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

By J. Lechat* and G. A. Jeffrey†

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, *U.S.A.*

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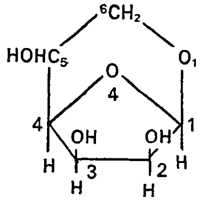
The crystal structure of 1,6-anhydro-β-D-mannofuranose, $C_6H_{10}O_5$, has been determined from X-ray automatic diffractometer data with Cu $K\alpha$ radiation. The crystal data are: space group $P2_12_12_1$, $a=5{\cdot}877$ (5), $b=11{\cdot}396$ (9), $c=9{\cdot}915$ (8) Å, $Z=4$, $D_m=1{\cdot}613$ g.cm^{-3}. The phase problem was solved by symbolic addition and tangent refinement, and the parameters were refined to give a final $R=0{\cdot}03$. The molecular conformation is that with a chair six-membered anhydro ring and an envelope furanose ring, having the oxygen out of the plane. There are small, but apparently systematic, differences in the C–O bond lengths, which range from 1·409 to 1·466 Å. The hydrogen bonding is intermolecular and consists of infinite spirals and isolated links.

Introduction

This crystal-structure determination is part of a study of the effect of anhydro ring formation on the bond lengths, valence and torsion angles of carbohydrates. Previous investigations in this series are those of 1,6-anhydro-β-D-glucopyranose (Park, Kim & Jeffrey, 1971) and 1,6:2,3-dianhydro-β-D-gulopyranose (Berking & Seeman, 1971). 1,6-Anhydro-β-D-mannofuranose (I), $C_6H_{10}O_5$, is formed by the dry pyrolysis of D-mannose (Heyns, Köll & Paulsen, 1971) and crystals were provided by Professor H. Paulsen of the Institute of Organic Chemistry and Biochemistry, University of Hamburg.



(I)

Experimental

The unit-cell constants, and the three-dimensional intensity data were measured on a Nonius CAD-3 automatic diffractometer using (Ni-filtered) Cu $K\alpha$ radiation with a crystal, $0{\cdot}4\times0{\cdot}2\times0{\cdot}3$ mm, mounted along the a axis. The θ–2θ scanning mode with varying interval was used up to $2\theta=120°$. Of the 602 recorded reflections, 589 were observed above background, $[I_m>2\sigma(I_m)]$, where σ is the estimated standard deviation of I_m from the counting statistics. Two standards were measured every thirty reflections and used to scale the data. The data were reduced to structure factors without absorption correction. Crystal data are given in Table 1.

Table 1. *Crystal data*

1,6-Anhydro-β-D-mannofuranose, $C_6H_{10}O_5$
M.W. 162·08, m.p. 192–3 °C.
Space group $P2_12_12_1$, from systematic extinctions $h00$ with $h=2n+1$, $0k0$ with $k=2n+1$, $00l$ with $l=2n+1$.
$a=5{\cdot}877$ (5), $b=11{\cdot}396$ (9), $c=9{\cdot}915$ (8) Å
$D_m=1{\cdot}613$ g.cm^{-3}(flotation), $D_x=1{\cdot}625$ g.cm^{-3}, $Z=4$, μ(Cu$K\alpha$) $=12{\cdot}5$ cm^{-1}.

Determination and refinement of the structure

The structure was solved by application of the $\sum_2$ symbolic addition method to the 30 reflections with the higher E values, using the reflections 033; 1,10,0; 2,11,0, to define the origin and 023 to define the en-

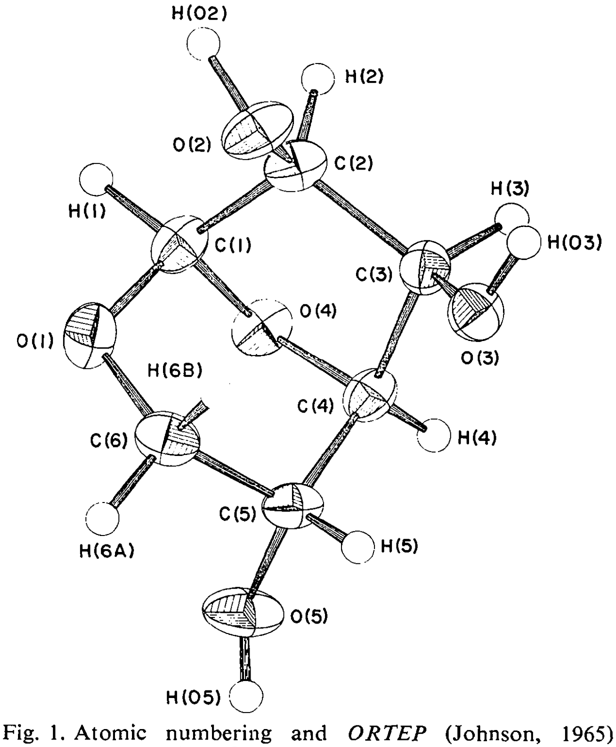


Fig. 1. Atomic numbering and *ORTEP* (Johnson, 1965) representation of 1,6-anhydro-β-D-mannofuranose.

