

## The Crystal and Molecular Structure of 1,2:4,5-Di-*O*-isopropylidene- $\beta$ -D-fructopyranose

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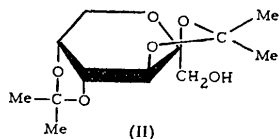
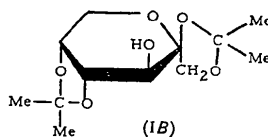
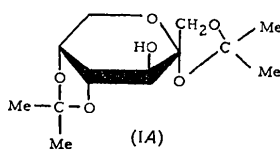
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The crystal structure of 1,2:4,5-di-*O*-isopropylidene- $\beta$ -D-fructopyranose, C<sub>12</sub>H<sub>20</sub>O<sub>6</sub>, has been determined. The crystals are monoclinic, *P*2<sub>1</sub>, with  $a=11.094(7)$ ,  $b=5.626(4)$ ,  $c=11.917(7)$  Å,  $\beta=115.53(8)^\circ$  and  $Z=2$ . The structure was refined by the full-matrix least-squares technique to an  $R$  value of 0.047, using 1281 independent three-dimensional single-crystal X-ray data collected with an automatic four-circle diffractometer. The  $\beta$ -anomer configuration previously assumed without proof was confirmed. Each 1,3-dioxolane ring has an envelope conformation (*E*) and the six-membered ring is a chair (<sup>2</sup>*C*<sub>5</sub>) somewhat distorted towards a half-chair (<sup>2</sup>*H*<sub>0</sub>). The molecules are arranged in a polar helix joined together by hydrogen bonds around the screw axis and they fit together well by tilting in the direction of the pitch of the screw.

### Introduction

Emil Fischer (1895) isolated two crystalline diisopropylidene acetals from the condensation of D-fructose with acetone in the presence of acid: ' $\alpha$ -' and ' $\beta$ -diacetone-fructose' (' $\alpha$ -' and ' $\beta$ -' had no anomeric significance). The ' $\alpha$ -' and ' $\beta$ -' derivatives were shown by chemical evidence to be 1,2:4,5-di-*O*-isopropylidene-D-fructopyranose (*I*A or *I*B) by Ohle (1927), Anderson, Charlton, Haworth & Nicholson (1929) and 2,3:4,5-di-*O*-isopropylidene-D-fructopyranose (*II*) by Wolfrom, Shilling & Binkley (1950), respectively. It has been generally accepted that both derivatives were the  $\beta$ -anomers, as shown in *I*B and *II*. Recently, Brady (1970) has established the conditions for obtaining *I* (*A* or *B*) free from traces of *II*, which greatly predominates in the mixture at equilibrium.



The rare sugar  $\beta$ -D-psicose, which differs from  $\beta$ -D-fructose by inversion about C(3), can be obtained in high yields via *IB* by an elegant sequence of stereospecific reactions (Tipson, Brady & West, 1970). The removal of the protective groups in the final

step exploits the smooth and rapid hydrolysis of the isopropylidene derivatives of ketoses to the free sugars by dilute oxalic acid (Tipson, West & Brady, 1969). In order to be certain that the starting material was the  $\beta$ -anomer (*IB*), since this could not be proved by n.m.r. spectroscopy, Dr R. S. Tipson provided us with the compound used in this structure determination.

### Experimental

Monoclinic crystals were obtained by extremely slow evaporation at room temperature of a solution in a mixture of distilled water and ethyl alcohol. The crystals were colorless prisms with pinacoids on the edges. They had a pronounced cleavage parallel to the  $b$  axis, but bent when cut perpendicular to  $b$ . The crystal density was measured by flotation in a liquid mixture of carbon tetrachloride and benzene. Preliminary unit-cell parameters and probable space group were determined from oscillation and Weissenberg photographs. The precise unit-cell parameters and three-dimensional intensity data were measured on a Picker four-circle automated diffractometer using Ni-filtered Cu  $K\alpha$  radiation ( $\lambda_{\text{ave}}=1.5418$  Å) with a scintillation counter, at  $\sim 16$ – $18^\circ\text{C}$ .

### Crystal data

1,2:4,5-Di-*O*-isopropylidene- $\beta$ -D-fructopyranose  
(C<sub>12</sub>H<sub>20</sub>O<sub>6</sub>),

M.W. 260.29; m.p.  $119^\circ\text{C}$ .

Monoclinic, space group *P*2<sub>1</sub>, from systematic absences ( $0k0$  absent when  $k=2n+1$ ),  $Z=2$ .

$a=11.094(7)$ ,  $b=5.626(4)$ ,  $c=11.917(7)$  Å,  $\beta=115.53(8)^\circ$

$D_x=1.288$  g cm<sup>-3</sup>,  $D_m=1.273$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha_{\text{ave}})=8.78$  cm<sup>-1</sup>.

The intensity data were collected with  $\theta$ - $2\theta$  scans of  $2^\circ$  per 60 sec up to  $130^\circ$  in  $2\theta$  from a crystal  $0.2$  mm  $\times$   $0.65$  mm  $\times$   $0.17$  mm, mounted with the principal axis  $b$  parallel to the  $\varphi$  axis of the diffractometer. Four reflections, 020, 006, 303 and 211, were measured as

standard reflections every one hundred reflections. 10-sec background measurements were taken at both ends of the  $2^\circ$  scan range of each peak. Out of 1281 independent reflections, not including systematic absences, 26 reflections with  $I_{\text{meas}} \leq 2\sigma(I_{\text{meas}})$  were considered as unobserved reflections, where  $\sigma(I_{\text{meas}})$  is the estimated standard deviation derived from counting statistics. Unobserved reflections were arbitrarily given values of  $|I_{\text{unobs}}| = \frac{1}{2}\sigma(I_{\text{meas}})$ . Lorentz and polarization corrections were made (Shiono, 1969) with no correction for other possible systematic errors (*i.e.* absorption, extinction and Renninger effect) in the structure analysis.

