Acta Cryst. (1971). B27, 220

The Crystal Structure of 1,6-Anhydro-β-D-glucopyranose

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(*Received* 14 *November* 1969)

The crystal structure of 1,6-anhydro-β-D-glucopyranose, $C_6H_{10}O_5$, levoglucosan, has been determined by the direct method using the tangent formula for phase determination. The structure was refined by anisotropic least-squares using Cu $K\alpha$ data to give a final R value of 0·035 for 687 reflections. The space group is $P2_12_12_1$, with $Z=4$ and unit-cell dimensions $a=6·684$ (2), $b=13·266$ (7), $c=7·547$ (2) Å. The molecule has a dicyclic structure, with an anhydro bridge across a pyranose ring forming a boat-shaped seven-membered ring. The three hydroxyl substituents are axial relative to the pyranose ring, two *exo*-axial at C(2) and (4) and one *endo*-axial at C(3). The pyranose ring has the 1C chair conformation which is distorted by the formation of the anhydride, so as to compress C(1) and C(5) and extend C(2) and C(4). The pyranose ring oxygen angle is less and the two *syn*-hydroxyl groups at C(2) and C(4) are further apart than in an unstrained pyranose ring system.

Introduction

1,6-Anhydro-β-D-glucopyranose, levoglucosan, $C_6H_{10}O_5$ is an internal glycoside with a dicyclic ring system, which is formed by the dry distillation of D-glucose. It is one of the more important anhydro sugars (Peat, 1946), since it is easily hydrolyzed to glucose by aqueous acid, and can therefore be used in the synthesis of glucose derivatives substituted in the positions 2, 3 or 4 and in the polymerization to dextrans (Carvalho, Prins & Schuerch, 1959).

The anhydride formation must take place through conversion of D-glucose to its less stable 1C conformation, as shown in Fig. 1. The anhydro molecule II*a* has three hydroxyls in the axial orientation, and it is not immediately obvious that this conformer will be preferred over that shown in II*b*, in which the pyranose ring is boat-shaped and the hydroxyl groups are equatorially oriented.

The structure was determined in order to establish the conformation in the crystalline state and to examine the strain effect of anhydride formation on the shape of the pyranose ring and the orientation of the three hydroxyl groups.

Experimental

Large, transparent crystals of 1,6-anhydro-β-D-glucopyranose were provided by the Chemical Institute of the Slovak Academy of Sciences, Bratislava, Czechoslovakia. The crystal data are as follows:

1,6-anhydro-β-D-glucopyranose, $C_6H_{10}O_5$,
M.W. 162·08, m.p. 184°C.

Space group $P2_12_12_1$, from systematic absences,
$h00$, $h=2n+1$; $0k0$, $k=2n+1$, $00l$, $l=2n+1$.

$a=6·684(2)$ Å
$b=13·266(7)$
$c=7·547(2)$
$Z=4$
$D_m=1·618$ g.cm³, $D_x=1·608$ g.cm³.
$\mu_{\mathrm{Cu}\,K\alpha}=12·45$ cm⁻¹.

The cell parameters and three-dimensional intensity data were measured on a Picker FACS I diffractometer using Cu $K\alpha$ radiation with a crystal of dimensions 0·3 × 0·3 × 0·25 mm mounted along the diagonal axis [101]. A 2θ scanning mode with varying interval was used up to $2\theta=130°$. Of the 687 recorded data,

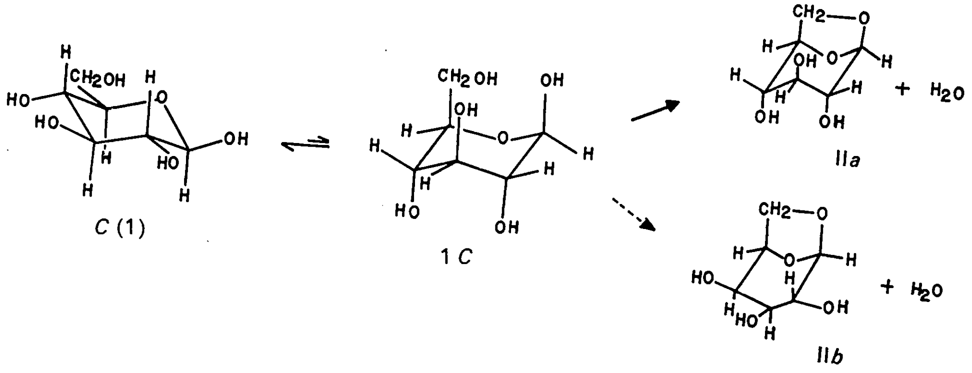


Fig. 1. Formation of 1,6-anhydro-β-D-glucopyranose from β-D-glucose.

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters in 1,6-anhydro-β-D-glucopyranose*

Key to the atomic numbering is given in Fig. 2. The temperature factor expression used was exp $\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}$.

The estimated standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·1984 (5)	0·0482 (2)	0·3060 (5)	0·0160 (6)	0·0024 (1)	0·0138 (6)	0·0009 (3)	−0·0001 (6)	0·0009 (3)
C(2)	0·2536 (4)	0·1311 (2)	0·1761 (4)	0·0101 (6)	0·0029 (1)	0·0104 (5)	0·0000 (2)	0·0009 (5)	−0·0003 (2)
C(3)	0·0717 (4)	0·1964 (2)	0·1275 (4)	0·0124 (6)	0·0025 (1)	0·0089 (4)	−0·0003 (3)	−0·0012 (5)	0·0005 (2)
C(4)	−0·0730 (4)	0·2105 (2)	0·2844 (4)	0·0100 (6)	0·0026 (1)	0·0120 (5)	−0·0000 (2)	−0·0006 (5)	0·0000 (2)
C(5)	−0·0834 (5)	0·1170 (2)	0·3995 (4)	0·0136 (7)	0·0029 (2)	0·0128 (5)	−0·0006 (3)	0·0036 (5)	0·0002 (2)
C(6)	−0·1427 (5)	0·0231 (2)	0·2947 (6)	0·0162 (8)	0·0028 (2)	0·0171 (7)	−0·0018 (3)	0·0032 (7)	−0·0001 (3)
O(1)	0·0472 (4)	−0·0153 (2)	0·2330 (3)	0·0191 (6)	0·0022 (1)	0·0182 (5)	−0·0004 (2)	0·0033 (5)	−0·0013 (2)
O(2)	0·4133 (3)	0·1900 (2)	0·2469 (3)	0·0121 (5)	0·0043 (1)	0·0102 (4)	−0·0015 (2)	−0·0001 (3)	0·0003 (2)
O(3)	−0·0278 (4)	0·1497 (2)	−0·0180 (3)	0·0192 (5)	0·0038 (1)	0·0109 (4)	−0·0010 (2)	−0·0049 (4)	0·0002 (2)
O(4)	−0·0055 (4)	0·2903 (1)	0·3966 (3)	0·0186 (5)	0·0023 (1)	0·0115 (4)	0·0005 (2)	0·0015 (4)	−0·0004 (2)
O(5)	0·1149 (3)	0·0903 (2)	0·4590 (3)	0·0172 (5)	0·0032 (1)	0·0103 (3)	0·0002 (2)	−0·0009 (4)	0·0014 (2)
H(1)	0·333	0·003	0·339						
H(2)	0·305	0·109	0·062						
H(3)	0·124	0·266	0·086						
H(4)	−0·201	0·220	0·225						
H(5)	−0·170	0·126	0·506						
H(6)	−0·192	−0·024	0·384						
H(6′)	−0·227	0·045	0·192						
H(O2)	0·407	0·205	0·369						
H(O3)	−0·061	0·200	−0·097						
H(O4)	−0·035	0·349	0·352						

643 reflections were observed above background. The data were reduced to structure amplitudes using an IBM 1130 program (Shiono, 1969). No absorption corrections were applied. The crystal density was measured by the flotation method in a mixture of carbon tetrachloride and bromoform at 23° C.