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[*] On leave from Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, S. P., Brazil.

[†] To whom all correspondence should be addressed.

antiomorph. The tangent refinement formula was then applied to 140 reflections with $E \geq 1{\cdot}20$. The eleven highest peaks which appeared in the resulting E map clearly corresponded to the eleven heavy atoms (carbon and oxygen) of the structure. The conventional R value calculated from the trial structure was 0·27 for all reflections. The refinement was by several cycles of isotropic and anisotropic block-diagonal and full-matrix least squares. The function minimized was $\omega_1(K|F_o|-|F_c|)^2$ where $\omega_l = 1/(A+B|F_o|+C|F_o|)^2$ with $A=16$, $B=1$, $C=0{\cdot}0014$ for the observed reflections and $\omega_l=0$ for the unobserved. The non-hydroxyl hydrogen atoms were found close to their calculated positions on a difference synthesis map calculated at $R=0{\cdot}095$. The hydroxyl hydrogen atoms were located on a difference synthesis map calculated at $R=0{\cdot}046$. The hydrogen atoms were given the thermal parameters of the atoms to which they are attached and their coordinates only were refined. The final refinement cycle gave $R=0{\cdot}039$ for all reflections and $R=0{\cdot}032$ for the observed reflections only. Nine reflections which appeared to be seriously affected by extinction were given zero weight as indicated in Table 2, which gives the observed and calculated structure factors. The atomic parameters are given in Table 3. Fig. 1 gives the atomic numbering and an *ORTEP* plot (Johnson, 1965) of the thermal parameters. The atomic scattering factors used were those of Cromer & Waber (1965) for carbon and oxygen and of Stewart, Davidson & Simpson (1965) for hydrogen.

Table 2. *Observed and calculated structure factors for* 1,6-*anhydro-β-*D-*mannofuranose*

Columns are: Index, $10|F_{obs}|$, $10|F_{calc}|$; * indicates unobserved reflections, + indicates reflections eliminated from last refinement cycle.