### The structure determination and refinement

The structure was determined in two stages. Initially, the direct method was used: starting phases were derived by the symbolic addition procedure (Karle & Karle, 1963, 1964, 1966) after fixing the origin (Hauptman & Karle, 1956) and the *DP5* (Hall 1967) tangent refinement and extension program was applied. In the resulting *E* synthesis 13 of the 21 highest peaks were consistent with molecule *IB*, and the carbon and oxygen structure could be completed with five lower peaks. It was obvious, however, that the inferred molecule was too close to the twofold screw axis; more-

Table 1. Fractional coordinates ( $\times 10^4$ ) and anisotropic temperature factors ( $\times 10^4$ ) for 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose

The thermal parameters are of the form  $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . The quantity  $U_i$  is the r.m.s. atomic displacement ( $\text{\AA}$ ) along the direction of the  $i$ th principal axis of the thermal ellipsoid. These are calculated from the experimental values of  $\beta_{ij}$ . The estimated standard deviations for the last decimal place ( $10^4$  for heavier atoms and  $10^3$  for hydrogen atoms) are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$U_1$	$U_2$	$U_3$
O(1)	725 (2)	10200 (7)	2070 (2)	105 (2)	306 (8)	66 (2)	-19 (3)	18 (8)	-8 (3)	0.19	0.22	0.26
O(2)	2220 (2)	7491 (6)	3333 (1)	113 (2)	297 (7)	58 (2)	-38 (3)	33 (1)	19 (3)	0.17	0.21	0.26
O(3)	172 (2)	7134 (6)	4168 (2)	75 (2)	318 (7)	85 (2)	25 (3)	21 (1)	-2 (3)	0.19	0.22	0.25
O(4)	1966 (2)	5491 (7)	6692 (1)	97 (2)	321 (8)	56 (2)	44 (3)	24 (1)	-3 (3)	0.18	0.20	0.26
O(5)	3827 (2)	7846 (6)	7476 (2)	87 (2)	360 (8)	60 (1)	41 (3)	17 (1)	11 (3)	0.18	0.22	0.26
O(6)	3331 (2)	10204 (6)	4955 (2)	77 (2)	325 (8)	66 (1)	26 (3)	25 (1)	8 (3)	0.19	0.21	0.24
C(1)	1262 (3)	11208 (7)	3260 (2)	103 (2)	258 (9)	74 (2)	-6 (4)	35 (2)	-8 (4)	0.20	0.21	0.23
C(2)	2076 (2)	9217 (7)	4129 (2)	76 (2)	250 (8)	58 (2)	-8 (4)	25 (2)	6 (3)	0.18	0.19	0.21
C(3)	1445 (2)	8078*	4923 (2)	67 (2)	236 (8)	53 (2)	-2 (3)	22 (2)	11 (3)	0.17	0.19	0.20
C(4)	2313 (2)	6069 (7)	5690 (2)	91 (2)	233 (9)	57 (2)	1 (4)	25 (2)	11 (4)	0.18	0.20	0.22
C(5)	3781 (2)	6775 (8)	6376 (2)	73 (2)	366 (11)	77 (2)	-28 (4)	23 (2)	-4 (4)	0.18	0.22	0.25
C(6)	4286 (2)	8472 (9)	5682 (2)	68 (2)	497 (14)	78 (2)	-18 (5)	27 (2)	3 (5)	0.18	0.22	0.28
C(7)	2719 (3)	9538 (12)	1772 (3)	135 (3)	606 (21)	107 (3)	55 (8)	65 (3)	19 (7)	0.23	0.26	0.32
C(8)	883 (3)	6478 (9)	1211 (3)	157 (4)	365 (12)	78 (3)	13 (6)	30 (2)	20 (5)	0.21	0.25	0.30
C(9)	1645 (2)	8405 (8)	2088 (2)	95 (2)	323 (10)	54 (2)	11 (5)	26 (2)	0 (4)	0.18	0.22	0.23
C(10)	2943 (2)	6515 (8)	7830 (2)	95 (2)	339 (10)	58 (2)	43 (5)	16 (2)	4 (4)	0.18	0.21	0.26
C(11)	3701 (4)	4549 (11)	8710 (3)	163 (4)	475 (16)	90 (3)	-10 (8)	15 (3)	-79 (6)	0.19	0.29	0.34
C(12)	2264 (3)	8209 (10)	8361 (2)	127 (3)	513 (15)	77 (2)	40 (6)	44 (2)	55 (6)	0.20	0.25	0.30

Table 1 (cont.)

#### Hydrogen atom parameters

H(O3)	-0.040 (2)	0.829 (8)	0.398 (2)
H(C1)	0.186 (2)	1.251 (9)	0.324 (2)
H'(C1)	0.056 (2)	1.162 (8)	0.352 (2)
H(C3)	0.137 (2)	0.933 (7)	0.547 (2)
H(C4)	0.224 (2)	0.464 (7)	0.523 (2)
H(C5)	0.434 (2)	0.540 (9)	0.653 (2)
H(C6)	0.459 (2)	0.758 (10)	0.512 (2)
H'(C6)	0.509 (2)	0.936 (10)	0.629 (2)
H(C7)	0.331 (3)	0.809 (12)	0.175 (3)
H'(C7)	0.232 (2)	1.037 (14)	0.098 (2)
H''(C7)	0.320 (4)	1.070 (13)	0.239 (3)
H(C8)	0.140 (3)	0.497 (9)	0.144 (3)
H'(C8)	0.065 (3)	0.690 (9)	0.043 (3)
H''(C8)	0.005 (3)	0.622 (9)	0.140 (3)
H(C11)	0.417 (3)	0.348 (10)	0.834 (2)
H'(C11)	0.436 (3)	0.511 (11)	0.944 (3)
H''(C11)	0.300 (3)	0.363 (12)	0.883 (2)
H(C12)	0.296 (2)	0.914 (12)	0.895 (2)
H'(C12)	0.181 (3)	0.727 (12)	0.878 (2)
H''(C12)	0.162 (3)	0.930 (12)	0.767 (2)

\* Fixed parameter (polar space group).

over a set of structure factors based on the trial parameters gave poor agreement with the observed data for the *h00* and *00l* reflections, also implying that the molecule had to be shifted. A method related to Bragg-Lipson structure-factor charts was then used for the shifts  $\Delta X$  and  $\Delta Z$ . The best agreement was obtained with  $\Delta X, \Delta Z = \frac{1}{8}, \frac{1}{8}$ , and the close contacts between symmetry-related molecules were eliminated.

