Table 2. *Molecular geometry*

	TMAT BrCu		TMAT BrZn	
	Uncorrected	Corrected	Uncorrected	Corrected
(*a*) Bond lengths (Å)				
M–Br(1)	2·364 (5)	2·426	2·393 (3)	2·445
M–Br(2)	2·360 (3)	2·423	2·398 (2)	2·452
M–Br(3)	2·366 (5)	2·430	2·390 (3)	2·443
N(1)–C(11)	1·42 (4)	1·62	1·38 (3)	1·66
N(1)–C(12)	1·46 (3)	1·68	1·48 (3)	1·77
N(1)–C(13)	1·49 (4)	1·71	1·46 (3)	1·75
N(2)–C(21)	1·51 (4)	1·74	1·47 (3)	1·73
N(2)–C(22)	1·42 (3)	1·63	1·41 (2)	1·65
N(2)–C(23)	1·42 (5)	1·64	1·44 (3)	1·69
Br(1)–Br(2)	3·670 (4)	3·768	3·896 (3)	3·981
Br(1)–Br(3)	4·226 (5)	4·338	3·969 (5)	4·057
Br(2)–Br(3)	3·689 (4)	3·787	3·889 (3)	3·974
Br(2)–Br′(2)	4·155 (4)	4·267	3·926 (3)	4·013
(*b*) Angles (°)				
Br(1)–*M*–Br(2)	102·0 (1)		108·8 (1)	
Br(1)–*M*–Br(3)	126·6 (2)		112·2 (1)	
Br(2)–*M*–Br(3)	102·6 (1)		108·6 (1)	
Br(2)–*M*–Br′(2)	123·4 (2)		109·9 (1)	
C(11)–N(1)–C(12)	109 (2)		110 (2)	
C(11)–N(1)–C(13)	107 (4)		115 (3)	
C(12)–N(1)–C(13)	112 (2)		109 (2)	
C(12)–N(1)–C′(12)	107 (4)		104 (4)	
C(21)–N(2)–C(22)	113 (2)		110 (2)	
C(21)–N(2)–C(23)	107 (3)		114 (3)	
C(22)–N(2)–C(23)	107 (3)		107 (2)	
C(22)–N(2)–C′(22)	108 (3)		108 (3)	

The primed atoms correspond to the atom obtained from the original atom by the symmetry plane at $y = \frac{1}{4}$.

This study is part of a more general study of tetramethylammonium tetrabromometallate compounds. In particular, a study at low temperature is planned in the near future.

The authors thank C. Carpentier and M. Muller for growing crystals and G. Odou for the technical assistance during the experiments. We are grateful to F. Baert and M. Foulon for stimulating discussions.

Table 3. *Rigid-body vibration parameters for the heavy tetrahedra*

	$[CuBr_4]^{2-}$			$[ZnBr_4]^{2-}$		
T(Å² × 10⁴)	653 (34)	0	48 (45)	474 (10)	0	12 (14)
		765 (37)	0		636 (12)	0
			768 (44)			537 (12)
L(rad² × 10⁴)	272 (10)	0	64 (18)	215 (3)	0	−8 (7)
		114 (18)	0		88 (5)	0
			150 (11)			136 (5)
S(Å rad × 10⁴)	0	−45 (19)	0	0	−16 (6)	0
	28 (18)	0	7 (15)	29 (6)	0	5 (5)
	0	−44 (16)	0	0	29 (5)	0
R.m.s. ($U^o - U^c$) (Å² × 10⁴)		55			17	
E.s.d. U^o_{ij} (Å² × 10⁴)		57			17	

References

Clay, R., Murray-Rust, J. & Murray-Rust, P. (1975). *Acta Cryst.* **B31**, 289–290.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Gesi, K. (1982). *J. Phys. Soc. Jpn*, **51**, 203–207.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Kallel, A., Bats, J. W. & Daoud, A. (1981). *Acta Cryst.* **B37**, 676–677.

Kamenar, B. & Nagl, A. (1976). *Acta Cryst.* **B32**, 1414–1417.

Sawada, S., Shiroishi, Y., Yamamoto, A., Takashige, M. & Matsuo, M. (1978). *J. Phys. Soc. Jpn*, **44**, 687–688.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

Scott, R. A. & Sheraga, H. A. (1965). *J. Chem. Phys.* **42**, 2209–2215.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Templeton, D. & Templeton, L. (1973). *ABSORB*. An analytical absorption correction program. Univ. of California, Berkeley.

Wiesner, J. R., Srivastava, R. C., Kennard, C. H. L., DiVaira, M. & Lingafelter, E. C. (1967). *Acta Cryst.* **23**, 565–574.