Determination and refinement of the structure

The structure was solved by the application of the tangent formula (Karle & Hauptman, 1956) using an IBM 7090 version of the Hall (1968) direct phasing methods. Four reflections were selected as starting phases, three to define the origin (3,11,0; 5,8,0; 0,2,1) and one to define the enantiomorph (0,15,2) with E's of 2·90, 2·25, 1·82 and 1·94 respectively. The tangent formula refinement was then applied to 148 reflections with E value > 1·40. The eleven highest peaks on the resulting E map corresponded to the eleven oxygen and carbon atoms of the molecule. The first trial structure gave an R value of 0·30 for all reflections. Refinement was by several cycles of isotropic and of anisotropic structure factor calculations using the block-diagonal least-squares program for IBM 1130 (Shiono, 1968) and the full-matrix least-squares program for IBM 7090 (Shiono, 1966). The function minimized was $\omega_i(K|F_o|-|F_c|)^2$ where $\omega_i=|F_o|^{-2}$ for $|F_o|\geq 4|F_{\min}|$ and $\omega_i=4|F_{\min}|^{-2}$ for $|F_o|<4\,|F_{\min}|$, with $|F_{\min}|=8{\cdot}4$. The final cycle gave an R value of 0·035 and an average Δ/σ of 0·7. All the hydrogen atoms were clearly located on a difference synthesis at an R value of 0·090. Their coordinates were not refined and they were assigned the thermal parameters of the atoms to which they are attached. Atomic parameters are given in Table 1. The observed and calculated structure factors are

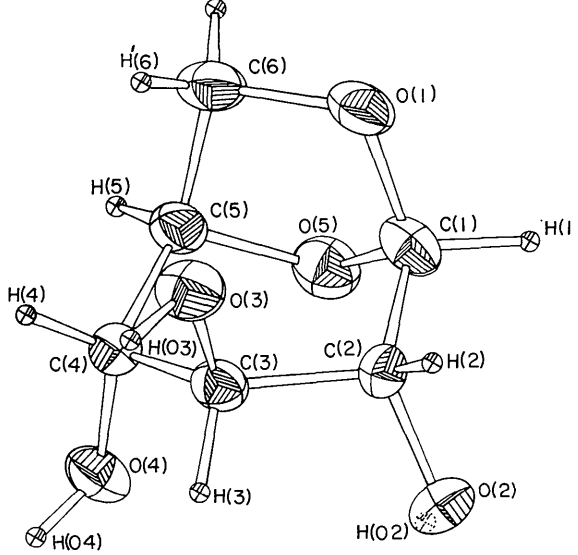


Fig. 2. Molecular conformation and atomic numbering of 1,6-anhydro-β-D-glucopyranose. *ORTEP* plot of thermal ellipsoids.

Table 2. *Observed and calculated structure factors*

Columns are: Index, $10|F_{\mathrm{obs}}|$, $10|F_{\mathrm{calc}}|$, $10A_{\mathrm{calc}}$, $10B_{\mathrm{calc}}$.

* Indicates unobserved reflections.