The atomic positional and thermal parameters were refined isotropically with an IBM 1130 computer for two cycles using a block-diagonal least-squares program (Shiono, 1968) reducing *R* from 0.35 to 0.25 for 596 reflections. All 1281 reflections were then used to refine the parameters isotropically until  $R=0.13$  and anisotropically until  $R=0.09$ . Positional parameters for all hydrogen atoms were found on a difference Fourier map computed using reflections with  $\sin \theta \leq 0.6$ . Block-diagonal least-squares calculations with fixed atomic parameters for hydrogen atoms reduced the *R* index to 0.072. At this stage, full-matrix least-

squares refinement (Shiono, 1966) was used for all parameters except those for hydrogen atoms. The function minimized was  $\sum_H \omega \Delta^2$ , where  $\Delta = |F_{\text{meas}}| -$

$|F_{\text{calc}}/K|$ .  $\omega$  is the weight to be attached to an observation and  $K$  is a scale factor. The weighting function suggested by Cruickshank (1961),  $\omega = (A + B|F_{\text{meas}}| + C|F_{\text{meas}}|^2)^{-1}$ , was employed with  $A = 0.20 \times 10^{-2}$ ,  $B = 6.30 \times 10^{-2}$ ,  $C = 0.40 \times 10^{-2}$  for the final refinement. Hydrogen positional parameters were refined separately using the block-diagonal approximation, giving  $R = 0.051$ . Refinement was terminated with the discrepancy index  $R (= \sum ||F_{\text{meas}}| - |F_{\text{c}}|| / \sum |F_{\text{meas}}|)$  of 0.047 when the ratio of shift/error for all parameters was less than 0.4 except that of  $\beta_{23}$  for O(1), O(5) and C(2) (0.9, 0.7 and 0.7, respectively). Four low-order strong reflections (marked + in Table 2) considered to be affected by extinction, were omitted in the final two cycles of full-matrix least-squares refinement. The final positional and anisotropic thermal parameters with their estimated standard errors and the principal r.m.s. atomic vibrational amplitudes are shown in Table 1. The thermal parameters for hydrogen atoms were assigned values which were the same as those for the atoms bonded to them and were fixed during the refinement. The atomic scattering factors for carbon and oxygen were those from *International Tables for X-ray Crystallography* (1962). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used.

### Discussion of the structure

#### Conformation

The molecular structure and atomic numbering of 1,2:4,5-di-*O*-isopropylidene- $\beta$ -D-fructopyranose is illustrated in Fig. 1(a). Fig. 1(b) shows the molecule in a view more closely resembling the convention used in carbohydrate chemistry. The crystal structure determination confirms that the molecule is the  $\beta$ -anomer.

The pyranose ring, C(2)–C(3)–C(4)–C(5)–C(6)–O(6), has a chair [ ${}^2C_5$  or  $1C(D)$ ] conformation, which is distorted in the direction of the half-chair ( ${}^2H_0$ ) conformation as a result of the fusion of the five- and six-membered rings. The deviations from the best least-squares plane passing through atoms C(3)–C(4)–C(6)–O(6), as compared to  $\beta$ -D-fructopyranose (Rosenstein, 1968), are shown in Fig. 2 and Table 3. The *cis*-fused ring bridging O(4) and O(5) tends to flatten the chair at C(5), while the *spiro*-fusion at C(2) slightly tilts up the other side of the chair.

The dihedral angles are shown in Fig. 3; those of the carbon atoms are compared with  $\beta$ -D-fructopyranose in Table 4. The largest difference (about  $25^\circ$ ) from those of the unstrained pyranose ring occurs around the C(4)–C(5) bond, where the *cis*-fused 1,3-dioxolane ring is attached. The distortion introduced by the *cis*-fusion progressively lessens in going around the ring away from the C(4)–C(5) bond and is least for C(2)–C(3), which is furthest away. (The conformation of O(1) and O(2) around the C(1)–C(2) bond is *anti-clinal* rather than *antiperiplanar* because of the formation of the *spiro* 1,3-dioxolane ring.) A similar distortion of a chair form was also found in the 1,2-*O*-amine

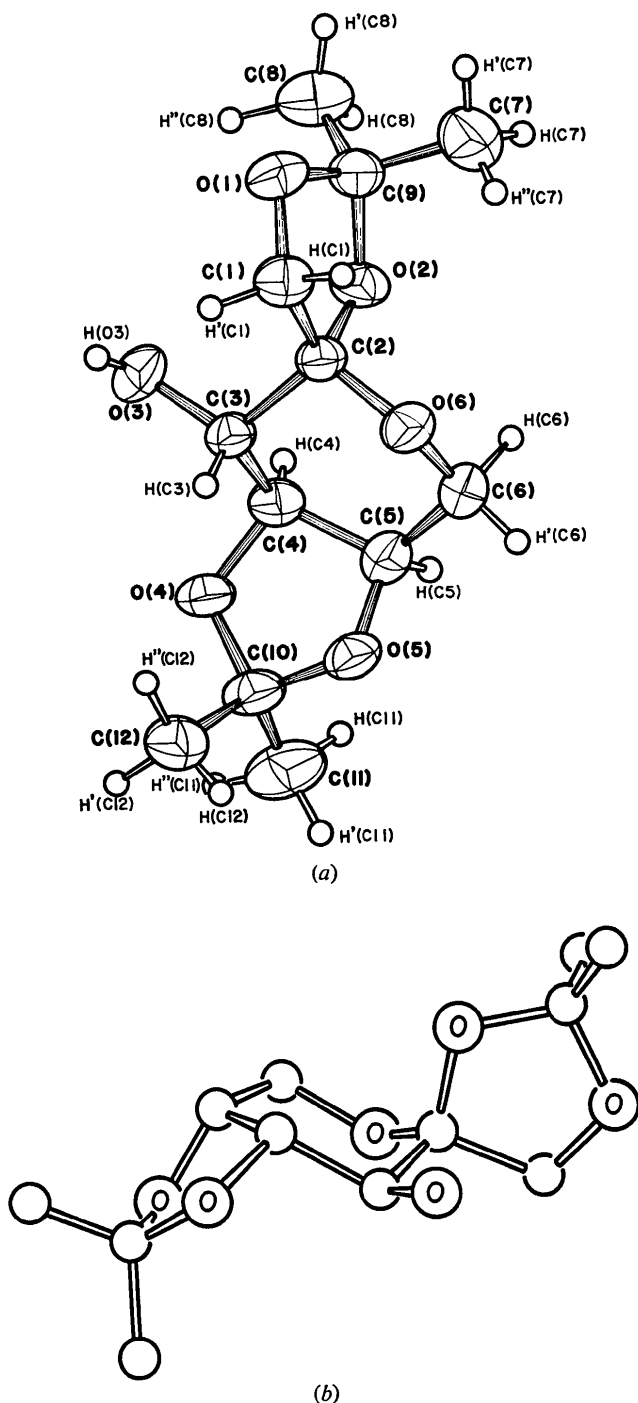


Fig. 1. (a) Structure of 1,2:4,5-di-*O*-isopropylidene- $\beta$ -D-fructopyranose, and atomic numbering. Thermal vibrational ellipsoids are scaled to contain 50% probability (ORTEP, Johnson, 1965). (b) 1,2:4,5-Di-*O*-isopropylidene- $\beta$ -D-fructopyranose in conventional view for carbohydrate chemistry.