H= 0 K= 0		
2	786+	841
4	49	45
6	58	53
8	13	6
10	165	158
H= 0 K= 1		
2	428	420
3	149	150
4	35	36
5	47	51
6	345	361
7	62	67
8	66	63
9	73	74
10	34	38
11	22	22
H= 0 K= 2		
0	84	90
1	397	396
2	307+	357
3	576+	625
4	83	86
5	139	137
6	68	64
7	15	7
8	88	91
9	145	146
10	46	46
11	108	110
H= 0 K= 3		
1	58	60
2	305	314
3	742+	784
4	101	106
5	281	293
6	159	160
7	46	46
8	124	124
9	182	184
10	5*	11
H= 0 K= 4		
0	280	280
1	232	227
2	136	154
3	225	228
4	116	110
5	268	272
6	108	105
7	27	27
8	40	43
9	15	17
10	53	52
H= 0 K= 5		
1	502+	537
2	203	200
3	365	348
4	163	159
5	23	20
6	258	254
7	43	34
8	80	76
9	38	37
10	30	33
H= 0 K= 6		
0	389	386
1	167	160
2	98	102
3	43	38
4	188	180
5	18	8
6	129	123
7	90	85
8	82	86
9	55	54
H= 0 K= 7		
1	1*	16
2	386	387
3	32	28
4	43	38
5	56	53
6	9	10
7	73	71
8	55	52
9	9	7
H= 0 K= 8		
0	195	204
1	117	113
2	218	222
3	53	51
4	14	12
5	98	95
6	29	30
7	25	25
8	153	161
H= 0 K= 9		
1	67	67
2	87	85
3	35	35
4	84	83
5	62	66
6	77	71
7	10	7
H= 0 K= 10		
0	117	123
1	235	241
2	96	95
3	22	16
4	28	31
5	144	141
6	5*	3
H= 0 K= 11		
1	48	52
2	60	57
3	128	127
4	61	60
5	39	41
H= 0 K= 12		
0	59	57
1	24	24
2	5*	2
3	93	95
H= 1 K= 0		
1	375	376
2	124	137
3	61	68
4	171	161
5	375	387
6	143	157
7	39	39
8	66	67
9	62	64
10	5*	5
11	13	12
H= 1 K= 1		
0	564+	630
1	572	572
2	164	165
3	310	312
4	282	281
5	94	93
6	57	55
7	119	121
8	80	78
9	84	84
10	100	95
H= 1 K= 2		
0	234+	303
1	112	114
2	284+	339
3	348	343
4	97	96
5	7	7
6	115	114
7	191	198
8	155	157
9	69	68
10	57	54
H= 1 K= 3		
0	41	40
1	142	141
2	316+	367
3	277	272
4	273	273
5	35	36
6	60	56
7	91	85
8	80	82
9	92	91
10	54	55
H= 1 K= 4		
0	294	287
1	107	105
2	309	308
3	170	165
4	174	171
5	216	218
6	114	114
7	177	173
8	111	118
9	140	138
10	108	106
H= 1 K= 5		
0	112	105
1	310	296
2	105	97
3	257	257
4	122	117
5	66	72
6	199	204
7	80	83
8	129	125
9	46	48
10	19	19
H= 1 K= 6		
0	210	207
1	103	102
2	257	259
3	136	129
4	170	168
5	176	179
6	238	236
7	168	163
8	71	68
9	30	31
H= 1 K= 7		
0	241	240
1	76	76
2	152	146
3	202	192
4	167	167
5	132	128
6	125	130
7	90	54
8	37	38
9	55	56
H= 1 K= 8		
0	81	79
1	107	111
2	96	103
3	172	169
4	66	68
5	116	119
6	44	47
7	42	39
8	47	48
H= 1 K= 9		
0	15	15
1	244	254
2	84	83
3	125	129
4	90	90
5	41	40
6	29	34
7	45	49
H= 1 K= 10		
0	299	295
1	137	142
2	137	133
3	104	99
4	52	48
5	86	88
6	42	42
H= 1 K= 11		
0	20	15
1	49	45
2	71	69
3	47	48
4	96	95
5	23	28
H= 1 K= 12		
0	68	68
1	97	91
2	34	26
3	20	29
H= 2 K= 0		
0	173	191
1	60	63
2	61	63
3	242	242
4	10	7
5	196	198
6	77	74
7	39	43
8	27	30
9	20	23
10	78	76
H= 2 K= 1		
0	336	352
1	320	323
2	382	392
3	256	258
4	305	303
5	258	263
6	65	64
7	66	59
8	100	98
9	65	63
10	48	39
H= 2 K= 2		
0	78	79
1	386	367
2	304	309
3	275	274
4	128	125
5	143	149
6	126	129
7	12	14
8	113	119
9	33	34
10	85	81
H= 2 K= 3		
0	85	93
1	92	93
2	150	137
3	30	24
4	170	174
5	100	101
6	25	24
7	92	84
8	85	85
9	83	78
10	47	51
H= 2 K= 4		
0	255	251
1	134	122
2	90	92
3	73	67
4	22	20
5	210	214
6	119	122
7	168	170
8	145	145
9	26	27
10	19	14
H= 2 K= 5		
0	63	64
1	207	209
2	173	165
3	67	64
4	118	116
5	66	68
6	123	120
7	59	59
8	46	43
9	75	74
H= 2 K= 6		
0	10	10
1	72	71
2	141	135
3	138	138
4	68	68
5	34	28
6	110	105
7	177	177