H= 0 K= 0				
2	430	452	452-	0
4	250	250	250	0
6	92	95	95-	0
8	65	63	63	0
H= 0 K= 1				
1	96	97	0	97-
2	220	223	0	223-
3	95	103	0	103
4	110	118	0	118-
5	110	114	0	114
6	140	141	0	141-
8	18	19	0	19-
7	127	127	0	127
H= 0 K= 2				
0	146	149	149-	0
1	695	739	739-	0
2	184	190	190-	0
3	93	92	92	0
4	166	174	174-	0
5	44	41	41-	0
6	72	73	73	0
8	110	106	106-	0
7	16	15	15-	0
H= 0 K= 3				
1	207	213	0	213-
2	294	300	0	300-
3	53	53	0	53-
4	164	158	0	158
5	16	14	0	14-
6	102	103	0	103
8	16	14	0	14
7	22	20	0	20
H= 0 K= 4				
0	77	68	68	0
1	148	141	141	0
2	632	637	637-	0
3	437	428	428-	0
4	18	17	17	0
5	6*	5	5	0
6	131	133	133-	0
8	21	20	20	0
7	128	132	132-	0
H= 0 K= 5				
1	351	361	0	361-
2	308	303	0	303
3	60	63	0	63
4	264	264	0	264
5	225	226	0	226-
6	87	90	0	90-
8	5*	5	0	5-
7	27	26	0	26
H= 0 K= 6				
0	328	326	326	0
1	150	154	154-	0
2	313	300	300-	0
3	341	328	328	0
4	144	146	146	0
5	51	54	54-	0
6	8*	6	6-	0
8	74	77	77	0
7	37	37	37-	0
H= 0 K= 7				
1	163	165	0	165
2	77	71	0	71-
3	197	198	0	198
4	164	162	0	162-
5	121	124	0	124-
6	150	153	0	153
7	64	65	0	65
H= 0 K= 8				
0	34	33	33-	0
1	68	67	67	0
2	75	66	66	0
3	6*	9	9-	0
4	20	18	18	0
5	160	153	153	0
6	61	58	58	0
7	28	28	28	0
H= 0 K= 9				
1	170	171	0	171
2	58	57	0	57
3	138	147	0	147
4	40	42	0	42-
5	29	29	0	29
6	6*	5	0	5
7	19	14	0	14
H= 0 K= 10				
0	267	268	268	0
1	6*	1	1	0
2	81	88	88-	0
3	30	24	24	0
4	37	39	39-	0
5	88	92	92	0
6	146	139	139-	0
H= 0 K= 11				
1	134	142	0	142-
2	6*	2	0	2
3	6*	7	0	7
4	69	70	0	70-
5	38	37	0	37-
6	5*	5	0	5
H= 0 K= 12				
0	196	203	203-	0
1	46	45	45-	0
2	116	120	120	0
3	89	84	84-	0
4	101	105	105	0
5	43	38	38-	0
H= 0 K= 13				
1	29	29	0	29-
2	6*	14	0	14-
3	25	29	0	29-
4	47	50	0	50-
H= 0 K= 14				
0	72	72	72	0
1	147	151	151	0
2	20	24	24	0
3	67	69	69-	0
H= 0 K= 15				
1	20	19	0	19-
2	102	100	0	100
H= 1 K= 0				
1	698	801	0	801
2	238	238	238-	0
3	231	229	0	229
4	126	130	130	0
5	35	29	0	29-
6	49	48	48	0
8	44	45	45	0
7	70	72	0	72-
H= 1 K= 1				
0	335	344	0	344
1	243	247	50-	242-
2	358	363	352	89-
3	32	31	22	22-
4	136	133	121	56
5	21	22	6	21-
6	111	115	111	29
8	57	57	46-	34-
7	71	68	58	36-
H= 1 K= 2				
0	489	505	0	505
1	221	224	5	223
2	465	463	142	440
3	434	432	211	377-
4	59	58	5-	58
5	205	208	31	206
6	107	108	20	106
8	14	15	12	8-
7	45	45	3-	45
H= 1 K= 3				
0	155	153	0	153-
1	373	381	364-	110-
2	185	179	132	121
3	64	64	60-	20-
4	95	84	79	29
5	55	52	46	24-
6	56	56	55	10-
8	59	58	58	3-
7	148	149	97-	113-
H= 1 K= 4				
0	190	189	0	189
1	388	384	153	352
2	86	87	79	36-
3	202	205	80-	188-
4	74	69	65-	21-
5	84	84	55	63
6	113	113	44-	104-
8	23	22	10	20-
7	26	26	23-	11-
H= 1 K= 5				
0	83	78	0	78-
1	456	454	442	103
2	91	94	40	85-
3	113	106	24-	103-
4	102	101	92-	42-
5	179	177	177-	3-
6	71	73	16	72-
8	90	89	42-	78
7	35	33	33	3
H= 1 K= 6				
0	342	329	0	329-
1	102	78	70	35
2	188	190	113-	152-
3	189	181	115-	140-
4	48	51	13	49-
5	95	103	11	103-
6	123	125	71-	103
8	63	61	17-	58-
7	48	49	7-	49-
H= 1 K= 7				
0	92	93	0	93-
1	48	46	40	22-
2	123	115	50-	103-
3	150	152	152	6
4	117	117	116-	15-
5	227	230	228	26
6	68	67	63	21
7	70	68	30-	61
H= 1 K= 8				
0	5*	8	0	8-
1	110	113	35-	108
2	173	170	113-	127
3	172	174	45-	168-
4	74	83	69	47-
5	98	93	4-	93
6	62	63	51-	37
7	49	47	3	47-
H= 1 K= 9				
0	47	45	0	45-
1	90	90	59-	69
2	75	72	14	71
3	88	85	85-	6
4	74	66	66-	10
5	98	95	48-	82
6	26	26	14-	22
7	46	43	8-	42-
H= 1 K= 10				
0	30	25	0	25-
1	169	164	83-	141
2	76	77	49-	60-
3	133	146	50	137
4	72	73	70	21
5	50	51	44-	26
6	6*	10	6	8
H= 1 K= 11				
0	42	38	0	38
1	89	92	73-	56
2	113	115	95	64
3	113	113	110-	26-
4	55	55	29-	46
5	30	26	1-	26
6	65	60	21	56-
H= 1 K= 12				
0	60	58	0	58-
1	100	95	20-	93-
2	94	93	65	66
3	72	73	40	61-
4	137	138	17	137-
5	39	43	2-	43
H= 1 K= 13				
0	34	34	0	34-
1	81	85	33	78
2	55	55	33-	44
3	56	56	21	51-
4	22	21	14-	16-
H= 1 K= 14				
0	6*	9	0	9-
1	82	82	57	59
2	68	68	13-	67
3	32	29	16	24-
H= 1 K= 15				
0	43	45	0	45
1	103	106	65	84
2	72	73	58	44-
H= 2 K= 0				
0	640	707	707	0
1	4*	5	0	5-
2	146	144	144	0
3	361	362	0	362-
4	93	90	90	0
5	79	86	0	86-
6	149	154	154-	0
8	135	138	138.	0
7	23	25	0	25-
H= 2 K= 1				
0	309	326	326	0
1	83	84	53	65-
2	293	287	285-	31
3	239	242	75-	230
4	201	196	168	100-
5	115	110	64-	90
6	75	79	79-	5-
8	66	65	37	54-
7	93	98	66-	72
H= 2 K= 2				
0	458	466	466-	0
1	210	201	156	126-
2	77	76	30-	70-
3	51	50	50	5
4	124	121	107	56
5	40	46	25-	38
6	99	100	10	100
8	58	57	23-	52
7	96	96	95	13-
H= 2 K= 3				
0	151	167	167-	0
1	242	237	228-	61
2	81	71	8	71
3	232	227	226	15
4	211	200	159-	122-
5	132	129	128-	18
6	176	168	3	168
8	42	41	36	19
7	76	74	68	28-
H= 2 K= 4				
0	136	142	142	0
1	271	266	213	160
2	316	326	275-	175
3	303	294	294-	19
4	58	62	53-	33
5	130	135	21	133
6	62	62	38-	49
8	27	27	14-	23
7	28	25	13-	22-
H= 2 K= 5				
0	134	134	134-	0
1	201	195	150	125-
2	372	329	139-	298
3	257	251	151-	200-
4	26	28	8-	27
5	145	162	162	5
6	48	50	12-	48-
8	26	26	1-	26-
7	74	72	67	28-
H= 2 K= 6				
0	241	241	241	0
1	137	131	40	125
2	64	55	49-	26-
3	84	82	79	21-
4	139	131	123	45
5	42	41	17	38
6	34	30	4-	30-
7	77	76	70-	29-
H= 2 K= 7				
0	181	177	177	0
1	127	114	35-	108
2	208	209	86-	190-
3	190	192	187	44-
4	212	216	208	60-
5	63	64	55-	33
6	57	56	28-	48
7	37	38	37	5
H= 2 K= 8				
0	74	66	66-	0
1	155	156	149	46
2	29	30	30	3
3	126	126	124-	24-
4	115	110	72	83-
5	55	57	55	16
6	51	53	3-	53-
7	78	75	56	49-
H= 2 K= 9				
0	146	150	150	0
1	96	96	64	72
2	114	114	114	3
3	104	101	13	100
4	75	78	24-	74
5	30	30	27-	13
6	46	46	32	32-
H= 2 K= 10				
0	225	221	221	0
1	150	150	146	35
2	176	178	163-	71-
3	120	121	41-	114-
4	63	64	64-	3-
5	24	23	14	17
6	73	70	53-	46-
H= 2 K= 11				
0	172	162	162	0
1	131	121	1-	121-
2	134	137	134-	27
3	82	83	81-	16
4	63	63	57	28-
5	23	25	18-	16-
H= 2 K= 12				
0	6*	7	7-	0
1	101	101	32-	95-
2	76	75	48-	58-
3	66	63	62-	13-
4	80	81	74	35
5	78	27	19	19
H= 2 K= 13				
0	6*	6	6	0
1	53	54	46-	29
2	88	89	86-	22-
3	48	48	10	47-
4	5*	6	4-	4-
H= 2 K= 14				
0	87	88	[illegible]	0
1	28	26	24	10-
2	51	50	3	48
3	29	29	3-	18-
H= 2 K= 15				
0	40	41	41	0
H= 3 K= 0				
1	34	35	0	35
2	210	211	211-	0
3	23	26	0	26
4	107	104	104	0
5	58	61	0	61-
6	32	29	29	0
