ by a 2θ–ω

TABLE III

BOND LENGTHS (Å), BOND ANGLES (DEGREES), AND TORSION ANGLES (DEGREES) IN D-GLUCOSE 6-(SODIUM HYDROGEN PHOSPHATE)

Bond	*Bond distance*	*Bond*	*Bond distance*
C-1–C-2	1.528(7)	C-5–O-5	1.437(6)
C-1–O-1	1.387(6)	O-5–C-1	1.431(6)
C-2–C-3	1.523(6)	C-5–C-6	1.519(7)
C-2–O-2	1.418(6)	C-6–O-6	1.443(6)
C-3–C-4	1.526(7)	O-6–P	1.584(3)
C-3–O-3	1.433(6)	O-7–P	1.517(3)
C-4–C-5	1.518(7)	O-8–P	1.495(3)
C-4–O-4	1.419(6)	O-9–P	1.592(3)

Bonds	*Bond angle*	*Bonds*	*Bond angle*
O-5–C-1–O-1	106.4(4)	C-4–C-5–O-5	110.3(4)
O-5–C-1–C-2	107.8(4)	C-5–O-5–C-1	111.3(4)
O-1–C-1–C-2	111.9(4)	C-4–C-5–C-6	111.1(4)
C-1–C-2–C-3	106.2(4)	O-5–C-5–C-6	106.5(4)
C-1–C-2–O-2	111.4(4)	C-5–C-6–O-6	108.0(4)
O-2–C-2–C-3	110.0(4)	C-6–O-6–P	119.8(3)
C-2–C-3–O-3	108.9(4)	O-6–P–O-7	107.5(2)
O-3–C-3–C-4	109.7(4)	O-6–P–O-8	107.3(2)
C-2–C-3–C-4	110.9(4)	O-6–P–O-9	106.3(2)
C-3–C-4–C-5	111.2(4)	O-7–P–O-8	117.8(2)
C-3–C-4–O-4	108.9(4)	O-7–P–O-9	105.5(2)
O-4–C-4–C-5	108.0(4)	O-8–P–O-9	111.9(2)

Bonds	*Torsion angle*	*Bonds*	*Torsion angle*
C-6–O-6–P–O-7	−48.0(7)	O-1–C-1–C-2–C-3	−178.3(8)
C-6–O-6–P–O-8	−175.5(6)	C-1–C-2–C-3–O-3	−177.8(7)
C-6–O-6–P–O-9	64.7(7)	O-2–C-2–C-3–O-3	61.5(7)
C-5–C-6–O-6–P	−144.8(7)	C-1–C-2–C-3–C-4	−57.1(7)
O-6–C-6–C-5–O-5	64.2(8)	O-2–C-2–C-3–C-4	−177.7(6)
O-6–C-6–C-5–C-4	−175.6(7)	C-2–C-3–C-4–O-4	170.1(6)
C-5–O-5–C-1–O-1	171.0(6)	O-3–C-3–C-4–O-4	−69.7(7)
C-5–O-5–C-1–C-2	−68.9(9)	C-2–C-3–C-4–C-5	51.2(8)
C-1–O-5–C-5–C-6	−178.3(5)	O-3–C-3–C-4–C-5	171.4(7)
C-1–O-5–C-5–C-4	61.0(8)	C-3–C-4–C-5–C-6	−168.9(7)
O-5–C-1–C-2–O-2	−175.2(7)	O-4–C-4–C-5–C-6	71.6(7)
O-1–C-1–C-2–O-2	−58.6(8)	C-3–C-4–C-5–O-5	−51.1(7)
O-5–C-1–C-2–C-3	65.1(8)	O-4–C-4–C-5–O-5	−170.5(7)
H-9–O-9–P–O-6	99		

scan technique. Two reflexions, which were monitored periodically, exhibited no significant variations in intensity during the period of data collection. The intensities were corrected for Lorentz and polarisation factors, only. The crystals data are listed in Table I.