8	16	16
9	57	62
H= 2 K= 7		
0	21	23
1	165	158
2	143	147
3	29	31
4	111	110
5	69	78
6	91	90
7	28	29
8	43	44
H= 2 K= 8		
0	29	28
1	37	36
2	157	154
3	158	162
4	81	84
5	52	53
6	27	33
7	51	50
H= 2 K= 9		
0	13	10
1	51	51
2	81	74
3	116	112
4	210	215
5	54	52
6	74	75
7	3*	6
H= 2 K= 10		
0	31	27
1	71	72
2	129	129
3	84	89
4	16	22
5	44	47
6	39	46
H= 2 K= 11		
0	185	184
1	81	76
2	84	84
3	12	13
4	28	28
H= 2 K= 12		
0	86	81
1	55	58
H= 3 K= 0		
1	232	240
2	224	223
3	342	338
4	17	17
5	48	51
6	79	72
7	13	7
8	5*	16
9	59	61
H= 3 K= 1		
0	156	153
1	162	165
2	36	40
3	84	86
4	197	195
5	23	24
6	92	87
7	64	48
8	41	38
9	66	61
H= 3 K= 2		
0	16	15
1	333	321
2	267	252
3	136	129
4	35	30
5	92	89
6	127	126
7	115	116
8	73	74
9	35	36
H= 3 K= 3		
0	74	71
1	147	147
2	57	55
3	144	141
4	40	40
5	182	189
6	90	91
7	95	96
8	47	46
9	32	31
H= 3 K= 4		
0	54	51
1	136	131
2	232	233
3	136	126
4	76	76
5	103	103
6	45	41
7	74	79
8	75	72
9	36	36
H= 3 K= 5		
0	36	39
1	64	63
2	87	91
3	100	98
4	304	307
5	163	159
6	109	101
7	50	49
8	58	58
H= 3 K= 6		
0	120	124
1	174	172
2	158	163
3	59	57
4	15	15
5	15	13
6	81	78
7	43	53
8	33	31
H= 3 K= 7		
0	143	144
1	90	85
2	97	92
3	102	96
4	115	119
5	30	27
6	51	53
7	113	114
H= 3 K= 8		
0	59	102
1	226	239
2	131	133
3	134	133
4	115	108
5	152	150
6	36	34
7	12	12
H= 3 K= 9		
0	98	91
1	125	122
2	64	66
3	100	104
4	86	92
5	65	65
6	61	59
H= 3 K= 10		
0	22	20
1	60	60
2	60	63
3	48	49
4	52	56
H= 3 K= 11		
0	60	64
1	50	52
2	49	49
H= 4 K= 0		
0	67	64
1	228	233
2	124	115
3	102	104
4	36	36
5	63	69
6	47	46
7	102	100
8	117	110
H= 4 K= 1		
0	22	20
1	255	252
2	202	197
3	155	196
4	86	88
5	192	200
6	55	49
7	50	55
8	36	39
H= 4 K= 2		
0	4*	6
1	81	77
2	64	63
3	140	137
4	170	172
5	200	201
6	140	137
7	103	108
8	72	70
H= 4 K= 3		
0	143	144
1	109	106
2	247	240
3	92	96
4	84	84
5	29	30
6	105	110
7	85	82
8	78	74
H= 4 K= 4		
0	107	108
1	51	52
2	78	77
3	120	120
4	245	245
5	111	114
6	147	151
7	16	16
8	4*	1
H= 4 K= 5		
0	112	114
1	81	83
2	49	50
3	87	91
4	103	105
5	54	57
6	28	24
7	40	41
H= 4 K= 6		
0	155	156
1	89	88
2	34	32
3	131	130
4	95	90
5	151	143
6	54	56
7	50	54
H= 4 K= 7		
0	57	54
1	121	122
2	73	73
3	88	87
4	21	24
5	65	62
6	65	67
H= 4 K= 8		
0	86	89
1	119	118
2	61	51
3	65	64
4	20	25
5	59	60
H= 4 K= 9		
0	79	82
1	14	12
2	67	70
3	43	40
4	52	56
H= 4 K= 10		
0	116	121
1	63	58
H= 5 K= 0		
1	133	129
2	162	174
3	131	138
4	86	84
5	78	79
6	5*	21
7	13	8
H= 5 K= 1		
0	85	82
1	111	113
2	165	167
3	127	130
4	60	56
5	26	26
6	49	50
7	23	19
H= 5 K= 2		
0	16	12
1	170	165
2	58	56
3	44	47
4	95	99
5	67	66
6	66	67
7	16	20
H= 5 K= 3		
0	83	86
1	107	104
2	94	97
3	89	93
4	105	109
5	82	83
6	76	79
H= 5 K= 4		
0	156	153
1	125	123
2	79	81
3	22	20
4	31	31
5	71	70
6	54	53
H= 5 K= 5		
0	13	4
1	134	135
2	59	63
3	49	52
4	30	29
5	16	12
H= 5 K= 6		
0	5*	6
1	162	160
2	46	45
3	61	59
4	172	173
5	12	8
H= 5 K= 7		
0	18	19
1	67	70
2	126	124
3	101	100
H= 5 K= 8		
0	113	116
1	14	13
H= 6 K= 0		
0	95	89
1	24	29
2	143	133
3	65	75
4	78	81
H= 6 K= 1		
0	5*	3
1	7*	18
2	22	19
3	34	33
4	35	34
H= 6 K= 2		
0	61	61
1	51	52
2	24	21
3	41	36
4	49	50
H= 6 K= 3		
0	145	150
1	49	51
2	62	64
3	69	70
H= 6 K= 4		
0	63	66
1	71	69
2	88	79
3	19	16
H= 6 K= 5		
0	20	20
1	30	35