8	113	109	109	0
7	135	138	0	138-
H= 3 K= 1				
0	38	32	0	32
1	290	292	291	16-
2	133	126	124	21-
3	38	41	39-	15-
4	135	135	75	112
5	136	146	117	87-
6	89	85	21-	82-
8	49	52	23-	47
7	59	58	38-	44
H= 3 K= 2				
0	101	98	0	98-
1	198	204	110	172-
2	120	119	79	89
3	183	178	152	93-
4	94	90	68	59
5	113	116	112	31
6	44	46	20-	41
8	25	25	7	24
7	35	38	37	8
H= 3 K= 3				
0	75	74	0	74
1	295	283	199-	201
2	192	186	177-	53
3	162	153	147-	42-
4	50	40	13-	38
5	115	114	84	77-
6	53	53	33-	41
8	47	46	24	38-
7	98	98	75-	63-
H= 3 K= 4				
0	196	198	0	198-
1	92	85	57	63
2	133	120	108-	53
3	78	81	7-	81
4	200	199	130	152-
5	64	68	12-	67
6	116	116	102-	55-
7	19	20	18-	9-
H= 3 K= 5				
0	235	229	0	229
1	93	94	53	78
2	206	202	43-	197-
3	203	163	128-	132-
4	72	67	22	63-
5	74	73	44-	58
6	108	108	82-	70-
7	35	33	21-	26-
H= 3 K= 6				
0	259	270	0	270-
1	116	112	100-	52
2	73	71	60-	38
3	105	113	112	15-
4	37	38	36-	9-
5	157	149	148-	12
6	60	57	55-	13
7	6*	6	2-	6-
H= 3 K= 7				
0	164	166	0	166-
1	73	73	31-	66-
2	125	122	1-	122-
3	76	66	54	38-
4	111	99	85	51
5	126	123	16	39
6	42	40	10-	39-
7	79	74	6	73
H= 3 K= 8				
0	48	49	0	49
1	27	21	3	21
2	229	234	53	228
3	78	81	50-	63-
4	102	100	93-	35-
5	17	19	15	11
6	5*	4	1-	4
H= 3 K= 9				
0	22	22	0	22-
1	220	224	29	223
2	54	55	30-	46
3	21	23	15-	17-
4	74	76	62	44
5	65	66	58-	32
6	44	42	23	35
H= 3 K= 10				
0	92	94	0	94-
1	120	126	40-	119
2	105	100	69-	72
3	38	37	36-	8
4	58	56	56	4-
5	20	17	17	4
H= 3 K= 11				
0	242	238	0	238
1	85	88	26-	84
2	65	67	33	58-
3	34	33	21	26-
4	56	57	20	53
5	43	41	13-	39
H= 3 K= 12				
0	87	87	0	87-
1	49	49	48-	5-
2	68	68	68	1
3	93	90	34	83-
4	81	78	32	71-
H= 3 K= 13				
0	6*	0	0	0
1	45	45	20	40-
2	49	48	47-	12
3	59	59	58	11-
H= 3 K= 14				
0	28	29	0	29-
1	102	101	78	65
H= 4 K= 0				
0	6*	10	10	0
1	59	60	0	60
2	28	36	36	0
3	263	247	0	247-
4	76	79	79-	0
5	35	35	0	35-
6	66	65	65	0
7	52	52	0	52-
H= 4 K= 1				
0	227	236	236	0
1	92	88	38-	79
2	195	196	110-	163
3	62	64	21	60
4	140	144	141	32-
5	134	127	31-	123
6	69	70	51-	49
7	6*	9	3-	9
H= 4 K= 2				
0	83	92	92-	0
1	110	106	101	32-
2	194	192	139-	133-
3	115	125	117	45
4	66	64	64	9
5	133	134	127	42
6	20	18	14-	11
7	32	32	29-	13-
H= 4 K= 3				
0	32	30	30	0
1	311	305	182-	245
2	79	80	32	73-
3	189	190	190	11
4	76	79	79-	8-
5	119	127	125-	20-
6	59	61	17	59
7	64	65	65	1-
H= 4 K= 4				
0	36	23	23-	0
1	104	103	92-	46
2	97	92	76	52
3	23	17	1	17
4	46	45	45-	6
5	96	97	3	97
6	79	81	81-	1
7	66	67	67	6
H= 4 K= 5				
0	6*	4	4-	0
1	107	104	34-	99-
2	116	115	114-	17
3	97	110	110-	5
4	49	53	22-	48-
5	76	74	71	18-
6	16	19	0	19-
7	46	43	36	24-
H= 4 K= 6				
0	108	104	104	0
1	178	181	179	28-
2	136	138	133	40-
3	54	57	50-	27-
4	67	87	36	79
5	30	31	21-	22-
6	31	29	25	14-
H= 4 K= 7				
0	111	102	102	0
1	151	153	128-	83-
2	104	104	99-	30-
3	161	160	160	8
4	195	198	141	139-
5	74	75	73-	18
6	5*	7	5-	5-
H= 4 K= 8				
0	66	65	65	0
1	44	48	43-	19-
2	65	60	50-	34
3	99	95	88-	37
4	72	71	60	38-
5	29	28	4-	28-
6	22	18	18	2-
H= 4 K= 9				
0	58	59	59	0
1	70	72	45-	56
2	138	138	72	118
3	90	95	57	76-
4	41	40	40-	1
5	5*	7	0	7
H= 4 K= 10				
0	107	113	113-	0
1	70	71	28	65
2	27	26	13-	22-
3	6*	11	0	11-
4	74	74	73-	13-
5	19	14	0	14-
H= 4 K= 11				
0	55	53	53	0
1	54	57	46-	34-
2	79	79	76-	22-
3	46	45	10-	44-
4	61	59	36	46
H= 4 K= 12				
0	66	65	65-	0
1	118	116	92	71-
2	35	35	30-	17-
3	61	61	40-	46
H= 4 K= 13				
0	29	28	28-	0
1	64	63	48-	41
H= 5 K= 0				
1	59	56	0	56
2	163	167	167-	0
3	133	129	0	129-
4	6*	14	14	0
5	6*	12	0	12-
6	22	23	23-	0
H= 5 K= 1				
0	104	104	0	104
1	118	117	110	38-
2	207	205	65	195-
3	59	61	61	6
4	29	32	25	20
5	40	43	14-	41
6	50	50	50-	7-
H= 5 K= 2				
0	71	71	0	71-
1	45	41	36-	20-
2	114	107	65	85-
3	97	103	96	37-
4	121	116	45-	109
5	53	52	27	47-
6	21	22	1-	22
H= 5 K= 3				
0	87	86	0	86
1	108	99	98-	18-
2	91	87	87-	2-
3	60	59	12-	58
4	164	168	116-	122
5	31	30	9-	29
6	56	58	54	22-
H= 5 K= 4				
0	6*	6	0	6
1	72	71	20-	68
2	62	72	61	38-
3	155	143	106-	96
4	114	116	3	116-
5	43	43	18	38
6	31	33	26	19
H= 5 K= 5				
0	133	146	0	146
1	83	88	42-	77
2	34	35	28	21-
3	64	62	58-	23-
4	37	38	36-	9
5	31	32	29	13
6	57	58	25-	53-
H= 5 K= 6				
0	6*	5	0	5
1	30	31	8	30
2	69	67	10-	66-
3	48	49	49-	7-
4	57	57	23	52
5	52	51	8	51
H= 5 K= 7				
0	70	72	0	72
1	29	30	13-	27-
2	149	154	90	126-
3	47	45	5-	45-
4	51	52	25	45
5	29	29	22	19-
H= 5 K= 8				
0	173	176	0	176
1	130	121	80	90-
2	54	51	12-	50
3	19	20	4	20
4	16	16	16	2
5	65	63	56	29-
H= 5 K= 9				
0	24	26	0	26
1	72	71	71	10-
2	23	23	22-	7-
3	61	62	62-	0
4	5*	10	4-	9
H= 5 K= 10				
0	66	65	0	65-
1	28	27	4-	27-
2	66	65	48-	43
3	17	14	14	2-
H= 5 K= 11				
0	20	19	0	19
1	6*	14	4	13
2	28	25	7	24-
H= 5 K= 12				
0	53	52	0	52-
H= 6 K= 0				
0	159	161	161-	0
1	6*	8	0	8
2	118	118	118	0
3	6*	10	0	10
4	21	20	20-	0
5	53	53	0	53-
H= 6 K= 1				
0	73	71	71	0
1	110	104	101-	23-
2	57	57	56	12-
3	103	106	82	68
4	80	83	50	65
5	43	40	11	39
H= 6 K= 2				
0	85	89	89	0
1	157	159	159	4
2	121	123	123-	9-
3	88	86	43	75
4	86	82	50	65-
5	20	21	18	12-
H= 6 K= 3				
0	29	33	33	0
1	106	107	81-	70
2	76	73	72	13-
3	94	94	84	43
4	29	29	28	8-
5	100	99	29-	94-
H= 6 K= 4				
0	79	81	81	0
1	173	174	174-	7
2	38	33	6-	33
3	47	46	46	3
4	93	92	62-	67-
5	28	26	25-	7
H= 6 K= 5				
0	48	51	51-	0
1	87	89	85-	26-
2	6*	10	7-	7-
3	26	25	7-	25-
4	44	43	23-	36-
H= 6 K= 6				
0	7*	10	10-	0
1	68	68	30	60-
2	63	62	58	22
3	58	58	16-	56-
4	6*	12	0	12-
H= 6 K= 7				
0	57	55	55-	0
1	60	63	29-	56-
2	52	53	3-	53-
3	30	31	19	25
4	21	22	9	20
H= 6 K= 8				
0	6*	11	11	0
1	100	97	95-	29-
2	57	55	28-	47
3	5*	7	3	6-
H= 6 K= 9				
0	5*	3	3-	0
1	24	23	1-	23
2	58	58	6-	58
H= 6 K= 10				
0	92	91	91-	0
H= 7 K= 0				
1	27	28	0	28-
2	22	24	24	0
3	18	16	0	16-
4	68	68	68-	0
H= 7 K= 1				
0	21	22	0	22-
1	54	54	17	52
2	65	64	31	56-
3	27	25	7-	24-
4	53	49	44	22-
H= 7 K= 2				
0	32	32	0	32-
1	35	36	36	2
2	6*	7	3	7-
3	49	51	51-	2-
H= 7 K= 3				
0	113	115	0	115
1	30	29	29-	1-
2	66	63	46-	42-
3	18	14	12	7
H= 7 K= 4				
0	57	56	0	56
1	42	42	42-	5-
2	37	34	32-	10
3	64	64	36-	53
H= 7 K= 5				
0	48	48	0	48
1	23	24	10-	22-
2	6*	12	8	9
H= 7 K= 6				
0	59	57	0	57-
1	35	31	18-	25
2	5*	10	10	3-
H= 7 K= 7				
0	5*	3	0	3-