Table 2. Observed and calculated structure amplitudes

Columns are: l index, 10|F<sub>meas</sub>|, 10|F<sub>calc</sub>|. Asterisks indicate unobserved reflections, crosses indicate reflections omitted from the final refinement.

Table with multiple columns containing numerical data for reflections, including indices and amplitudes. The table is organized into rows and columns, with some cells containing asterisks or crosses as per the caption's instructions.

Table 3. *Least-squares planes in 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose, with displacements of atoms from the plane*

The equation for the plane is in the form  $AX + BY + CZ = D$ .  $X$ ,  $Y$ , and  $Z$  are  $|a|x$ ,  $|b|y$ , and  $|c|z$  respectively, where  $|a|$ ,  $|b|$ ,  $|c|$  are lattice parameters in  $\text{\AA}$  and  $x, y, z$  are fractional coordinates.  $D$  is the distance of the plane from the origin. Asterisks indicate atoms which were not included in the calculation of the plane. The estimated standard error in a distance is given in parentheses ( $10^{-3} \text{\AA}$ ).

A	B	C	D	Atom	Distance to the plane ( $\text{\AA}$ )
Pyranose ring					
-0.285	0.469	0.878	6.819	C(2)*	-0.728 (3)
				C(3)	0.001 (2)
				C(4)	-0.001 (3)
				C(5)*	0.439 (3)
				C(6)	0.001 (3)
				O(6)	-0.001 (3)
1,2 isopropylidene group					
0.885	0.444	-0.254	3.065	O(1)*	-0.433 (3)
				O(2)	-0.025 (2)
				C(1)	-0.015 (3)
				C(2)	0.024 (3)
				C(9)	0.016 (3)
4,5 isopropylidene group					
-0.555	0.810	0.069	1.825	O(4)	0.020 (2)
				O(5)	0.013 (3)
				C(4)	-0.013 (3)
				C(5)*	-0.538 (3)
				C(10)	-0.020 (3)

isopropylidene- $\alpha$ -D-glucopyranose hydroiodide (Trotter & Fawcett, 1966) derived from  $\alpha$ -D-glucose, which has a *cis*-glycol grouping on C(1) and C(2). The

displacements of atoms C(5) and C(2) from the best least-squares plane through C(4)-C(3)-C(1)-O(1) in the glucose derivative are  $-0.77$  and  $0.25 \text{\AA}$ , respectively. The dihedral angle around the C(1)-C(2) bond is  $12^\circ$  and the system C(1)-C(2)-O(1)-O(2) is approximately planar showing that the C(1)-O(1) and C(2)-O(2) bonds are nearly coplanar. The pyranose ring in the glucose derivative is therefore more flattened towards the half-chair conformation than in this structure.

Table 4. *Comparison of dihedral angles for 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose (IB) and  $\beta$ -D-fructopyranose (IV)*

+ signifies turning the plane  $IJK$  to  $JKL$ , advancing in the direction of a right-handed screw.

Bond involved		Atoms	(IB)	(IV)
J	K	I L		
C(1)	C(2)	O(1), O(2)	$+15.2^\circ$	$+177.8^\circ$
C(2)	C(3)	O(2), O(3)	$-60.1$	$-51.7$
C(3)	C(4)	O(3), O(4)	$-76.2$	$-65.9$
C(4)	C(5)	O(4), O(5)	$-33.3$	$-57.2$
C(5)	C(6)	O(5), O(6)	$-79.6$	$-63.7$

Trotter & Fawcett (1966) showed conclusively by re-interpretation of the proton magnetic resonance spectra that the molecular conformation found in crystals of the isopropylidene glucose derivative is the same as that of the predominant species in solution. They found that the interpreted p.m.r. dihedral angles are