Table 3. *Fractional atomic coordinates and anisotropic thermal parameters in* 1,6-*anhydro-β-*D-*mannofuranose*

The temperature factor expression used was $\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times 10\}$. Estimated standard deviations are in parentheses.

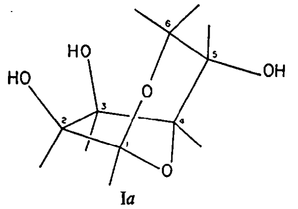
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·4801 (6)	0·3842 (3)	0·2495 (3)	140 (9)	42 (2)	71 (3)	−2 (4)	18 (5)	−8 (2)
C(2)	0·5721 (5)	0·4750 (3)	0·1485 (3)	117 (9)	38 (2)	76 (3)	−4 (4)	−4 (5)	−3 (2)
C(3)	0·7352 (5)	0·4027 (3)	0·0589 (3)	172 (9)	34 (2)	51 (3)	−2 (4)	16 (5)	−1 (2)
C(4)	0·7195 (5)	0·2784 (2)	0·1182 (3)	156 (9)	30 (2)	58 (3)	−1 (4)	9 (5)	−10 (2)
C(5)	0·8795 (5)	0·2553 (3)	0·2330 (3)	127 (10)	31 (2)	72 (3)	4 (4)	−1 (5)	6 (2)
C(6)	0·8456 (6)	0·3458 (3)	0·3462 (3)	148 (10)	49 (3)	65 (4)	−3 (4)	−33 (5)	2 (2)
O(1)	0·6106 (4)	0·3715 (2)	0·3693 (2)	189 (8)	61 (2)	55 (2)	−2 (3)	12 (3)	−10 (2)
O(2)	0·6847 (4)	0·5720 (2)	0·2062 (2)	175 (7)	32 (2)	107 (3)	1 (3)	13 (4)	−16 (2)
O(3)	0·9640 (4)	0·4427 (2)	0·0580 (2)	169 (7)	40 (2)	63 (2)	−10 (3)	18 (3)	5 (2)
O(4)	0·4889 (4)	0·2779 (2)	0·1746 (2)	143 (7)	36 (2)	73 (2)	−11 (3)	5 (3)	−7 (2)
O(5)	0·8334 (4)	0·1382 (2)	0·2793 (3)	216 (7)	33 (2)	124 (3)	4 (3)	−3 (5)	25 (2)

Table 3 (*cont.*)

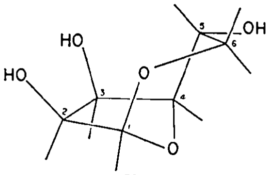
	x	y	z
H(1)	0·303 (6)	0·398 (3)	0·293 (3)
H(2)	0·428 (6)	0·497 (3)	0·093 (3)
H(3)	0·665 (6)	0·398 (3)	−0·042 (3)
H(4)	0·708 (6)	0·214 (3)	0·055 (3)
H(5)	1·027 (7)	0·258 (3)	0·200 (3)
H(6*A*)	0·915 (6)	0·312 (3)	0·429 (4)
H(6*B*)	0·938 (6)	0·419 (3)	0·313 (4)
H(O2)	0·554 (7)	0·620 (3)	0·229 (4)
H(O3)	0·960 (7)	0·500 (4)	0·006 (4)
H(O5)	0·939 (7)	0·097 (3)	0·302 (5)

Results and discussion

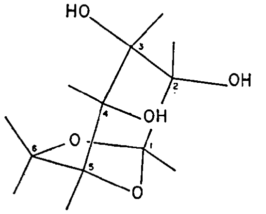
As in 1,6-anhydro-β-D-glucopyranose (II), the conformation observed for 1,6-anhydro-β-D-mannofuranose is that with a chair-shaped six-membered ring, (I*a*), rather than the alternative conformation with the boat-shaped ring, (I*b*). In 1,6:2,3-dianhydro-β-D-gulopyranose, the presence of the 2,3 ring constrains the six-membered ring to be half-chair, as shown in (III). The similarities between the fused-ring systems of the four anhydro sugar molecules which have been studied by crystal-structure determination are illustrated in Fig. 2.



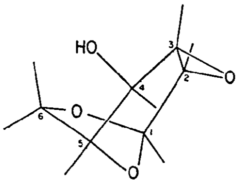
I*a*



I*b*



II



III

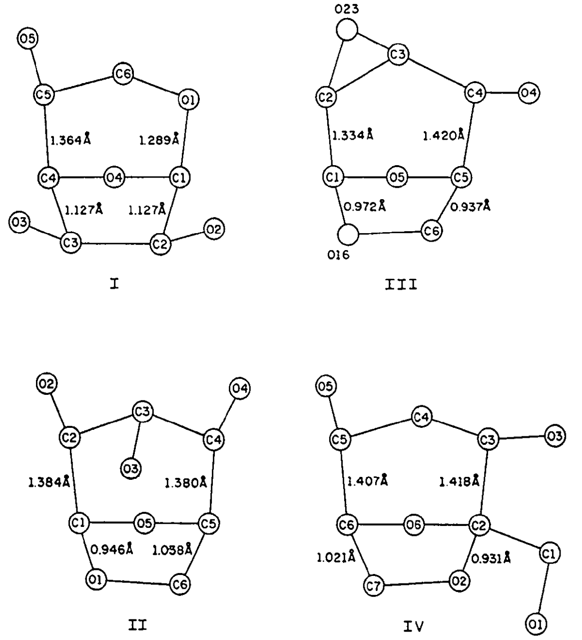


Fig. 2. Projections of 1,6-anhydro-β-D-mannofuranose (I), 1,6-anhydro-β-D-glucopyranose (II), 1,6:2,3-dianhydro-β-D-gulopyranose (III), and sedoheptulosan (IV), in a plane normal to the plane of the C, O, C, atoms common to both rings. The numbers are distances from this common plane.