Table 3. *Least-squares planes in* 1,6-*anhydro-β-*D-*glucopyranose*

Equation for plane: $Ax+By+Cz=D$, where x,y,z are in Å.

	Atoms in plane		Distance from best plane	Constants	
Pyranose ring	C(1)		0·001	A	0·501
	C(2)		−0·001	B	0·477
	C(4)		0·001	C	0·722
	C(5)		−0·001	D	2·638
		C(3)	−0·460		
		O(5)	0·820		
Anhydride ring	C(1)		0·012	A	0·049
	C(5)		−0·011	B	−0·563
	C(6)		0·017	C	0·825
	O(1)		−0·018	D	1·599
		O(5)	0·623		
	C(2)		0·019	A	0·019
	O(2)		−0·015	B	−0·610
	C(4)		−0·018	C	0·792
	O(4)		0·014	D	0·005

Table 4. *Values of A, B, B′ and μ used in the energy function*

Energies are expressed in kcal.mole^{-1}.

	A	$B\,(\times 10^{-4})$	$B'\,(\times 10^{-4})$	μ
$\mathrm{H\cdots H}$	49	0·4682	1·0000	4·60
$\mathrm{H\cdots O_h}$*	93	1·4365	0·7978	4·12
$\mathrm{H\cdots O_r}$*	100	1·5446	0·8478	4·12
$\mathrm{H\cdots C}$	125	3·0118	1·2900	4·12
$\mathrm{O_h\cdots O_h}$	201	4·8430	0·6364	3·63
$\mathrm{O_h\cdots O_r}$	214	5·1562	0·6763	3·63
$\mathrm{O_h\cdots C}$	250	9·1125	1·0278	3·63
$\mathrm{O_r\cdots O_r}$	227	5·4695	0·7187	3·63
$\mathrm{O_r\cdots C}$	266	9·6957	1·0923	3·63
$\mathrm{C\cdots C}$	325	17·4483	1·6600	3·63

* $\mathrm{O_h}$ and $\mathrm{O_r}$ represent hydroxyl and ring oxygen, respectively.