All calculations were performed on a NOVA 1200 computer with the Syntex XTL/XTLE Structure Determination System (1976)[2]. The structure was solved by direct methods. An E-map with 269 values ≥ 1.2 provided the positions of 12 of the 17 non-hydrogen atoms in the structure. The remainder were located from several difference-Fourier syntheses. Refinement was by full-matrix least-squares, minimising $\Sigma w(|F_o| - |F_c|)^2$, with $w = \sigma^{-2}(F_o)$, where $\sigma(F_o)$ was based on counting statistics. The positions of 7 hydrogen atoms were calculated by using a C–H distance of 1.0 Å and tetrahedral angles. The O-bonded hydrogen atoms were located as the five largest peaks in a difference-Fourier synthesis. Further refinement, with fixed hydrogen atoms, yielded a final R value of 0.034 and an R_w value of 0.033 for 977 reflexions with $I > 1.96\,\sigma(I)$, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. During the last cycle of refinement, no parameter shifted more than 0.01 of its standard deviation. The atomic scattering factors were those listed in International Tables for X-Ray Crystallography (1974)[3]. The anomalous dispersion was included for P, Na, O, and C atoms. A final difference synthesis was featureless.

The final atomic* parameters are listed in Table II; interatomic distances and angles for the D-glucose 6-phosphate monoanion are given in Table III.

DISCUSSION

The crystals of the title compound are composed of D-glucose 6-phosphate monoanions and sodium cations. The molecular configuration and conformation and the atom-numbering scheme of one anion are illustrated in Fig. 1. The ring conformation in the monoanion, like that of the dianion in the barium salt[1], is the $^4C_1$ chair form, with little distortion from the ideal, having Cremer–Pople[4] puckering parameters of $Q = 0.606$ Å, $\theta = 9.9°$, and $\varphi = 62°$. The most interesting feature is the conformation about the exocyclic C-5–C-6 bond, which is distinctly different in the monoanion from that in the dianion[1]; the ester O-6 atom is *trans* to C-4 in the former and *gauche* in the latter [the torsion angles C-4–C-5–C-6–O-6 are −175.6(7)° and 48.6(14)°, respectively]. The intramolecular hydrogen-bond between O-4 and one of the phosphate oxygen atoms present in the dianion[1] cannot be formed in the monoanion. The conformation about the C-6–O-6 bond in the monoanion differs slightly from that found in the dianion [the torsion angles C-5–C-6–O-6–P are −144.8(7)° and −118.3(14)°, respectively].

All of the bond distances and angles in the monoanion are normal. The phosphate group is essentially tetrahedral with O–P–O angles ranging from 105.5 to 117.8°. The phosphorus hydroxyl (P–O-9) distance, 1.592(3) Å, belongs to the longest phosphorus hydroxyl distances and the ester phosphorus bond (P–O-6), 1.584(3) Å, belongs to the shortest ester phosphorus bonds[5]. The ester phosphorus bond is significantly shorter than that in D-glucopyranosyl dipotassium phosphate

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*The Tables of observed, and calculated, structure factors and of anisotropic, thermal parameters may be obtained from the author, or from Elsevier Science Publishers B.V., B.B.A. Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/301/*Carbohydr. Res.*, 135 (1984) 187–194.