Acta Cryst. (1984). C**40**, 389–393

Structure of Disodium Uridine Diphosphoglucose Dihydrate, $C_{15}H_{22}N_2O_{17}P_2^{2-}.2Na^+.2H_2O$, and Refinement of Dipotassium Glucose 1-Phosphate Dihydrate, $C_6H_{11}O_9P^{2-}.2K^+.2H_2O$ (Monoclinic Form)

By Yoko Sugawara and Hitoshi Iwasaki

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, *Japan*

(*Received* 23 *July* 1983; *accepted* 16 *November* 1983)

Abstract. $C_{15}H_{22}N_2O_{17}P_2^{2-}.2Na^+.2H_2O$: $M_r = 646·3$, monoclinic, $P2_1$, $a = 8·950\ (2)$, $b = 18·724\ (4)$, $c = 7·289\ (2)$ Å, $\beta = 101·98\ (2)°$, $V = 1194·9\ (4)$ Å³, $Z = 2$, $D_x = 1·796$, $D_m = 1·80$ Mg m⁻³, $\lambda(\text{Mo}\ K\alpha) = 0·71073$ Å, $\mu(\text{Mo}\ K\alpha) = 0·329$ mm⁻¹, $F(000) = 668$, $T = 293$ K, $R = 0·049$ for 5895 observed reflections. $C_6H_{11}O_9P^{2-}.2K^+.2H_2O$: $M_r = 372·3$, $P2_1$, $a = 10·458\ (3)$, $b = 9·027\ (1)$, $c = 7·532\ (2)$ Å, $\beta =$

110·39 (3)°, $V = 666·5$ (2) Å^3, $D_x = 1·855$ Mg m^{-3}, $Z = 2$, μ(Mo $K\alpha$) = 0·878 mm^{-1}, $F(000) = 384$, $T = 293$ K, $R = 0·029$ for 3761 observed reflections. The structure of glucose 1-phosphate given by Beevers & Maconochie [*Acta Cryst.* (1965). **18**, 232–236] was refined. Uridine diphosphoglucose takes the extended form. Uracil is *anti* to ribose, ribose is C(2′)-*endo* (^2E) and the pyrophosphate linkage takes a staggered form. O(4″) and C(6″), which are known as reaction sites and/or essential sites for enzymic specificity, are very close to the mean plane through the pyranose ring. Esterified P—O bond lengths of uridine diphosphoglucose are nearly equal to those of nucleoside diphosphate and triphosphate while P—O(1) of glucose 1-phosphate is longer than the corresponding bond of uridine diphosphoglucose. Geometrical differences are recognized also at the anomeric centres of these two compounds.

Introduction. Sugar nucleotide is one of the 'high-energy' compounds in biological systems and acts as a key material in the metabolism of carbohydrate. Although the specificity and mechanism of the enzymic reactions of sugar nucleotide have been studied by isotope-labelling and chemical-modification techniques (Kochetkov & Shibaev, 1973), structural studies have been very limited to date. We determined the structure of uridine diphosphoglucose (UDP-Glc), and this is the first report on the crystal structure of sugar nucleotide.

Glucose 1-phosphate (Glc-1-P) is a precursor of UDP-Glc and their structural analogy attracted our attention. Although the crystal structure of the monoclinic form of Glc-1-P had been reported (Beevers & Maconochie, 1965), the R value was 0·17 and the accuracy of the parameters was not sufficient. Therefore the refinement of Glc-1-P was also performed. The orthorhombic form of Glc-1-P was studied by Rosenstein (1968; $R = 0·08$) but the structural details have not yet been published.

Experimental. UDP-Glc and Glc-1-P purchased from Yamasa Shoyu Co. Ltd and Nakarai Chemicals, Ltd, respectively.

UDP-Glc. Plate-like crystals from water–dioxane solution, 0·08 × 0·25 × 0·28 mm. D_m by flotation in chloroform/bromoform mixture. Cell constants: least-squares on 24 reflections. Rigaku automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, $2\theta \leq 60°$. 5895 reflections ($-12 \leq h \leq 12$, $-26 \leq k \leq 26$, $0 \leq l \leq 10$) with $|F_o| > 3\sigma(F_o)$ obtained. ω–2θ scan mode. Three standard reflections (073, $\bar{2}14$, $\bar{4}32$): variation within 3%. Intensities corrected for Lorentz and polarization factors but not for absorption. Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Anisotropic block-diagonal least squares. Anomalous-dispersion corrections. Two water molecules and H atoms from a difference Fourier map. H atoms with isotropic temperature factors. $w = 0·3$ for $|F_o| < 8·0$, $w = 1·0$ for $8·0 \leq |F_o| < 20·0$, $w = (20·0/|F_o|)^2$ for $20·0 \leq |F_o|$. Final $R = 0·049$, $R_w = 0·055$, $S = 0·73$. $(\Delta/\sigma)_{\max}$ 0·3. No peak higher than 0·4 e Å^{-3} observed in final $\Delta\rho$ map. Calculations performed on a FACOM M-380 computer of this Institute using the *UNICS*III program system (Sakurai & Kobayashi, 1979). Atomic scattering factors and correction terms for anomalous scattering from *International Tables for X-ray Crystallography* (1974).