Table 5. *Bond lengths and angles in* 1,6-*anhydro-β-*D-*glucopyranose*

The estimated standard deviations given in parentheses refer to the last decimal positions at respective values.

i	j	$D(ij)$
C(1)	C(2)	1·518 (4) Å
C(2)	C(3)	1·537 (4)
C(3)	C(4)	1·540 (4)
C(4)	C(5)	1·516 (5)
C(5)	C(6)	1·527 (5)
C(2)	O(2)	1·426 (3)
C(3)	O(3)	1·425 (4)
C(4)	O(4)	1·429 (4)
C(1)	O(1)	1·427 (4)
C(6)	O(1)	1·444 (4)
C(1)	O(5)	1·399 (4)
C(5)	O(5)	1·443 (4)
Mean value		
C–C		1·528 (11)
C–O(H)		1·427 (2)
C–O		1·428 (21)

i	j	k	$\angle(ijk)$
C(1)	C(2)	C(3)	111·7 (2)°
C(2)	C(3)	C(4)	112·4 (2)
C(3)	C(4)	C(5)	111·7 (2)
C(4)	C(5)	C(6)	112·5 (3)
C(4)	C(5)	O(5)	109·6 (3)
C(5)	O(5)	C(1)	102·0 (2)
O(5)	C(1)	C(2)	110·0 (2)
O(1)	C(1)	C(2)	110·5 (2)
C(5)	C(6)	O(1)	103·1 (3)
C(6)	O(1)	C(1)	106·8 (2)
O(1)	C(1)	O(5)	105·8 (2)
O(5)	C(5)	C(6)	101·5 (3)
C(1)	C(2)	O(2)	109·6 (2)
O(2)	C(2)	C(3)	111·9 (2)
C(2)	C(3)	O(3)	107·9 (2)
O(3)	C(3)	C(4)	110·6 (2)
C(3)	C(4)	O(4)	110·3 (2)
O(4)	C(4)	C(5)	106·4 (2)
Mean value			
C–C–C			112·1 (4)
C–C–O(H)			109·5 (18)
Five-membered ring formed by C(1)–O(1)–C(6)–C(5)–O(5)			103·8 (24)

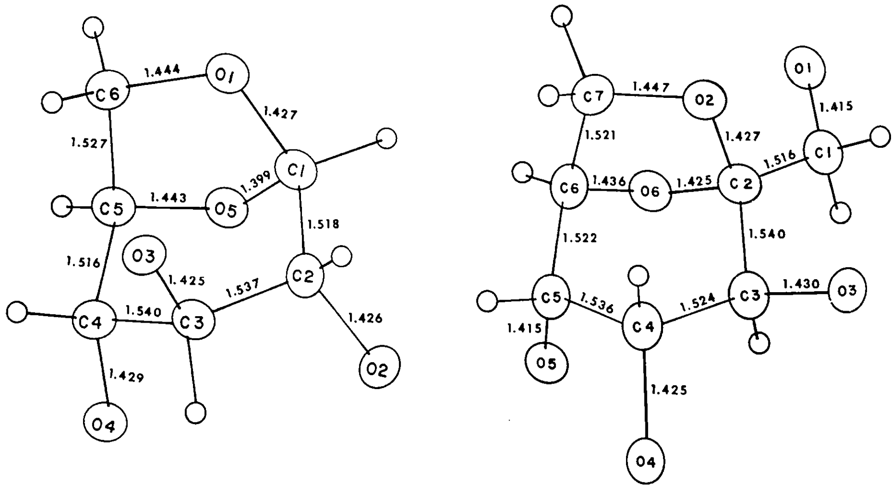


Fig. 3. Comparison of bond lengths in 1,6-anhydro-β-D-glucopyranose (left) and in sedoheptulosan (right) (Brown & Thiessen, 1969).

given in Table 2. The atomic scattering factors used were those of Cromer & Waber (1965) for carbon and oxygen and of Stewart, Davidson & Simpson (1965) for hydrogen.

Description of the structure

The molecular conformation and atomic numbering are shown in Fig. 2. The molecule has the conformation shown in II*a*, in which the pyranose ring has the 1*C* chair form with the hydroxyl groups axial at C(2), C(3) and C(4). The seven-membered ring which includes the six carbon atoms and O(1) is boat-shaped with the atoms lying in the three planes containing the atoms C(1) C(5) C(6) O(1), C(1) C(2) C(4) C(5), (see Table 3) and C(2) C(3) C(4), which make dihedral angles about C(1)···C(5) and C(2)···C(4) of 110·7° and 147·4°, respectively. The atoms C(2), O(2), C(4), O(4) are also in the same plane within 0·019 Å. In the unstrained conformation, the bonds C(2)–O(2) and C(4)–O(4), C(3)–O(3) and C(5)–C(6) will be eclipsed and parallel, thereby bringing O(2) and O(4), O(3) and C(6) to within non-bonded distances of 2·5 Å. These distances correspond to non-bonding interactions which in carbohydrates normally lead to instability relative to some alternate conformation, in this case the conformer shown in II*b*. However, in this molecule, the pyranose ring is strained by the formation of the anhydro ring in a manner such that the separations of O(2) and O(4), O(3) and C(6) are increased to 3·30 and 3·00 Å, respectively. The greater stability due to this reduction of the non-bonding repulsion by anhydro ring formation has been referred to as the 'reflex effect' by Sandris & Ourisson (1958).

The alternate conformation, II*b*, in which the pyranose has the boat form, the seven-membered ring is chair-shaped, and the substituent hydroxyl groups are all equatorial, might still be competitive in energy. A calculation was therefore made of the non-bonding interaction energies for all atom pairs separated by more than two covalent bonds and closer than 4 Å,

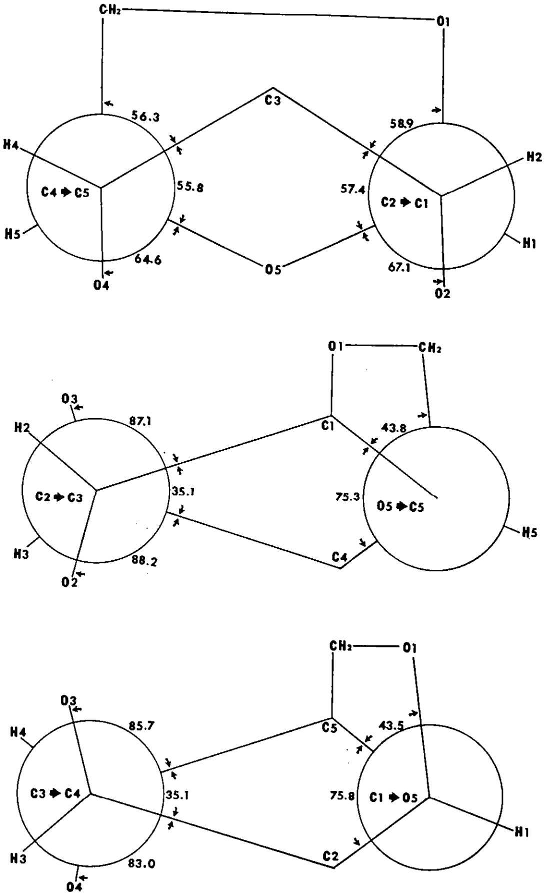


Fig. 4. The conformation angles about the C–C and C–O bonds of the pyranose ring in 1,6-anhydro-β-D-glucopyranose.