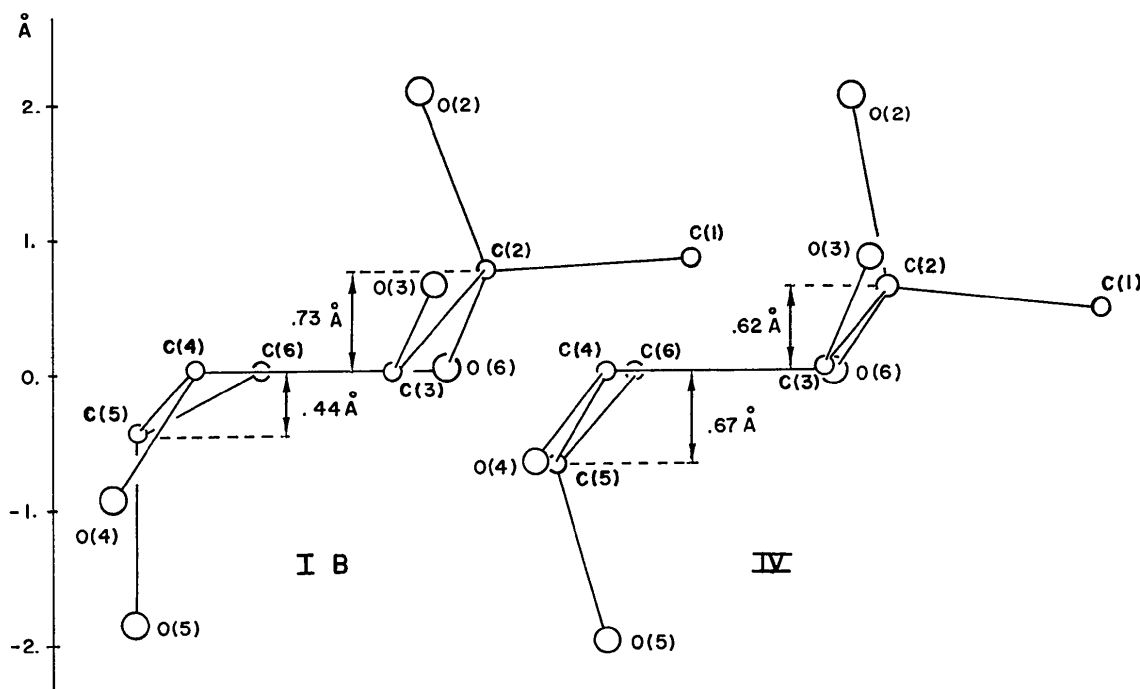
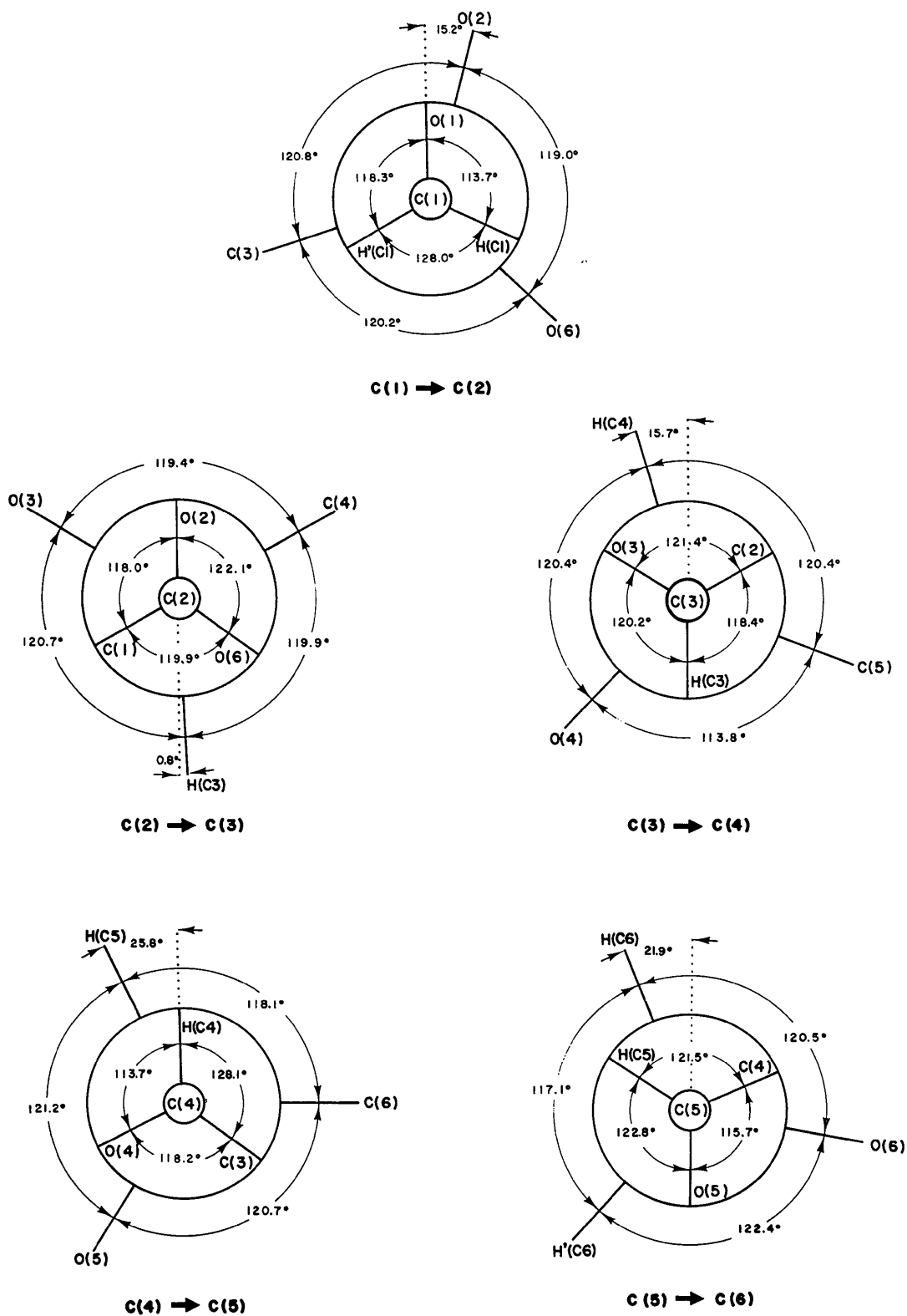


Fig. 2. Conformations of the pyranose rings. The number shows the deviation of the atom from the best least-squares plane passing through atoms C(3)-C(4)-C(6)-O(6) in  $\text{\AA}$ . The scale in the vertical direction is the same as that in the horizontal. 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose (IB), and  $\beta$ -D-fructopyranose (IV).

Fig. 3. Dihedral angles for 1,2:4,5-di-*O*-isopropylidene- $\beta$ -D-fructopyranose.

quite similar to the measured angles found by X-ray analysis. The p.m.r. spectra of the isopropylidene fructose derivatives (IB) and (II) have been measured at the Shionogi Research Laboratory (Maeda, Tori, Satoh & Tokuyama, 1969) as part of a series of conformational studies of diisopropylidene derivatives. Their measured value of the coupling constant  $J_{3,4}$  between H(C3) and H(C4) for (IB) is 7.8 Hz, which is consistent with the calculated value of 8.5 Hz derived

from the dihedral angles observed in the crystal structure using the equation  $J_{ik} = J_o \cos^2 \varphi_{ik} - 0.28$ , where  $J_o = 8.5$  for  $0^\circ \leq \varphi_{ik} \leq 90^\circ$ ,  $J_o = 9.5$  for  $90^\circ \leq \varphi_{ik} \leq 180^\circ$  and  $\varphi_{ik}$  is the dihedral angle between vicinal protons  $i$  and  $k$  (Karplus, 1959). The calculated value for  $J_{4,5}$  of 6.6 Hz compares well with the observed value of 5.0 Hz. The signals for  $J_{5,6}$  and  $J_{5,6'}$  were obscured, but the acetylated compound, which gave constants for  $J_{3,4}$  and  $J_{4,5}$  identical to those for (I), had constants  $\sim 1.8$