Glc-1-*P*. Plate-like crystals from water/ethanol solution, 0·10 × 0·80 × 0·28 mm. Conditions for intensity measurement and calculation procedure as for UDP-Glc except that the refinement was started from the coordinates of Beevers & Maconochie (1965). 3761 non-zero reflections ($-14 \leq h \leq 13$, $-12 \leq k \leq 12$, $0 \leq l \leq 10$). Three standard reflections (800, $\bar{3}05$, 152): variation within 1%. Anomalous-dispersion and absorption corrections. $w = 0·3$ for $|F_o| < 5·0$, $w = 1·0$ for $5·0 \leq |F_o| < 20·0$, $w = (7·0/|F_o|)^2$ for $20·0 \leq |F_o|$. Final $R = 0·029$, $R_w = 0·033$, $S = 0·33$. $(\Delta/\sigma)_{\max}$ 0·3. No peak higher than 0·3 e Å^{-3} observed in final $\Delta\rho$ map.

Discussion. Coordinates of the non-hydrogen atoms of Glc-1-P are listed in Table 1* and bond lengths and bond angles are shown in Fig. 1. The description in the literature (Beevers & Maconochie, 1965) was essentially confirmed, except that one of the non-esterified P—O bonds was shorter than the average. The refined bond lengths of three P—O bonds are nearly equal and charges are considered to be delocalized. The accuracy of the structural parameters is much increased and the structural features of Glc-1-P are discussed below and compared with those of UDP-Glc.

Coordinates of the non-hydrogen atoms and the structure parameters of UDP-Glc are listed in Tables 2 and 3,* and the molecular structure with the atom-numbering scheme and the crystal structure viewed along the **c** direction are shown in Figs. 2 and 3. The hydroxy groups of UDP-Glc and two water molecules are mainly hydrogen-bonded to the O atoms of the phosphate group, and coordinated to Na$^+$. The carbonyl groups coordinate to Na$^+$, and Na$^+$ ions are six-coordinated.

The conformation about the N—glycosidic bond is *anti* [$\chi = -105·0$ (3)°]. Uracil takes a diketo form. The puckering of the furanose ring is C(2′)-*endo* (^2E), the

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38983 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conformation about C(4′)—C(5′) is *gauche–gauche′* [$\varphi_{CO} = 56{\cdot}5\ (3)$, $\varphi_{OO} = 62{\cdot}0\ (3)°$], and that about C(5′)—O(5′) is *trans* [$\varphi_{CP} = -151{\cdot}0\ (2)°$].

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²) *of the non-hydrogen atoms of Glc*-1-*P with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j a_i a_j B_{ij}.$$

	x	*y*	*z*	B_{eq}
K(1)	9460 (1)	4558	4382 (1)	2·6
K(2)	4217 (1)	38 (1)	9889 (1)	2·1
P	2035 (1)	5090 (1)	−136 (1)	1·3
C(1)	2624 (2)	2606 (2)	1922 (2)	1·4
C(2)	2225 (2)	1946 (2)	3525 (2)	1·5
C(3)	3135 (2)	2559 (2)	5431 (2)	1·4
C(4)	4619 (2)	2272 (2)	5695 (2)	1·4
C(5)	4971 (2)	2798 (2)	3989 (2)	1·5
C(6)	6370 (2)	2250 (2)	4127 (3)	2·1
O(1)	2396 (1)	4146 (1)	1832 (2)	1·8
O(2)	843 (1)	2235 (2)	3312 (2)	2·3
O(3)	2814 (1)	1872 (1)	6929 (2)	2·0
O(4)	5480 (1)	3008 (2)	7345 (2)	2·3
O(5)	4012 (1)	2259 (1)	2228 (2)	1·7
O(6)	6846 (1)	2918 (2)	2761 (2)	2·4
O(7)	872 (1)	6083 (2)	−105 (2)	2·3
O(8)	3311 (1)	5972 (2)	40 (2)	2·4
O(9)	1632 (1)	4015 (1)	−1784 (2)	2·1
*W*O(1)	9534 (2)	2063 (2)	6873 (2)	3·1
*W*O(2)	8523 (2)	4340 (2)	265 (2)	2·8