Table 6. *Hydrogen bonding distances and angles*

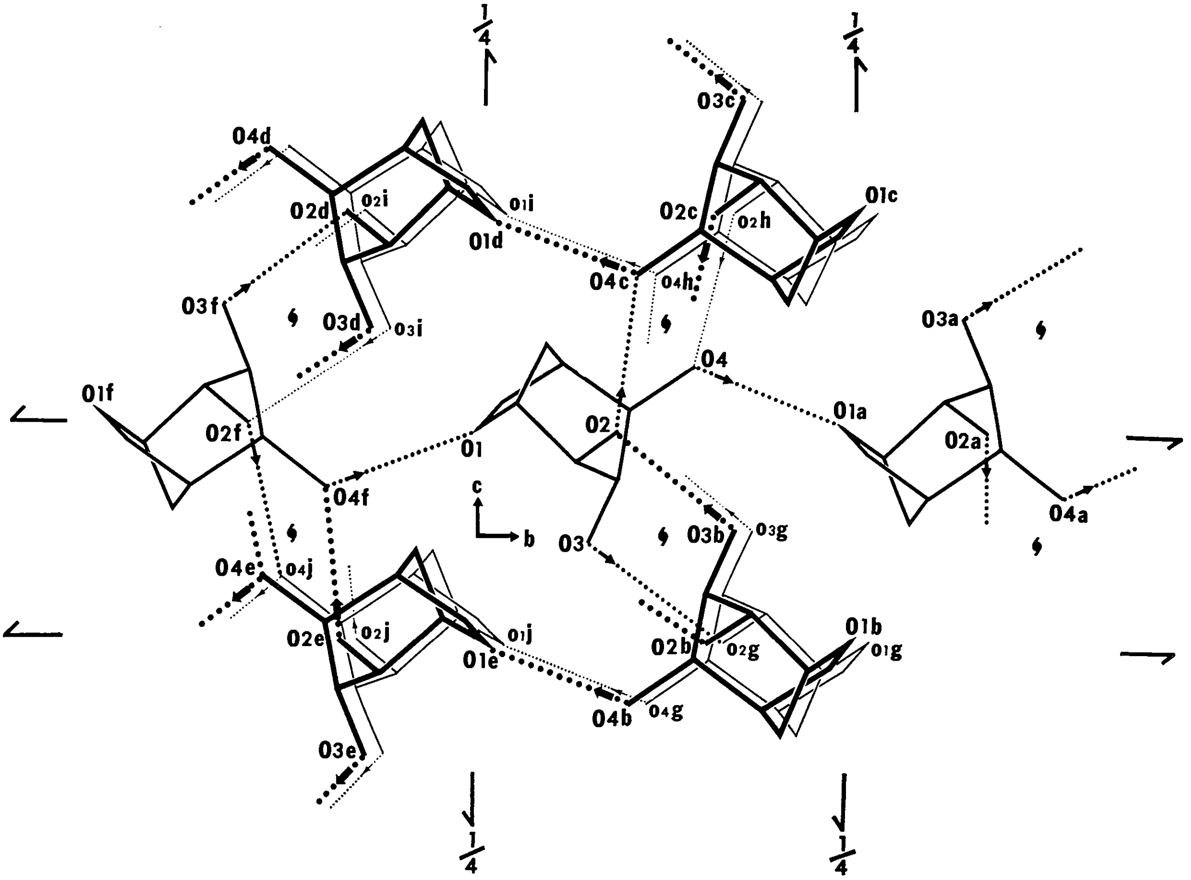
i	*j*	*k*	*D*(*ik*)	∠(*ijk*)	*i*	*j*	*k*	*D*(*jk*)	∠(*ijk*)
O(2)	H(O2)	O(4*c*)	2·756 Å	157°	C(2)	O(2)	O(4*c*)	2·756 Å	124·4°
O(3)	H(O3)	O(2*g*)	2·768	170	C(3)	O(3)	O(2*g*)	2·768	102·3
O(4)	H(O4)	O(1*a*)	2·771	168	C(4)	O(4)	O(1*a*)	2·771	116·7
O(2)	H(O2)	O(5)	2·878	100	C(2)	O(2)	O(5)	2·878	55·8

Non-bonded O···O distances less than 3·3 Å

O(1)	O(5*e*)	3·210 Å
O(2)	O(4)	3·299
O(3)	O(1)	2·938
O(4)	O(5)	2·812
O(4)	O(5*h*)	3·182

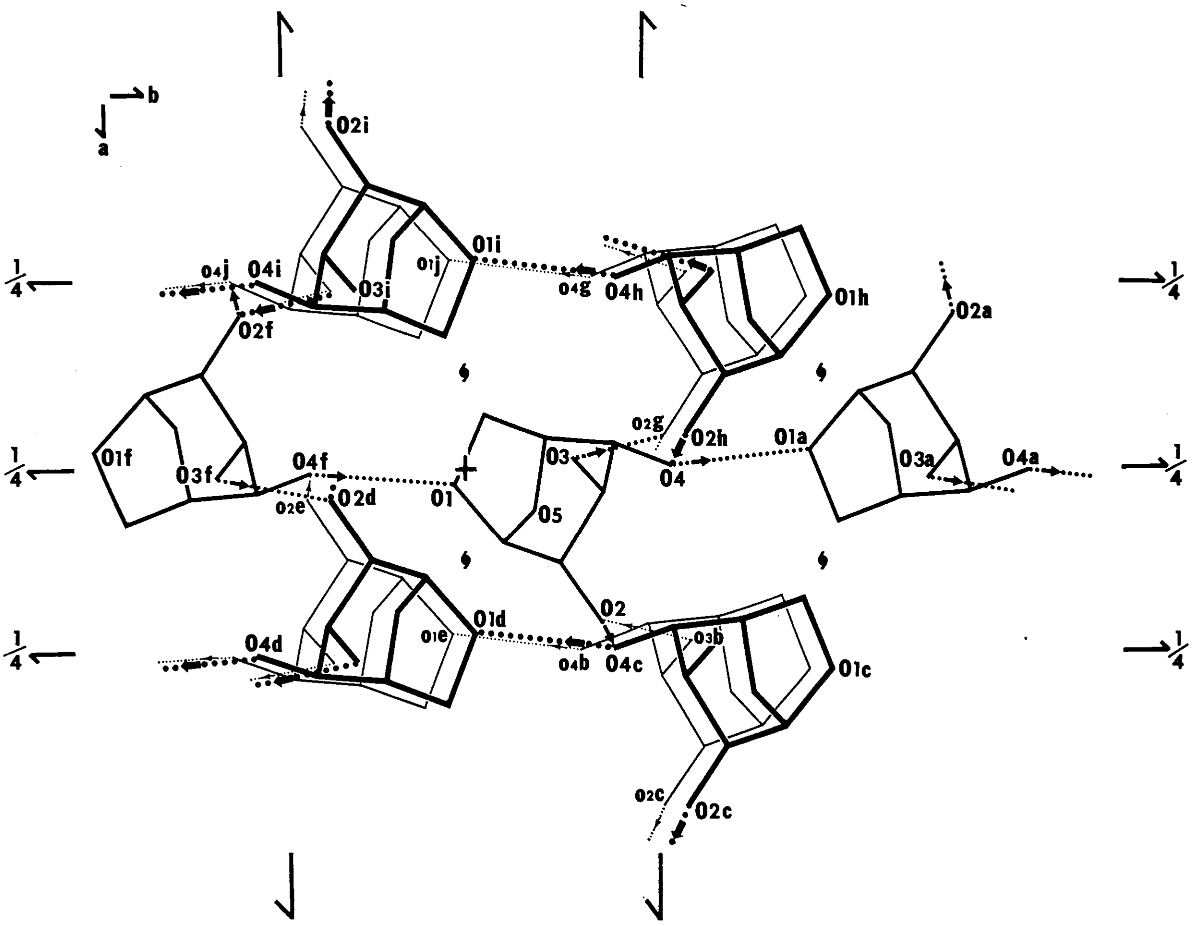
Symmetry code

No symbol	*x*	*y*	*z*
a	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
b	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
c	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
d	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
e	$\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$
f	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
g	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
h	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
i	$-\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
i	$-\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$