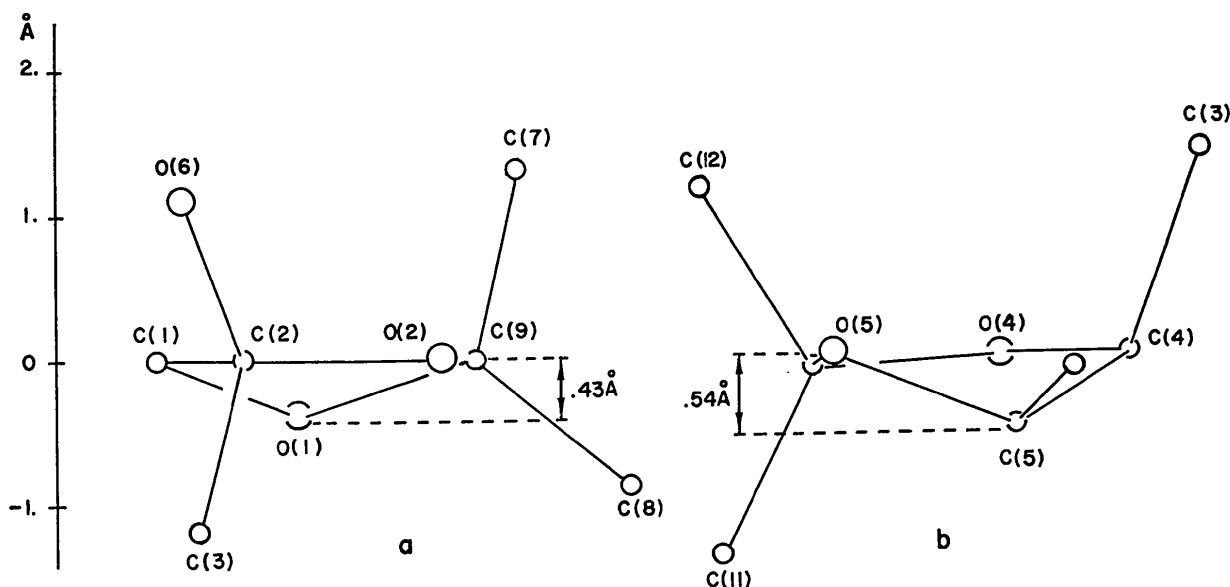


Fig. 4. Conformations of the five-membered rings. The number shows the deviations of the atom from the plane of the remaining four ring atoms. The scale in the vertical direction is the same as that in the horizontal. 1,2 isopropylidene group (a), and 4,5 isopropylidene group (b).

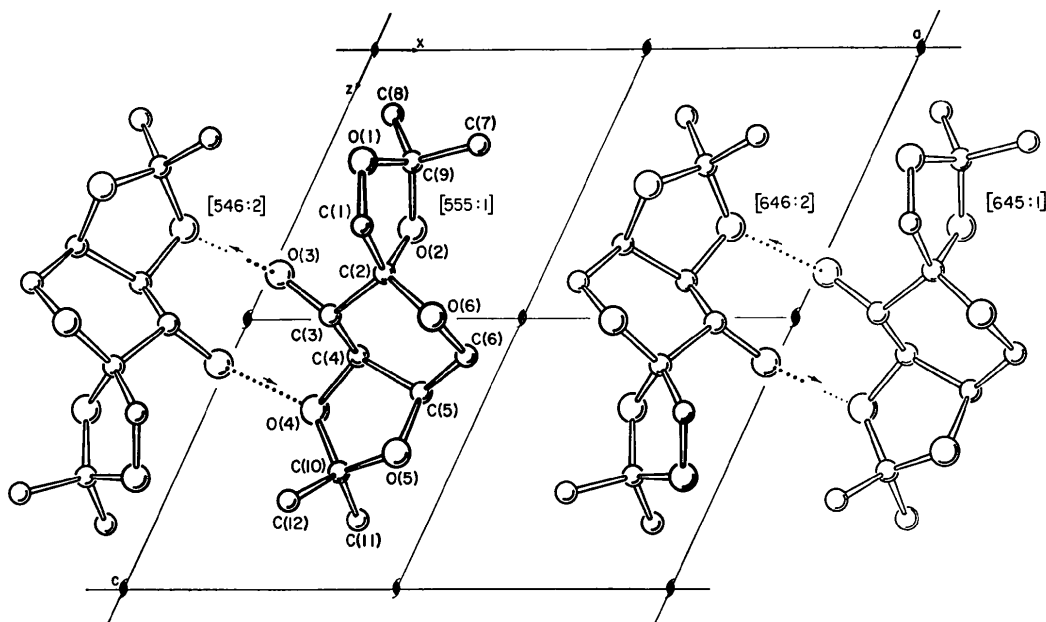


Fig. 5. Molecular packing and hydrogen bonding in 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose, [010] projection.

Hz for both  $J_{5,6}$  and  $J_{5,6'}$ , implying that the plane defined by H(C5)-C(5)-C(6) bisects the angles H(C6)-C(6)-H'(C6). As can be seen from Fig. 3, the dihedral angles of these hydrogen atoms in the crystal are appreciably different, and the derived constants are 5.3 and ~0 Hz respectively. This difference in dihedral angles could be related to a difference in conformation of the *cis*-fused dioxolane ring due to the bulky acyl group.

#### Conformations of the five-membered rings

Both the *spiro* and *cis*-fused five-membered rings in 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose have the envelope (*E*) conformation, as shown in Fig. 4. In the 1,2 isopropylidene ring, O(1) is out of the best least-squares plane by 0.43 Å, while in the 4,5 isopropylidene ring, C(5) is displaced from the best plane by 0.54 Å (see Table 3). Fused-dioxolane rings found in 1,2:3,4-di-*O*-isopropylidene-5-*O*-chloroacetyl-α-D-glucoseptanose (Jackobs & Sundaralingam, 1970) and in 1,2-*O*-aminoisopropylidene-α-D-glucopyranose hydroiodide (Trotter & Fawcett, 1966) also have envelope conformations. *Cis*-fused isopropylidene rings usually have the envelope conformation, but it is uncertain whether the different mode of puckering of a five-membered ring is a property of the isolated molecule or whether it is determined by the nature of its environment. For example, both dioxolane rings in ethyl 2,3:4,5-di-*O*-isopropylidene-1-thio-β-D-glucoseptanoside (Beale, Stephenson & Stevens, 1971) may be described as twist form.

#### Bond lengths and angles

The bond lengths and valency angles with their estimated standard deviations are given in Table 5.

Table 5. Bond distances and angles in 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose

The estimated standard deviations given in parentheses refer to the least significant figures of respective values.

#### (a) Bond lengths (Å)

C(1)—C(2)	1.528 (4)	C(1)—H(C1)	0.99 (3)
C(2)—C(3)	1.538 (4)	C(1)—H'(C1)	0.98 (3)
C(3)—C(4)	1.510 (4)	C(3)—H(C3)	0.99 (3)
C(4)—C(5)	1.526 (4)	C(4)—H(C4)	0.95 (3)
C(5)—C(6)	1.519 (4)	C(5)—H(C5)	0.96 (3)
C(7)—C(9)	1.534 (5)	C(6)—H(C6)	1.00 (3)
C(8)—C(9)	1.490 (5)	C(6)—H'(C6)	1.01 (3)
C(11)—C(10)	1.507 (6)	C(7)—H(C7)	1.06 (5)
C(12)—C(10)	1.512 (5)	C(7)—H'(C7)	0.97 (4)
		C(7)—H''(C7)	0.96 (5)
C(1)—O(1)	1.400 (4)	C(8)—H(C8)	0.99 (4)
C(9)—O(1)	1.428 (4)	C(8)—H'(C8)	0.88 (4)
C(2)—O(2)	1.413 (4)	C(8)—H''(C8)	1.05 (4)
C(9)—O(2)	1.434 (4)	C(11)—H(C11)	1.01 (4)
C(3)—O(3)	1.410 (4)	C(11)—H'(C11)	0.92 (4)
C(4)—O(4)	1.441 (4)	C(11)—H''(C11)	0.99 (4)
C(10)—O(4)	1.441 (4)	C(12)—H(C12)	0.95 (4)
C(5)—O(5)	1.423 (4)	C(12)—H'(C12)	1.00 (4)
C(10)—O(5)	1.433 (4)	C(12)—H''(C12)	1.03 (4)
C(2)—O(6)	1.426 (4)		
C(6)—O(6)	1.425 (4)		
O(3)—H(O3)	0.87 (3)		

Table 5 (cont.)