The detailed conformation of the fused ring system in (I*a*) can be described with reference to four planes.

(1) The plane through the carbon atoms of the furanose ring C(1), C(2), C(3), C(4), with $A=0{\cdot}755$, $B=0{\cdot}209$, $C=0{\cdot}622$, $D=0{\cdot}145$ Å. The four carbon atoms are coplanar within the standard deviation of 0·004 Å. The furanose ring oxygen is −0·676 Å out of this plane, *exo* to the anhydro ring. The ring conformation is therefore an *envelope* with the oxygen out of the plane, *i.e.* E_0, rather than the twist or envelope with C(2) or C(3) out of the plane as commonly observed in nucleosides and oligosaccharides.

(2) The plane through C(1), O(1), C(4), C(5) of the anhydro ring which is also exact within the standard

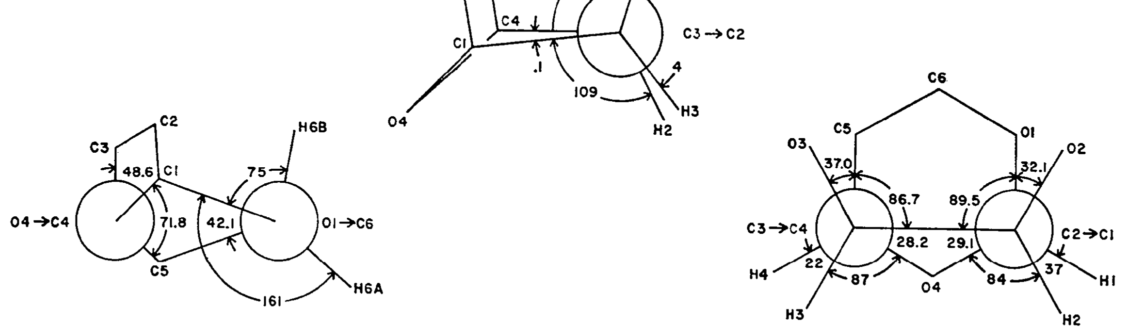


Fig. 3. Conformation angles around C–C and C–O bonds in 1,6-anhydro-β-D-mannofuranose.

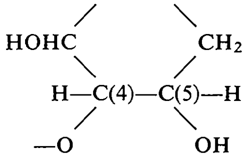
deviations, with $A=0{\cdot}505$, $B=0{\cdot}833$, $C=-0{\cdot}225$, $D=1{\cdot}544$ Å. O(4) and C(6) are, respectively −0·815 and 0·505 Å out of this plane, giving a chair-shaped dioxy six-membered ring.

(3) The plane through O(1), C(6), C(5) with $A=-0{\cdot}045$, $B=-0{\cdot}740$, $C=0{\cdot}671$, $D=-0{\cdot}568$ Å.

(4) The plane through C(2), C(3), O(2), O(3) with $A=0{\cdot}217$, $B=-0{\cdot}566$, $C=0{\cdot}796$, $D=-2{\cdot}449$ Å. This plane is not exact within the standard deviations, and the atoms are displaced +0·017, −0·017, −0·010, +0·010, respectively.

The dihedral angles between these four planes are 1 to 2, 114·6°, 2 to 3, 142·2°, and 1 to 4, 122·7°.

The torsion angles about the C–C and C–O bonds are given in Fig. 3, and the bond lengths and valence angles are listed in Table 4. Four of the C–C bond lengths lie within a narrow range from 1·536 to 1·544 Å and one, C(4)–C(5), is 0·040 Å shorter than their mean. We have no explanation for this, but it is noteworthy that the bonding environment of this linkage is unique in the four anhydro sugars that have been studied, *i.e.*



The C–O bond lengths show a variation between 1·409 and 1·466 Å; *i.e.* of the same magnitude as is observed in the vicinity of the ring oxygen and anomeric carbon in most pyranose sugars (*cf.* Berman, Chu & Jeffrey, 1967). Such differences are to be anticipated in view of the relationships between the electronic distribution, conformational energies, and bond lengths of the –O–C–O– acetal bond sequence shown by the studies on 2-aldoxytetrahydropyrans (de Hoog, Buys, Altona & Havinga, 1969), and by quantum-mechanical calculations (Radom, Hehre & Pople, 1971), which have been extrapolated to the pyranose sugars by Jeffrey, Pople & Radom (1972). In the anhydro sugars, the conformational angles about the C–O bonds are con-