(*a*)

Fig. 5. The hydrogen bonding in the crystal structure of 1,6-anhydro-β-D-glucopyranose. Solid lines indicate the molecules; dotted lines indicate the hydrogen bonds with the arrows pointing in the donor direction. (*a*) View down the *a* axis.



(b)

Fig 5 (*cont.*) (*b*) View down the *c* axis.

by means of the two commonly used Lennard-Jones type functions;

$$U_{ij}(r_{ij}) = -A/r_{ij}^{6} + B/r_{ij}^{12}$$

and

$$U_{ij}(r_{ij}) = -A/r_{ij}^{6} + B' \exp\{-\mu r_{ij}\}\,.$$

The values for A, B, B' and μ were calculated according to the methods suggested by Pitzer & Catalano, (1956) and Hendrickson (1961), with van der Waals radii for carbon, oxygen and hydrogen of 1·6, 1·4 and 1·25 Å respectively. The values of these constants are given in Table 4. Both expressions gave non-bonding interaction energies favoring the observed axially substituted conformer by 1·1 and 0·7 kcal.mole^{-1} respectively. The largest repulsion interaction in the conformer II*b* was between the ring oxygen and C(3), *i.e.*, that characteristic of the boat-shaped pyranose ring.

The intramolecular distances and valence angles are given in Table 5. The average values of C–C and C–O(H) bond lengths and C–C–C and C–C–O(H) angles are 1·528 (11), 1·427 (2) Å and 112·1 (4), 109·5 (18)° respectively. These values are not significantly different from those observed in other pyranose sugars (Berman, Chu & Jeffrey, 1967). The same ring system has been studied by Brown & Thiessen (1969) in sedoheptulosan in the crystal structure of the monohydrate. The bond distances are compared in Fig. 3.

It is most interesting to note that these bond distances agree to better than 0·015 Å, except for those which include C(1) where the configuration of the two molecules is different. There we observe differences of 0·026 Å in C(1)–O(5) and 0·022 Å in C(1)–C(2), both being longer in the molecule which has the primary alcohol group on C(1). This observation is of marginal significance and requires additional evidence before it can be regarded as a characteristic of the anhydropyranose carbohydrate derivates.

The chair conformation of the pyranose ring in this anhydro sugar is significantly strained. The conformation angles, shown in Fig. 4, differ by as much as 25° from those observed in unstrained pyranose rings (Berman & Kim, 1968). While the dihedral angles around C(1)–C(2) and C(4)–C(5) are close to the unstrained values, those around C(2)–C(3) and C(3)–C(4) are smaller, and those around C(5)–O(5) and O(5)–C(1) are larger, *i.e.*, 35·1, 35·1 and 75·3, 75·8° respectively. There are corresponding differences in the deviations of C(3) and O(5) from the plane of C(1), C(2), C(4), C(5) (Table 5). The angle at the pyranose ring oxygen, O(5), is about 10° smaller than normal and comparable with that at the oxygen in the anhydro ring.

The hydrogen bonding is shown in Table 6 and Fig. 5(*a*) and (*b*). The hydroxyls at O(2) and O(4) form two hydrogen bonds, one donor and one acceptor; that at O(3) forms only a donor bond to O(2). The molecules are linked by finite chains of hydrogen bonds through O(3*b*)H–O(2)H–O(4*c*)H–O(1*d*). The hydrogen H(O2) is '*anti*' to H(2) with respect to the C(2)–O(2) bond and O(2)–H(O2) is directed toward the mid-point of the triangle formed by O(5) and O(4) of the same molecule and O(4*c*) of an adjacent molecule. The distances from H(O2) to O(4*c*), O(5) and O(4) are 1·86, 2·57 and 2·98 Å. Therefore, only the intermolecular interaction can be regarded as a hydrogen bond. However, there is nuclear magnetic resonance and infrared spectral evidence that this '*anti*' conformation of H(O2) occurs in a 5% CCl_4 solution of the 3,4-dimethyl ether derivative and that this may be a characteristic 'conformational' property of certain levoglucosan derivatives (Seib, 1970). This would imply some intramolecular stabilization of the conformation observed in this structure.

This research is supported by Grant No. GM-11293 of the U.S. Public Health Service, National Institutes of Health.

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Acta Cryst. (1971). B27, 227

The Crystal Structure of the ν Phase, $Mn_{81\cdot5}$ $Si_{18\cdot5}$*

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(*Received* 17 *December* 1969)

The crystal structure of the ν phase, $Mn_{81\cdot5}Si_{18\cdot5}$ has been determined by single-crystal X-ray diffraction analysis. The lattice constants are $a_0 = 16{\cdot}992$ (4), $b_0 = 28{\cdot}634$ (7), $c_0 = 4{\cdot}656$ (1) Å, and the space group is *Immm* (D_{2h}^{25}), with 186 atoms in the unit cell. The structure has been refined by full-matrix least-squares analysis to a final *R* index of 0·041, based on the 2305 reflections observed with the diffractometer. The ν phase is related to the *P* phase, and belongs to the family of σ-phase related, layered, tetrahedrally close-packed structures, with percentages of sites with CN 12, 14, 15 and 16 respectively: 40, 43, 11 and 6. All positions with CN > 12 are occupied by Mn, except two CN 14 positions which have some Si present. The CN 12 positions are occupied by various mixtures of Mn and Si, except three positions which are occupied by Mn only, and two positions which are occupied by Si only. The structure may also be described as a stacking of two kinds of 'tiles' each consisting of 7 hexagons and 12 triangles, with the space in-between filled up by hexagons, pentagons and triangles.

Introduction

The ν phase was described by Gupta (1964) in the Mn–Fe–Si system as a binary Mn–Si phase about one at.% wide, centered at 81·5 at.% Mn and extending into the ternary system only up to 1·5 at.% Fe. Earlier the occurrence of a complex phase in the Mn–Si system in this region was mentioned by Åmark, Borén & Westgren (1936) and subsequently called the *N* phase by Kuzma & Hladyshevskii (1964). A specimen of the ν phase of stated composition $Mn_{81\cdot5}Si_{18\cdot5}$, annealed for 72 hours at 1000°C, was kindly made available to us

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* Research sponsored by the Army Research Office (Durham).

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