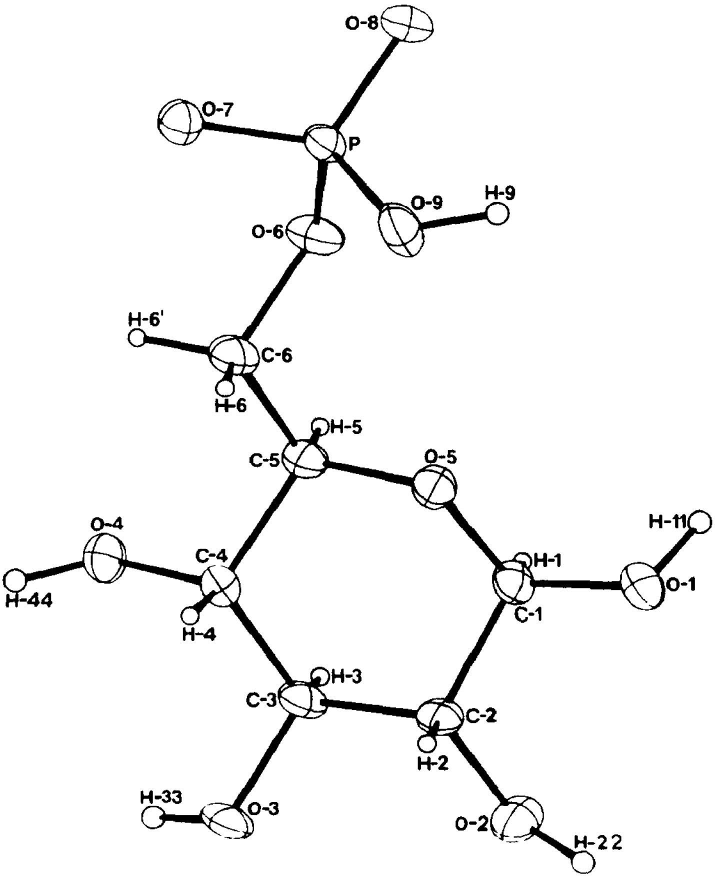

Fig. 1. The structure of the D-glucose 6-phosphate monoanion, showing the numbering of the atoms.

[1.636(2) Å][6], and that in trisodium 6-phospho-D-gluconate [1.614(2) Å][7]. Of the two remaining P–O bonds, the P–O-7 bond is a little longer than the P–O-8 bond (O-7 forms three intermolecular hydrogen-bonds, and O-8 is not utilised in hydrogen bonds).

The endocyclic C–O bond-lengths in the glucose ring are almost the same (contrary to the situation in the dianion) and the exocyclic C-1–O-1 bond distance is significantly shorter than that of the C-1–O-5 bond (in contrast to the dianion but similar to that in D-glucose[8]).

The crystal packing and hydrogen-bonding schemes are shown in Fig. 2. All of the hydrogen atoms that are covalently bonded to oxygen atoms participate in hydrogen bonding. Hydrogen-bond distances and angles are listed in Table IV. The O-1 atoms (as donors) form with O-7 atoms infinite chains parallel to *b*. The O-2 atoms (as donors) form with O-7 atoms infinite chains along *a* + *b*. The O-9 atoms (as donors) form the shortest hydrogen-bonds in the crystal with O-7. Thus,