Table 4. *Bond lengths and angles in* 1,6-*anhydro-β-*D-*mannofuranose*

The values in parentheses are the estimated standard deviations affecting the last decimal place.

i	*j*	D_{ij}	*i*	*j*	*k*	∠*ijk*
C(1)	C(2)	1·538 (4) Å	C(1)	C(2)	C(3)	103·5 (2)°
C(2)	C(3)	1·544 (4)	C(2)	C(3)	C(4)	103·6 (2)
C(3)	C(4)	1·536 (4)	C(3)	C(4)	C(5)	114·5 (2)
C(4)	C(5)	1·499 (4)	C(4)	C(5)	C(6)	110·8 (3)
C(5)	C(6)	1·537 (4)	C(1)	C(2)	O(2)	115·4 (3)
C(1)	O(1)	1·421 (4)	C(2)	C(1)	O(1)	115·0 (3)
C(2)	O(2)	1·409 (4)	C(2)	C(1)	O(4)	102·7 (2)
C(3)	O(3)	1·419 (4)	C(2)	C(3)	O(3)	114·8 (2)
C(4)	O(4)	1·466 (4)	C(3)	C(2)	O(2)	111·1 (2)
C(1)	O(4)	1·421 (4)	C(3)	C(4)	O(4)	101·8 (2)
C(5)	O(5)	1·436 (4)	C(4)	C(3)	O(3)	110·8 (2)
C(6)	O(1)	1·430 (4)	C(4)	C(5)	O(5)	106·7 (2)
C(1)	H(1)	1·14 (3)	C(5)	C(4)	O(4)	106·8 (2)
C(2)	H(2)	1·04 (3)	C(5)	C(6)	O(1)	112·3 (3)
C(3)	H(3)	1·08 (3)	C(6)	C(5)	O(5)	111·4 (3)
C(4)	H(4)	0·97 (3)	C(1)	O(4)	C(4)	103·3 (2)
C(5)	H(5)	0·93 (4)	C(6)	O(1)	C(1)	114·1 (2)
C(6)	H(6*A*)	0·99 (4)	O(1)	C(1)	O(4)	109·3 (2)
C(6)	H(6*B*)	1·05 (4)	Mean values:			
O(2)	H(O2)	0·97 (4)	C–C	1·539 (8) Å, excluding C(4)–C(5)		
O(3)	H(O3)	0·83 (4)	C–O(H)	1·420 (13)		
O(5)	H(O5)	0·81 (4)	C–O	1·434 (21)		

Table 5. *Comparison of bond lengths and torsion angles for* C–O *bonds in some anhydro sugars*

		Mean C–O	Difference from mean C–O				Torsion angles	
				θ	φ		θ	φ
			C–O–C–O–C					
I	1,6-Anhydro-β-D-mannofuranose (this work)	1·428	+37	−08	−08	+01	−74	+60
II	1,6-Anhydro-β-D-gulcopyranose (Park, Kim & Jeffrey, 1970)	1·428	+16	−01	−29	+15	+25	−44
III*	1,6:2,3-Dianhydro-β-D-gulopyranose (Berking & Seeman, 1971)	1·426	+11	−14	−21	+06	+34	−46
			+04	−23	−17	+13	+33	−46
IV	Sedoheptulosan (Brown & Thiessen, 1969)	1·427	+20	00	−02	+09	+23	−42

* Two symmetry-independent molecules.

strained by the ring formation and systematic relations between torsion angles and bond lengths can be sought. Table 5 shows a comparison of the bond length and torsion angle data for the C–O bonds of the C–O–C–O–C bond sequence in the four anhydro sugars which have been studied. In the mannofuranose derivative, this sequence is part of the chair-shaped six-membered ring with torsion angles close to 60°, whereas in the other three compounds, these bonds lie in the five-membered ring, which has characteristically smaller torsion angles. There is throughout the four compounds a systematic trend indicating a shortening of the inner bonds and a lengthening of the outer bonds. Although suggestive that a relationship may exist, the data are at present inadequate to establish an empirical connection with torsion angles. More precise measurements of bond lengths and some guidance from the theory is required at this stage.