#### (b) Bond angles (°)

C(1)—C(2)—C(3)	115.4 (2)	H(C1)—C(1)—H'(C1)	117 (3)
C(2)—C(3)—C(4)	110.0 (2)	O(1)—C(1)—H(C1)	106 (2)
C(3)—C(4)—C(5)	112.6 (2)	O(1)—C(1)—H'(C1)	112 (2)
C(4)—C(5)—C(6)	115.5 (3)	C(2)—C(1)—H(C1)	111 (2)
C(7)—C(9)—C(8)	113.3 (3)	C(2)—C(1)—H'(C1)	106 (2)
C(11)—C(10)—C(12)	113.6 (3)	C(3)—O(3)—H(O3)	107 (2)
O(1)—C(1)—C(2)	105.0 (3)	C(2)—C(3)—H(C3)	108 (2)
C(1)—C(2)—O(2)	104.7 (2)	O(3)—C(3)—H(C3)	110 (2)
C(1)—C(2)—O(6)	107.3 (2)	C(4)—C(3)—H(C3)	110 (2)
C(3)—C(2)—O(2)	109.8 (2)	C(3)—C(4)—H(C4)	114 (2)
C(3)—C(2)—O(6)	107.8 (2)	O(4)—C(4)—H(C4)	107 (2)
C(2)—C(3)—O(3)	111.1 (2)	C(5)—C(4)—H(C4)	110 (2)
C(4)—C(3)—O(3)	107.8 (2)	C(4)—C(5)—H(C5)	110 (2)
C(3)—C(4)—O(4)	110.0 (2)	O(5)—C(5)—H(C5)	114 (2)
C(5)—C(4)—O(4)	102.7 (2)	C(6)—C(5)—H(C5)	104 (2)
C(4)—C(5)—O(5)	102.1 (2)	C(5)—C(6)—H(C6)	111 (2)
C(6)—C(5)—O(5)	111.1 (3)	C(5)—C(6)—H'(C6)	110 (2)
C(5)—C(6)—O(6)	114.1 (3)	O(6)—C(6)—H(C6)	108 (2)
C(7)—C(9)—O(1)	109.1 (3)	O(6)—C(6)—H'(C6)	107 (2)
C(7)—C(9)—O(2)	110.9 (3)	H(C6)—C(6)—H'(C6)	106 (3)
C(8)—C(9)—O(1)	108.5 (3)	C(9)—C(7)—H(C7)	104 (2)
C(8)—C(9)—O(2)	109.2 (3)	C(9)—C(7)—H'(C7)	111 (2)
C(11)—C(10)—O(4)	109.2 (3)	C(9)—C(7)—H''(C7)	110 (3)
C(11)—C(10)—O(5)	109.9 (3)	H(C7)—C(7)—H'(C7)	112 (4)
C(12)—C(10)—O(4)	109.7 (3)	H(C7)—C(7)—H''(C7)	114 (4)
C(12)—C(10)—O(5)	108.7 (3)	H'(C7)—C(7)—H''(C7)	107 (4)
C(1)—O(1)—C(9)	106.4 (3)	C(9)—C(8)—H(C8)	110 (2)
C(2)—O(2)—C(9)	108.6 (2)	C(9)—C(8)—H'(C8)	111 (3)
C(4)—O(4)—C(10)	109.1 (2)	C(9)—C(8)—H''(C8)	104 (2)
C(5)—O(5)—C(10)	107.0 (2)	H(C8)—C(8)—H'(C8)	113 (3)
C(2)—O(6)—C(6)	113.7 (2)	H(C8)—C(8)—H''(C8)	106 (3)
O(2)—C(2)—O(6)	111.8 (2)	H'(C8)—C(8)—H''(C8)	113 (3)
O(1)—C(9)—O(2)	105.4 (2)	C(10)—C(11)—H(C11)	112 (2)
O(4)—C(10)—O(5)	105.3 (2)	C(10)—C(11)—H'(C11)	112 (3)
		C(10)—C(11)—H''(C11)	104 (2)
		H(C11)—C(11)—H'(C11)	106 (3)
		H(C11)—C(11)—H''(C11)	109 (3)
		H'(C11)—C(11)—H''(C11)	113 (4)
		C(10)—C(12)—H(C12)	105 (2)
		C(10)—C(12)—H'(C12)	109 (2)
		C(10)—C(12)—H''(C12)	110 (2)
		H(C12)—C(12)—H'(C12)	110 (3)
		H(C12)—C(12)—H''(C12)	109 (3)
		H'(C12)—C(12)—H''(C12)	113 (3)

These have not been corrected for the effects of thermal motion. The formula used for calculation of e.s.d.'s was derived by Cruickshank & Robertson (1953). The spread and mean values are given in Table 6. They are in good agreement with those found in other sugars (Jeffrey & Rosenstein, 1964; Berman, Chu & Jeffrey, 1967) and with the preliminary results of β-D-fructopyranose (Rosenstein, 1968).

#### Hydrogen bonding and molecular packing

As shown in Fig. 5, the only free hydroxyl in the molecule O(3)H donates to oxygen atom O(4), one of the two ring oxygens in the 4,5-isopropylidene group. The distances and angles for the hydrogen bonding are shown below, with their e.s.d.'s for the last decimal place given in parentheses:

$$d_{ik} = 2.854 (4) \text{ \AA} \quad d_{ij} = 2.00 (4) \text{ \AA} \quad d_{jk} = 0.87 (3) \text{ \AA}$$

$$\angle kji = 169 (3)^\circ \quad \angle jki = 8 (2)^\circ \quad \angle jik = 3.5 (9)^\circ$$

where *i* is O(4) [*x*, *y*, *z*], *j* is H(O3) [ $\bar{x}$ ,  $-\frac{1}{2} + y$ ,  $1 - z$ ], and *k* is O(3) [ $\bar{x}$ ,  $-\frac{1}{2} + y$ ,  $1 - z$ ]. This hydrogen bonding



forms an infinite polar chain along the twofold screw axis, as shown by the projection down  $[\bar{2}01]$  in Fig. 6. The non-bonded distances between molecules, given in Table 7, are consistent with van der Waals contacts. The molecular packing is illustrated in Fig. 7 with van der Waals radii of 1.6 Å for C and 1.4 Å for O. The molecules fit together well by tilting in the direction of the pitch of the screw axis.