Table 2. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²) *of UDP-Glc with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j a_i a_j B_{ij}.$$

	x	*y*	*z*	B_{eq}
Na(1)	7004 (2)	8261	304 (2)	3·6
Na(2)	429 (2)	7231 (1)	1954 (2)	2·5
N(1)	9360 (3)	4257 (1)	5801 (4)	1·9
C(2)	10413 (3)	3716 (2)	6200 (5)	2·0
N(3)	11274 (3)	3593 (2)	4886 (4)	2·7
C(4)	11132 (4)	3930 (2)	3147 (5)	2·6
C(5)	10005 (4)	4487 (2)	2827 (5)	2·6
C(6)	9169 (4)	4623 (2)	4113 (4)	2·2
O(2)	10599 (3)	3355 (1)	7636 (3)	2·4
O(4)	11931 (4)	3737 (2)	2077 (4)	3·9
C(1′)	8323 (3)	4373 (2)	7077 (4)	1·6
C(2′)	8093 (4)	5157 (2)	7562 (4)	1·8
C(3′)	6501 (4)	5122 (2)	8040 (4)	1·9
C(4′)	5679 (3)	4561 (2)	6665 (4)	1·8
C(5′)	4734 (4)	4855 (2)	4854 (5)	2·4
O(2′)	9280 (3)	5357 (1)	9063 (3)	3·0
O(3′)	6602 (3)	4853 (1)	9899 (3)	2·5
O(4′)	6867 (2)	4110 (1)	6219 (3)	2·2
O(5′)	5714 (2)	5280 (1)	3966 (3)	2·3
P(1)	5096 (1)	5938 (1)	2646 (1)	1·7
P(2)	5959 (1)	7183 (1)	5077 (1)	1·7
O(I)	3546 (3)	5771 (1)	1519 (4)	3·0
O(II)	6365 (3)	6117 (1)	1695 (4)	3·0
O(III)	4872 (3)	6549 (1)	4094 (4)	2·8
O(IV)	7446 (3)	6886 (2)	6077 (3)	3·1
O(V)	5925 (3)	7772 (1)	3717 (4)	3·2
C(1″)	3654 (3)	7767 (1)	6256 (4)	1·5
C(2″)	3305 (3)	8097 (1)	8052 (4)	1·6
C(3″)	2978 (3)	7519 (2)	9390 (4)	1·7
C(4″)	1684 (3)	7043 (1)	8348 (4)	1·4
C(5″)	2191 (3)	6727 (1)	6643 (4)	1·6
C(6″)	1076 (4)	6227 (2)	5428 (5)	2·1
O(1″)	5073 (2)	7396 (1)	6711 (3)	1·8
O(2″)	4525 (3)	8544 (1)	8929 (3)	2·2
O(3″)	2531 (3)	7826 (1)	10984 (3)	2·8
O(4″)	1272 (2)	6508 (1)	9544 (3)	1·8
O(5″)	2457 (2)	7305 (1)	5435 (3)	1·8
O(6″)	−222 (3)	6576 (2)	4353 (3)	2·8
*W*O(1)	7951 (3)	7093 (1)	31 (3)	2·7
*W*O(2)	2725 (4)	4627 (2)	−1153 (4)	3·9

Table 3. *Structural parameters of UDP-Glc with e.s.d.'s in parentheses*

Bond distances (Å)

N(1)—C(2)	1·373 (4)	P(1)—O(I)	1·491 (3)
C(2)—N(3)	1·368 (5)	P(1)—O(II)	1·487 (3)
N(3)—C(4)	1·397 (5)	P(1)—O(III)	1·596 (3)
C(4)—C(5)	1·436 (5)	P(2)—O(III)	1·607 (3)
C(5)—C(6)	1·340 (5)	P(2)—O(IV)	1·486 (3)
C(6)—N(1)	1·388 (4)	P(2)—O(V)	1·479 (3)
C(2)—O(2)	1·227 (4)	P(2)—O(1″)	1·612 (2)
C(4)—O(4)	1·217 (5)	C(1″)—C(2″)	1·537 (4)
N(1)—C(1′)	1·460 (4)	C(2″)—C(3″)	1·526 (4)
C(1′)—C(2′)	1·534 (4)	C(3″)—C(4″)	1·532 (4)
C(2′)—C(3′)	1·537 (5)	C(4″)—C(5″)	1·528 (4)
C(3′)—C(4′)	1·530 (5)	C(5″)—C(6″)	1·513 (4)
C(4′)—C(5′)	1·515 (5)	C(1″)—O(5″)	1·410 (4)
C(1′)—O(4′)	1·412 (4)	C(5″)—O(5″)	1·446 (4)
C(4′)—O(4′)	1·447 (4)	C(1″)—O(1″)	1·425 (4)
C(2′)—O(2′)	1·408 (4)	C(2″)—O(2″)	1·419 (4)
C(3′)—O(3′)	1·431 (4)	C(3″)—O(3″)	1·426 (4)
C(5′)—O(5′)	1·434 (4)	C(4″)—O(4″)	1·426 (4)
P(1)—O(5′)	1·591 (3)	C(6″)—O(6″)	1·419 (4)

