Short Communications

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Acta Cryst. (1960). **13**, 678

The crystal structure of β-D-glucose.

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(*Received* 8 *February* 1960)

Cellulose is a polymer of β-D-glucose in which glucose residues are linked 1 to 4. The author has undertaken a detailed examination of the crystal structure of β-D-glucose as a preliminary to a study of other more complex cellulose oligosaccharides. Sponsler & Dore (1931) studied the X-ray powder diagram of β-D-glucose but made no deductions regarding the size of the unit cell. McDonald & Beevers (1950, 1952) determined the crystal structure of α-D-glucose and showed that the pyranose ring possessed the Sachse *trans* configuration. It is to be expected, therefore, that β-D-glucose will also possess this form and this was confirmed by the present investigation.

The β-D-glucose was prepared by the method of Hudson & Dale (1917) and the crystals were grown from a solution of acetone and water at temperatures just above the ice point. Single crystals were orthorhombic with space group $P2_12_12_1$ and showed (101) and (10$\bar{1}$) as faces. The unit-cell dimensions are

$$a = 9{\cdot}29 \pm 0{\cdot}05,\ b = 12{\cdot}65 \pm 0{\cdot}03,\ c = 6{\cdot}70 \pm 0{\cdot}03\ \text{Å}\ .$$

On the assumption of 4 molecules in the unit cell, this gives a calculated density of 1·520 g.cm.$^{-3}$ compared with an observed density of 1·535 g.cm.$^{-3}$.

The intensities of the X-ray reflections were measured visually from Weissenberg photographs taken about each of the crystallographic axes using Cu $K\alpha$ radiation.

The structure was determined in the (001) projection from sign relationships using the method of Grant, Howells & Rogers (1957). This led to an interpretable electron-density map and the co-ordinates obtained were refined by successive Fourier syntheses. The positions of the atoms in this projection are shown in Fig. 1 and it can be seen that the pyranose ring possesses the Sachse *trans* configuration. Approximate z co-ordinates were obtained from a trial and error process using McDonald & Beevers bond lengths for α-D-glucose for the transfer from the (001) to the (100) projection. An initial Fourier synthesis was performed with the $0kl$ data and this showed resolution of all atoms except C_5, C_6 and O_6. This zone was then refined by successive Fourier syntheses. The $h0l$ structure factors were then calculated and a Fourier synthesis performed for this zone. This showed poor resolution but gave a good indication of the z co-ordinates of C_5 and C_6, particularly the latter. The only outstanding parameter is the z co-ordinate of the O_6 and this was determined at this stage by trial and error.

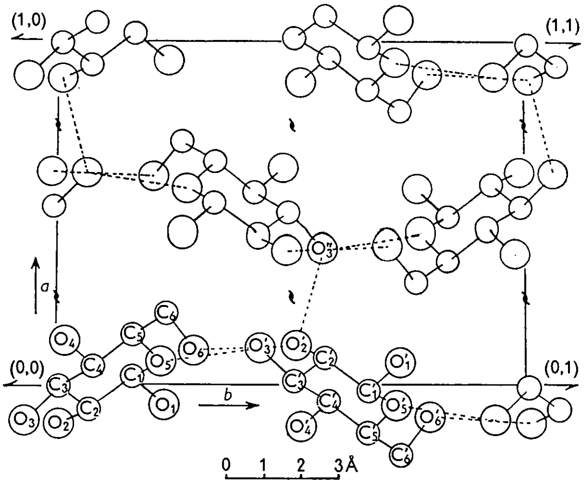

Fig. 1. The hydrogen bonding system in the (001) projection of β-D-glucose. Hydrogen bonds are shown as dashed lines.

The co-ordinates of the atoms are as follows:

	x (Å)	y (Å)	z (Å)
C_1	0·21	2·05	3·04
C_2	−0·72	0·87	2·62
C_3	−0·09	0·09	1·48
C_4	0·47	0·99	0·42
C_5	1·34	2·05	1·01
C_6	1·91	2·99	−0·06
O_1	−0·57	2·90	3·86
O_2	−1·05	0·06	3·77
O_3	−1·04	−0·82	0·93
O_4	1·15	0·24	−0·66
O_5	0·61	2·80	1·92
O_6	0·91	3·72	−0·67

These co-ordinates are not yet sufficiently accurate to enable much significance to be attached to the calculated bond lengths and angles but these appear to be very similar to the values found for α-D-glucose, except that, at this stage, there is no evidence of undue shortening of the C_1–O_1 and C_6–O_6 bonds such as was found for α-D-glucose.