We thank Dr R. L. Tipson, of the National Bureau of Standards, for suggesting the problem and fur-

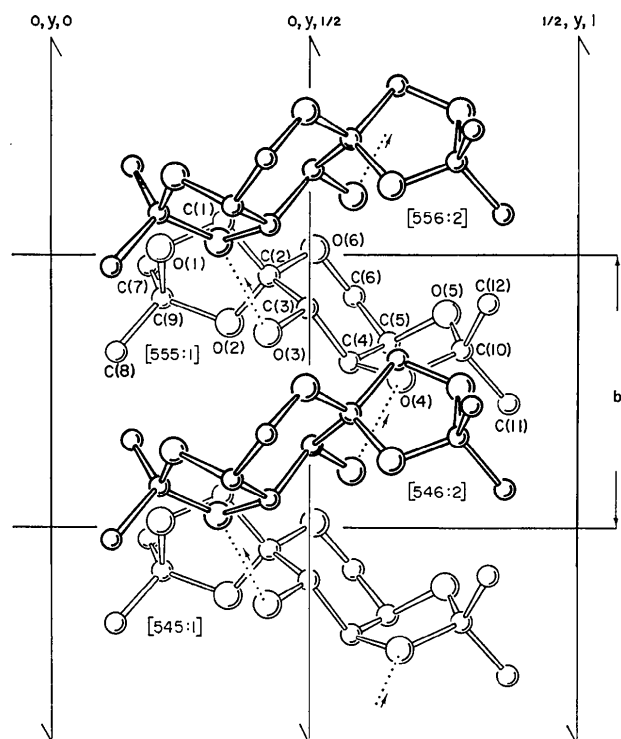


Fig. 6. Molecular packing and hydrogen bonding in 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose,  $[\bar{2}01]$  projection.

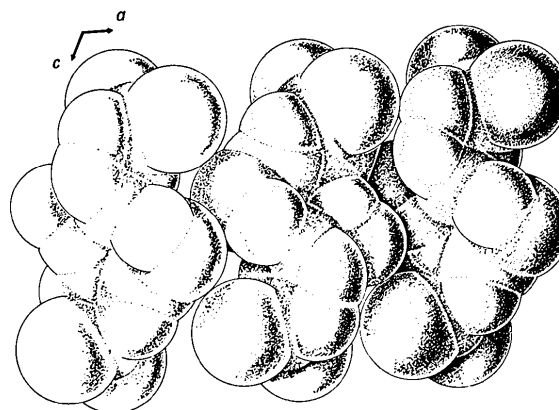


Fig. 7. Molecular packing in 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose,  $[010]$  projection.

Table 7. Non-bonded intermolecular distances less than 4.0 Å

All distances within 0.2 Å of the sum of the appropriate van der Waals radii (Pauling, 1960) are listed. The e.s.d.'s given in parentheses refer to the least significant figures in tabulated values.

C(7)—C(12)	$[x, y, -1 + z]$	3.945 (6) Å
C(7)—C(5)	$[1 - x, \frac{1}{2} + y, 1 - z]$	3.761 (5)
C(8)—C(8)	$[-x, \frac{1}{2} + y, -z]$	3.899 (5)
C(8)—O(1)	$[-x, -\frac{1}{2} + y, -z]$	3.601 (5)
C(11)—C(12)	$[x, -1 + y, z]$	3.855 (6)
C(12)—O(1)	$[-x, -\frac{1}{2} + y, 1 - z]$	3.558 (5)
O(6)—C(6)	$[1 - x, \frac{1}{2} + y, 1 - z]$	3.559 (4)
C(1)—C(4)	$[x, 1 + y, z]$	3.783 (4)
C(6)—C(6)	$[1 - x, \frac{1}{2} + y, 1 - z]$	3.908 (5)

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Table 6. Values of range and average of bond lengths and angles in 1,2:4,5-di-O-isopropylidene- $\beta$ -D-fructopyranose

The mean value and the standard deviation of the sample are calculated from

$$l = \frac{\sum_{i=1}^N l_i}{N} \left( \frac{1}{\sum_{i=1}^N \sigma_i^2} \right)^{1/2}, \quad \sigma_{\text{sample}} = \left( \frac{\sum_{i=1}^N (l_i - l)^2}{N - 1} \right)^{1/2}.$$

Bond lengths (Å)

	Range	Mean	C—C	C—O	C—O(H)
			1.490–1.538	1.400–1.441	1.410 (4)
			1.520 (15)	1.426 (13)	

Bond angles (°)

	C—C—C	C—C—O	C—C—OH	C—O—C	O—C—O
Range	110.0–115.5	102.1–114.1	107.8–111.1	106.4–113.7	105.3–111.8
Mean	113.1 (2.1)	107.7 (3.1)	109.4 (2.3)	109.3 (2.9)	107.5 (3.7)

Six-membered ring	
At carbon in ring	
Range	At oxygen in ring
Mean	113.7 (2)
	111.2 (3.2)

Five-membered ring	
Range	
Mean	
	106.4–109.1
	108.0 (1.3)

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## The Crystal Structure of 3-(*N*-Phenyl)aminopyrrolidine-2,5-dione

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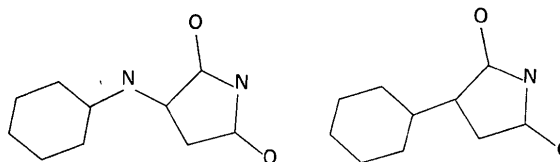
(Received 30 January 1973; accepted 2 February 1973)

The structure of 3-(*N*-phenyl)aminopyrrolidine-2,5-dione, C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>, has been determined from X-ray intensity data collected on a Stoe-Güttinger automatic off-line Weissenberg goniometer. The space group is *Pbca*, with *a* = 24.756, *b* = 7.453, *c* = 9.943 Å and *Z* = 8. The structure was solved by direct methods. The positional and vibrational parameters were refined by the method of least squares with anisotropic thermal parameters for the non-hydrogen atoms only. The final *R* was 0.049. The standard deviations of the bond lengths and angles were less than 0.003 Å and 0.2° respectively. Two molecules related by a centre of symmetry form a dimer through N–H...O bonds.

### Introduction

The synthesis of many succinimide compounds has recently been studied by Seres (1970). This work is part of a systematic programme to elucidate the crystal structure of these compounds. We present here the crystal and molecular structure of 3-(*N*-phenyl)aminopyrrolidine-2,5-dione [Fig. 1(a)] (hereafter PHA-PD).

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(a) PHA-PD. (b) PH-PD(O).