Bond angles (°)

C(2)—N(1)—C(6)	120·4 (3)	O(5′)—P(1)—O(III)	103·4 (1)
C(2)—N(1)—C(1′)	118·3 (3)	O(I)—P(1)—O(II)	120·2 (2)
C(6)—N(1)—C(1′)	120·9 (3)	O(I)—P(1)—O(III)	106·5 (1)
N(1)—C(2)—N(3)	115·9 (3)	O(II)—P(1)—O(III)	111·1 (2)
N(1)—C(2)—O(2)	123·5 (3)	P(1)—O(III)—P(2)	132·6 (2)
N(3)—C(2)—O(2)	120·5 (3)	O(III)—P(2)—O(IV)	109·9 (2)
C(2)—N(3)—C(4)	126·9 (3)	O(III)—P(2)—O(V)	109·0 (2)
N(3)—C(4)—C(5)	113·8 (3)	O(III)—P(2)—O(1″)	99·7 (1)
N(3)—C(4)—O(4)	119·5 (3)	O(IV)—P(2)—O(V)	119·9 (2)
C(5)—C(4)—O(4)	126·7 (4)	O(IV)—P(2)—O(1″)	105·0 (1)
C(4)—C(5)—C(6)	120·0 (3)	O(V)—P(2)—O(1″)	111·5 (1)
N(1)—C(6)—C(5)	122·8 (3)	P(2)—O(1″)—C(1″)	120·0 (2)
N(1)—C(1′)—C(2′)	115·0 (2)	C(2″)—C(1″)—O(1″)	109·1 (2)
N(1)—C(1′)—O(4′)	108·4 (2)	C(2″)—C(1″)—O(5″)	109·7 (2)
C(2′)—C(1′)—O(4′)	106·3 (2)	O(1″)—C(1″)—O(5″)	111·2 (2)
C(1′)—C(2′)—C(3′)	100·7 (2)	C(1″)—C(2″)—C(3″)	111·0 (2)
C(1′)—C(2′)—O(2′)	108·6 (2)	C(1″)—C(2″)—O(2″)	110·4 (2)
C(3′)—C(2′)—O(2′)	114·9 (3)	C(3″)—C(2″)—O(2″)	111·2 (2)
C(2′)—C(3′)—C(4′)	102·9 (2)	C(2″)—C(3″)—C(4″)	108·7 (2)
C(2′)—C(3′)—O(3′)	110·5 (3)	C(2″)—C(3″)—O(3″)	111·0 (2)
C(4′)—C(3′)—O(3′)	107·8 (3)	C(4″)—C(3″)—O(3″)	109·1 (2)
C(3′)—C(4′)—C(5′)	115·3 (3)	C(3″)—C(4″)—C(5″)	107·9 (2)
C(3′)—C(4′)—O(4′)	105·8 (2)	C(3″)—C(4″)—O(4″)	111·7 (2)
C(5′)—C(4′)—O(4′)	108·6 (3)	C(5″)—C(4″)—O(4″)	112·5 (2)
C(4′)—C(5′)—O(5′)	108·2 (3)	C(4″)—C(5″)—C(6″)	116·4 (2)
C(1′)—O(4′)—C(4′)	110·5 (2)	C(4″)—C(5″)—O(5″)	108·6 (2)
C(5′)—O(5′)—P(1)	122·3 (2)	C(6″)—C(5″)—O(5″)	106·2 (2)
O(5′)—P(1)—O(I)	109·7 (1)	C(5″)—C(6″)—O(6″)	113·8 (3)
O(5′)—P(1)—O(II)	104·7 (1)	C(1″)—O(5″)—C(5″)	114·1 (2)

Sodium coordination distances (Å)

	Symmetry*	Translation			
		a	*b*	*c*	
Na(1)···O(V)	1	0	0	0	2·993 (4)
Na(1)···O(2″)	1	0	0	−1	2·299 (3)
Na(1)···*W*O(1)	1	0	0	0	2·370 (3)
Na(1)···O(2)	2	2	0	1	2·356 (3)
Na(1)···O(4)	2	2	0	0	2·324 (4)
Na(1)···*W*O(2)	2	1	0	0	2·631 (4)
Na(2)···O(3″)	1	0	0	−1	2·415 (3)
Na(2)···O(4″)	1	0	0	−1	2·456 (3)
Na(2)···O(5″)	1	0	0	0	2·800 (3)
Na(2)···O(6″)	1	0	0	0	2·308 (3)
Na(2)···*W*O(1)	1	−1	0	0	2·379 (3)
Na(2)···O(2)	2	1	0	1	2·343 (3)