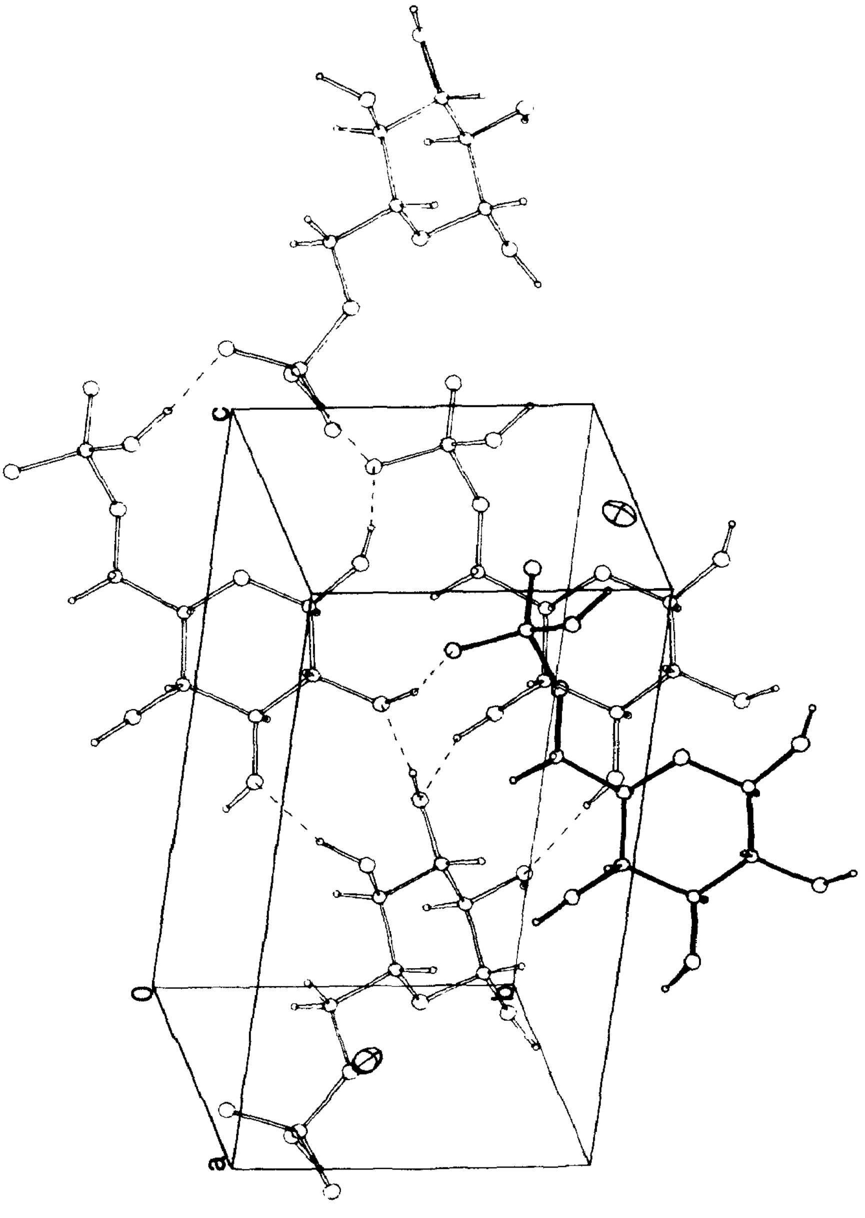

Fig 2 Molecular packing in the crystal structure of D-glucose 6-(sodium hydrogenphosphate). Hydrogen bonds are denoted by dashed lines.

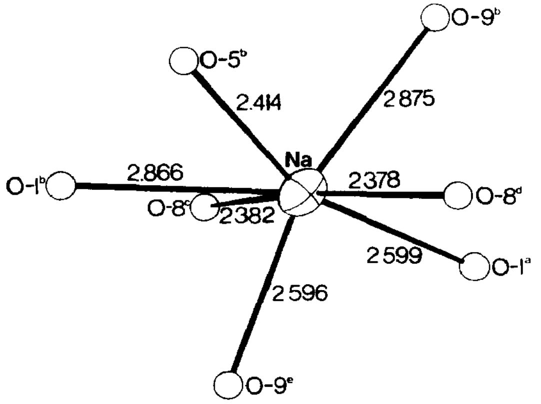

Fig. 3. Geometry of the sodium ion coordination-shell. Estimated standard deviations of Na–O distances are 0.004 Å. Symmetry codes: ^{a}x, y − 1, z − 1; ^{b}1 − x, y − 1/2, 1 − z; ^{c}1 + x, y, z − 1; ^{d}− x, y − 1/2, 1 − z; ^{e}x, y, z − 1.

TABLE IV

HYDROGEN-BOND DISTANCES (Å) AND ANGLES (DEGREES)

O–H · · · O	*O · · · O*	*O–H*	*H · · · O*	*O–H · · · O*
O-1–H-11 · · · O-7^{a}	2.783(5)	0.92	1.88	165
O-2–H-22 · · · O-7^{b}	2.876(4)	1.07	1.83	164
O-3–H-33 · · · O-2^{c}	2.784(4)	0.90	1.91	165
O-4–H-44 · · · O-3^{c}	2.716(5)	1.01	1.75	159
O-9–H-9 · · · O-7^{d}	2.606(5)	0.96	1.65	172

Symmetry codes: ^{a}x, 1 + y, z; ^{b}1 + x, 1 + y, z; ^{c}1 − x, y − 1/2, 1 − z; ^{d}− x, 1/2 + y, 2 − z.

each O-7 (as acceptor) is utilised in three independent hydrogen-bonds. The hydroxyl oxygens O-2 and O-3 from one anion accept hydrogens H-33 and H-44 from another anion; these pairs of hydrogen-bonded anions are related to each other by a two-fold screw axis, resulting in a helical hydrogen-bonding scheme which extends along *b*.

The coordination around sodium is shown in Fig. 3. Five distances between sodium cation and oxygen atoms range from 2.38 to 2.60 Å. The coordination of Na may best be described as a distorted tetragonal pyramid. Two slightly longer distances of 2.87 Å are observed. Each sodium ion is coordinated to five independent D-glucose 6-phosphate monoanions.

NOTE ADDED IN PROOF

A new refinement for D-glucose 6-(barium phosphate) (based on new diffractometer data collected by the author) showed that all the bond lengths of the D-glucose moiety have essentially the same values as in the crystal under investigation.

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