Intermolecular oxygen separations were calculated and four pairs of atoms had values in the region 2·7 to 2·8 Å and therefore must correspond to hydrogen bonds. Three of these O_5–O_3', O_6–O_2' and O_2'–O_3'' are shown in the figure. The only other possible bonds are between the oxygen atoms of one molecule and the oxygen atoms of the identically oriented molecule shifted one cell length along c. Two possibilities are found. One of these, O_6–O_1 (not shown in the two-dimensional figure) corresponds to the fourth hydrogen bond. The other O_4–O_2 has a separation of 3·2 Å and is rather large for a hydrogen bond. This distance is similar to some of the oxygen–oxygen separations found by Beevers, McDonald, Robertson & Stern (1952) in sucrose. Infrared spectra confirm this long O–O distance (Mann & Marrinan, 1958). β-D-glucose crystals show a band at 3540 cm.$^{-1}$, which is to be compared with a band at 3570 cm.$^{-1}$ in sucrose and approximately 3620 cm.$^{-1}$ for unbonded OH groups in dilute solution in carbon tetrachloride. The observed frequency in β-D-glucose must be due to an OH group, which interacts only weakly with its environment and it is concluded that O_4 and its associated hydrogen constitute this group.

The above co-ordinates were used to compute structure factors and the value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was calculated for all three zones using a temperature factor of $\exp(-1\cdot5\sin^2\theta/\lambda^2)$. The values obtained were

$$R(hk0)=0\cdot21,\quad R(0kl)=0\cdot22,\quad R(h0l)=0\cdot26$$

for all observed reflections.

It is intended to carry out three-dimensional refinement and full details of the crystallographic analysis will be published when the work is complete.

This work originally formed part of a programme of fundamental research undertaken by the British Rayon Research Association and the author wishes to express his sincere appreciation of their continued support and interest.

References

Beevers, C. A., McDonald, T. R. R., Robertson, J. H. & Stern, F. (1952). *Acta Cryst.* **5**, 689.

Grant, D. F., Howells, R. G. & Rogers, D. (1957). *Acta Cryst.* **10**, 489.

Hudson, A. & Dale, D. (1917). *J. Amer. Chem. Soc.* **39**, 320.

McDonald, T. R. R. & Beevers, C. A. (1950). *Acta Cryst.* **3**, 394.

McDonald, T. R. R. & Beevers, C. A. (1952). *Acta Cryst.* **5**, 654.

Mann, J. & Marrinan, H. J. (1958). Private communication.

Sponsler, O. L. & Dore, W. H. (1931). *J. Amer. Chem. Soc.* **53**, 1639.

Acta Cryst. (1960). **13**, 679

A new form of boron silicide, B_4Si.

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(*Received* 26 *October* 1959)

There has been much interest in compound formation in the boron–silicon system since the original work of Moissan & Stock (1900). Two phases only have been reported, namely B_3Si and B_6Si. The latter is well established (Cline, 1959), and while our work on the boron silicides was in progress, structural data for orthorhombic B_6Si were reported (Cline, 1958; Adamsky, 1958). A cubic form of B_6Si has also been suggested (Zhuravlev, 1956). The reported tetragonal B_3Si (Samsonov & Latysheva, 1955) has been questioned (Gurevich, Epel'baum & Ormont, 1957).

The investigation of the silicon–boron system has been conducted in this laboratory for some time and samples for this investigation were obtained from E. Colton. Samples were made from mixtures of silicon and amorphous boron or from silicon melts at temperatures ranging from 1350 to 1850 °C. Excess silicon was removed by treatment with a mixture of nitric and hydrofluoric acids.

At least four different crystalline forms were found, two of which were identified, namely, B_6Si and a new form, B_4Si. The former has been obtained as powder and crystals, the data on which agree very well with earlier work (Cline, 1958; Adamsky, 1958; Cline, 1959).

Purification of samples for chemical analysis was difficult because $HF–HNO_3$ acid mixture slowly decomposes B_4Si. Furthermore, some negligible quantity of B_6Si is also always present in the sample. Because B_6Si is not attacked by the acid mixture, purification results in enrichment of B_6Si. Some amount of boron nitride appears also to be formed during purification. Samples for analysis contained, therefore, either some metallic silicon or, when silicon was completely removed, some B_6Si and BN. The boron to silicon ratio was therefore found to vary between 3·7 and 4·3. The following is a chemical analysis of such a sample.

Silicon	36·6%	Aluminum	0·3%
Boron	60·2	Iron	0·2
Magnesium	0·2	Calcium	0·2
Nitrogen	0·6	Moisture	0·3
Oxygen	0·5		

A more detailed report on the preparation and purification of B_4Si will appear later.

The specific gravity of B_4Si, measured by heavy liquids method is 2·47 g.cm.$^{-3}$.

Table 1. *Powder diffraction data for* B_4Si

(Cr $K\alpha$ radiation)

hkl	*d* (Å)	I/I_0
101	4·985	20
012	4·147	30
110	3·159	20
104	2·745	90
021	2·674	100
202	2·518	1
015	2·308	5
006	2·120	1
024	2·076	1
211	2·043	20
116	1·762	20
107	1·724	10
303	1·677	10
125	1·606	50
220	1·582	30
018	1·527	5
027	1·516	1
131	1·510	30
223	1·485	1
312	1·480	20
306	1·384	10
401	1·361	1
315	1·3059	2
119	1·2925	1
226	1·2689	1
321	1·2518	1
1,0,10	1·2410	2
232	1·2342	1
045	1·2070	3
410	1·1962	3
324	1·1700	5