Hydrogen bonding

D···*A*	Symmetry*	Translation			*D*···*A* (Å)	H···*A* (Å)	*D*—H···*A* (°)
		a	*b*	*c*			
N(3)—H(3)···O(V)	2	2	−1	1	2·937 (4)	2·08 (4)	162 (4)
O(2′)—H(O2′)···O(4″)	1	1	0	0	2·772 (3)	2·15 (5)	156 (5)
O(3′)—H(O3′)···O(II)	1	0	0	1	2·735 (4)	2·07 (5)	149 (5)
O(2″)—H(O2″)···O(3′)	2	1	0	2	2·847 (4)	2·09 (4)	173 (4)
O(4″)—H(O4″)···O(I)	1	0	0	1	2·627 (3)	1·91 (5)	162 (5)
O(6″)—H(O6″)···O(IV)	1	−1	0	0	2·713 (4)	2·08 (9)	126 (7)
*W*O(1)—*W*H(1)···O(II)	1	0	0	0	2·745 (4)	2·06 (4)	162 (4)
*W*O(1)—*W*H(2)···O(IV)	1	0	0	−1	2·850 (4)	2·06 (6)	180 (5)
*W*O(2)—*W*H(4)···O(I)	1	0	0	0	2·886 (4)	2·30 (5)	142 (5)

* Symmetry code: (1) x, y, z; (2) $-x, y+\frac{1}{2}, -z$.

The pyrophosphate group takes a staggered form $\{\tau[O(5')-P(1)-P(2)-O(1'')] = -74\cdot6\ (1)°\}$ and UDP-Glc has a slightly twisted pyrophosphate linkage. The torsion angles of the main chain are: C(5')–O(5')–P(1)–O(III) 76·2 (3), O(5')–P(1)–O(III)–P(2) 93·5 (2), P(1)–O(III)–P(2)–O(1'') −164·9 (2), and O(III)–P(2)–O(1'')–C(1'') −72·6 (2)°. The bond lengths of the esterified P–O of UDP-Glc are 1·59–1·61 Å and are nearly equal to those of nucleoside diphosphate and triphosphate (*e.g.* Viswamitra, Post & Kennard, 1979; Larson, 1978). The bond lengths of non-esterified P–O are 1·48–1·49 Å and charges are considered to be delocalized. P–O(1) of Glc-1-P is slightly longer than the corresponding bond of UDP-Glc.

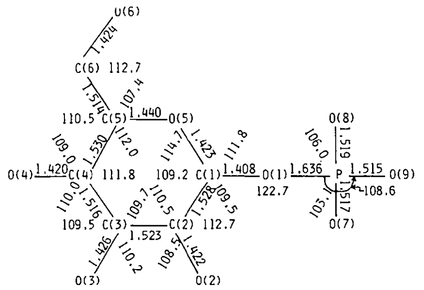

Fig. 1. Bond lengths (Å) and bond angles (°) of Glc-1-P. The averaged e.s.d.'s of the bond lengths are 0·002 Å and those of the bond angles are 0·1°.

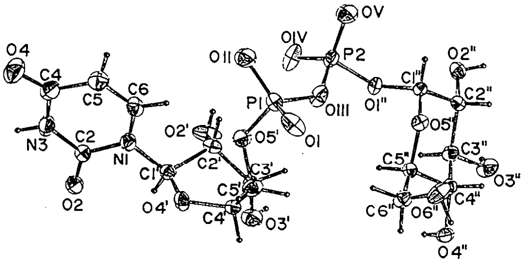

Fig. 2. Molecular structure of UDP-Glc with the atom numbering scheme.

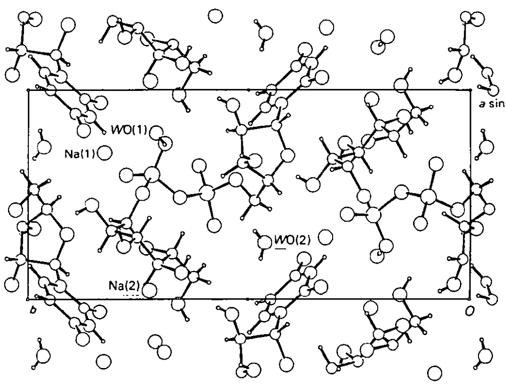

Fig. 3. Projection of the crystal structure of UDP-Glc down the *c* axis.

The pyranose ring of UDP-Glc takes the $^4C_1$ conformation and the Cremer & Pople (1975) ring-puckering parameters are $Q = 0\cdot595$ Å, $\theta = 5\cdot2°$ and $\varphi = 257°$. The ring-puckering parameters of Glc-1-P are $Q = 0\cdot552$ Å, $\theta = 6\cdot2°$ and $\varphi = 100°$. The distortions of the pyranose rings of the two molecules are slightly different. The pyranose ring of UDP-Glc is distorted towards $^4H_5$ and that of Glc-1-P is distorted to $^2H_1$.

The conformation about the glycosidic bond of UDP-Glc is *trans–gauche* $[\varphi_{CP} = -163\cdot2\ (2),\ \varphi_{OP} = 75\cdot7\ (3)°]$, and that about the C(5'')–C(6'') bond is *gauche–gauche'* $[\varphi_{CO} = 71\cdot8\ (3),\ \varphi_{OO} = -49\cdot3\ (3)°]$. The former is the standard form of the glycosidic bond. The latter takes either *gauche–gauche'* or *trans–gauche* in a crystal of glucose or glucose derivative (*e.g.* Hough, Neidle, Rogers & Troughton, 1973; Brown & Levy, 1979). In the case of Glc-1-P it takes *trans–gauche* $[\varphi_{CO} = -169\cdot6\ (1),\ \varphi_{OO} = 67\cdot9\ (2)°]$.

C(1'')–O(1'') of UDP-Glc is nearly equal to C(1'')–O(5'') while C(1)–O(1) of Glc-1-P is slightly shorter than C(1)–O(5). From the study on the anomeric effect, it is known that *X–A* bonds shorten when two electronegative substituents are bound to one centre (*X–A–X*). When the electronegativity of the two substituents is different (*X–A–Y*), a greater shortening effect appears at the *A–Y* bond and lengthening effect at the *A–X* bond, where *X* is a more electronegative group (Kirby, 1983). C(1)–O(1) is shorter than C(1)–O(5) in α-D-glucose (Brown & Levy, 1979; Hough, Neidle, Rogers & Troughton, 1973) and they are nearly equal in methyl α-D-glucopyranoside (Jeffrey, McMullan & Takagi, 1977). The electronegativity of the phosphate dianion is probably weak and C(1)–O(1) is shorter than C(1)–O(5) in Glc-1-P. On the other hand, the UDP^{2-} moiety is more electronegative and therefore C(1'')–O(1'') lengthens and C(1'')–O(5'') shortens. The free energy of hydrolysis of the glycosidic bond of UDP-Glc is −30·5 kJ mol^{-1} which is comparable to that of the P–O bond of ATP^{4-}, and 1·5 times larger than that of the corresponding bond of Glc-1-P (Jencks, 1976). The main function of sugar nucleotide is the participation in glycosidation reactions using the high energy of hydrolysis of the glycosidic bond, and the bond weakening related to the anomeric effect is an interesting problem.

Deviations of atoms from the mean planes through the pyranose ring are listed in Table 4, compared with some α anomers of 1-substituted glucose (Glc1α-*X*). UDP-Glc is a substrate in the 4''-epimerization of glucose into galactose and the 6''-oxidation of glucose into glucuronic acid. C(4'') and C(6'') are reaction sites

Table 4. *Deviations of atoms* (Å) *from the mean plane through the pyranose ring, and exocyclic torsion angles* (°)

Deviations of atoms from the mean plane[a]

	α-D-Glc[b]	Glc1α-Me[c]	*β*-Maltose[d]	Sucrose[e]	Glc-1-P[f]	UDP-Glc[f]
C(1)*	0·226	0·237	0·235	0·208	0·249	0·209
C(2)*	−0·209	−0·243	−0·235	−0·236	−0·254	−0·217
C(3)*	0·221	0·242	0·241	0·258	0·234	0·255
C(4)*	−0·231	0·223	−0·229	−0·241	−0·196	−0·269
C(5)*	0·246	0·217	0·224	0·212	0·190	0·262
O(5)*	−0·252	−0·231	−0·236	−0·201	−0·222	−0·240
C(6)	−0·267	−0·352	−0·370	−0·411	−0·467	−0·124
O(1)	1·611	1·636	1·648	1·626	1·655	1·627
O(2)	0·263	0·133	0·167	0·245	0·167	0·269
O(3)	−0·368	−0·287	−0·285	−0·258	−0·306	−0·235
O(4)	0·281	0·337	0·300	0·266	0·401	0·086

Exocyclic torsion angles[g]

O(1)···O(2)	56·9	60·7	61·7	54·9	57·8	55·9
O(2)···O(3)	63·2	58·8	60·5	63·4	59·6	61·5
O(3)···O(4)	−65·5	−67·4	−64·9	−64·7	−66·7	−56·3
O(4)···C(6)	62·9	64·5	65·5	64·6	68·5	55·4

Notes: (*a*) Atoms with asterisks were used for the calculation of the plane. Standard deviations are in the range 0·001 –0·003 Å. (*b*) α-D-Glucose (Brown & Levy, 1979). (*c*) Methyl α-D-glucopyranoside (Jeffrey *et al.*, 1977). (*d*) *β*-Maltose (Gress & Jeffrey, 1977). (*e*) Sucrose (Hanson, Sieker & Jensen, 1973). (*f*) This work. Equation of the plane of Glc-1-P is $-0{\cdot}116X + 0{\cdot}993Y + 0{\cdot}033Z = 1{\cdot}819$ and that of UDP-Glc is $0{\cdot}790X - 0{\cdot}541Y + 0{\cdot}119Z = -4{\cdot}955$. X, Y, and Z are the coordinates in Å along the *a*, *b*, and *c* axes, respectively. (*g*) O(1)···O(2) means O(1)—C(1)—C(2)—O(2). Standard deviations are in the range 0·1 – 0·3°.

and the hydroxyl groups of the glucose moiety are known as essential sites of enzymic specificity (Kochetkov & Shibaev, 1973). If the deviations of atoms from the mean plane of Glc1α-*X* are compared, the positions of C(6″) and O(4″) are characteristic of UDP-Glc. These atoms are very close to the mean plane in UDP-Glc while they stretch upward or downward from the plane of the pyranose ring in other compounds. From the fact that the deviation of each O atom takes similar values in different crystal forms of α-D-glucose (Brown & Levy, 1979; Hough, Neidle, Rogers & Troughton, 1973), these values are considered to be insensitive to hydrogen bonding but characteristic of the molecule. The exocyclic torsion angles [O(3)—C(3)—C(4)—O(4) and O(4)—C(4)—C(5)—C(6)] of UDP-Glc are about 10° smaller than those of other Glc1α-*X*, which corresponds to the difference in deviations of atoms from the mean plane. Oxidation at C(6″) couples with reduction of NAD$^+$ and epimerization at C(4) couples with oxidation–reduction of NAD$^+$–NADH (Kochetkov & Shibaev, 1973). The structural feature found in this work may be effective for fitting to the binding site of enzymes or enzyme-bound NAD$^+$ or NADH.

The partial structure of UDP-Glc was studied by NMR spectroscopy (Lee & Sarma, 1976; O'Connor, Nunez & Barker, 1979). The molecular conformation in the crystal coincides with the energetically favourable conformation of each segment in aqueous solution. It has been proposed that this molecule takes a folded conformation in enzymic reaction (Kochetkov & Shibaev, 1973). Intramolecular hydrogen bonds between glucose and uracil moieties were said to stabilize the folding. On the other hand, a ^{13}C NMR study using the lanthanide-induced-shift technique concluded that UDP-Glc takes an extended form in aqueous solution (London & Sherry, 1978). In the crystal the molecule also takes an extended form and no intramolecular hydrogen bond exists. From these facts the extended form seems to be favoured, at least when this molecule is not bound to the enzyme.

References

Beevers, C. A. & Maconochie, G. H. (1965). *Acta Cryst.* **18**, 232–236.

Brown, G. M. & Levy, H. A. (1979). *Acta Cryst.* B**35**, 656–659.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Gress, M. E. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 2490–2495.

Hanson, J. C., Sieker, L. C. & Jensen, L. H. (1973). *Acta Cryst.* B**29**, 797–808.

Hough, E., Neidle, S., Rogers, D. & Troughton, P. G. H. (1973). *Acta Cryst.* B**29**, 365–367.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Jeffrey, G. A., McMullan, R. K. & Takagi, S. (1977). *Acta Cryst.* B**33**, 728–737.

Jencks, W. P. (1976). *Handbook of Biochemistry and Molecular Biology*, Vol. 1, 3rd ed., edited by G. D. Fasman, pp. 296–304. Cleveland: CRC Press Inc.

Kirby, A. J. (1983). *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, pp. 37–77. Berlin, Heidelberg, New York: Springer-Verlag.

Kochetkov, N. K. & Shibaev, V. N. (1973). *Adv. Carbohydr. Chem. Biochem.* **28**, 307–399.

Larson, A. C. (1978). *Acta Cryst.* B**34**, 3601–3604.

Lee, C.-H. & Sarma, R. H. (1976). *Biochemistry*, **15**, 697–704.

London, R. E. & Sherry, A. D. (1978). *Biochemistry*, **17**, 3662–3666.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

O'Connor, J. V., Nunez, H. A. & Barker, R. (1979). *Biochemistry*, **18**, 500–507.

Rosenstein, R. D. (1968). Am. Crystallogr. Assoc. Abstr. Paper (Summer Meet.) 92.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

Viswamitra, M. A., Post, M. L. & Kennard, O. (1979). *Acta Cryst.* B**35**, 1089–1094.