The hydrogen bonding in the structure is shown in Fig. 4. It is entirely intermolecular and consists of an infinite spiral extending in the *a* axis direction, $\rightarrow O(5g)H \rightarrow O(2a)H \rightarrow O(5e)H \rightarrow$ with two short branch chains $O(2a)H \rightarrow O(4e)$ and $O(5g)H \rightarrow O(3a)H \rightarrow O(1b)$. The hydroxyls O(2)H and O(5)H form bifurcated hydrogen bonds to O(4), O(5) and O(2), O(3) respectively, as defined by the geometry given in Table 6; O(3)H forms a normal hydrogen bond to the anhydride ring oxygen O(1). The furanose ring oxygen O(4) accepts the bifurcated bond from O(2)H and there is a close intramolecular approach of 2·775 Å to O(5), but no intramolecular hydrogen bond, since the O(5)–H bond points away from O(4) to form the bifurcated intermolecular hydrogen bonds with O(2) and O(3). There is also a close approach of 2·649 Å between the vicinal hydroxyls O(2) and O(3), but again the hydrogen bonding is intermolecular. Other non-bonding approaches less than 3·3 Å are given in Table 6.

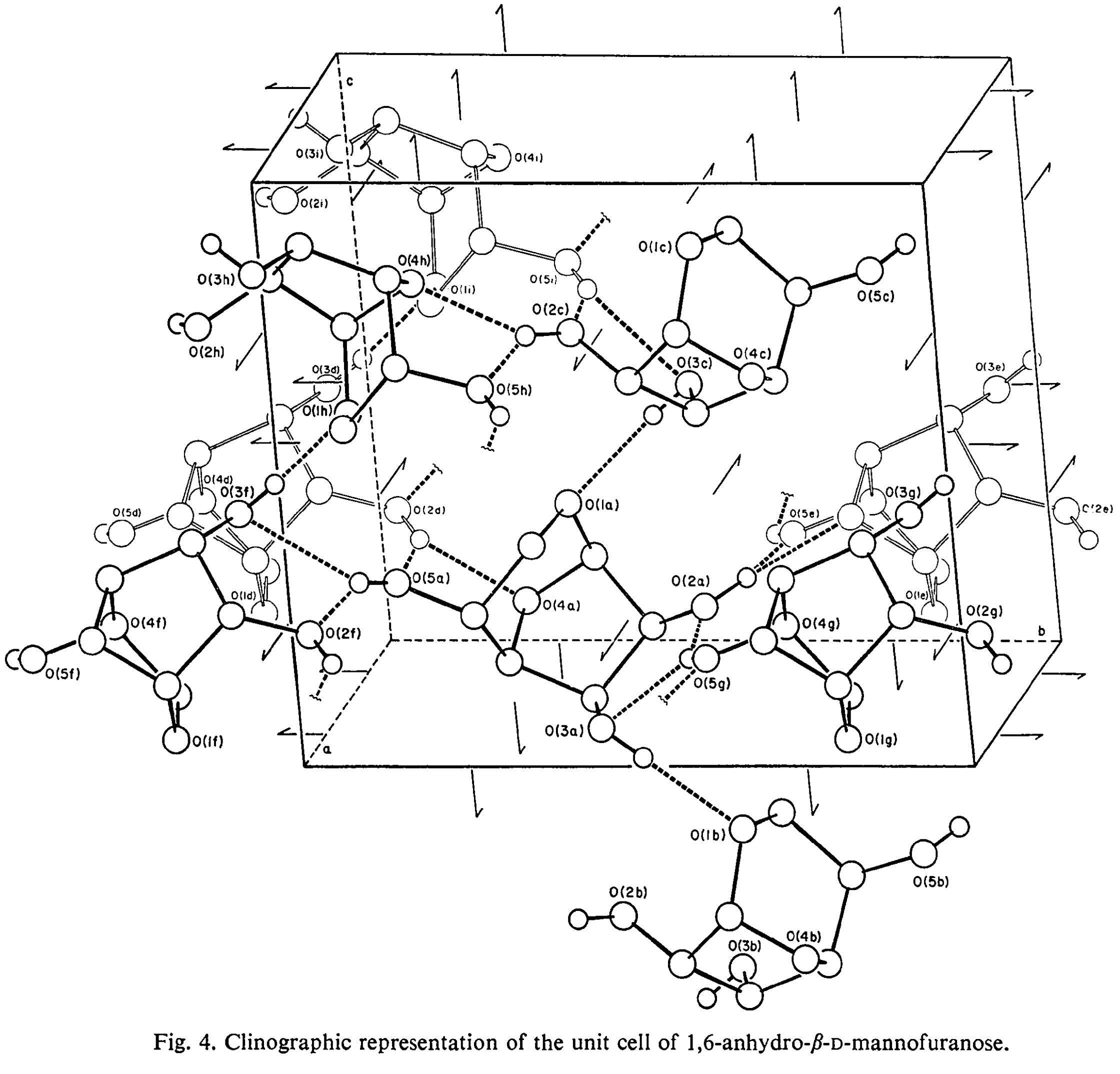


Fig. 4. Clinographic representation of the unit cell of 1,6-anhydro-β-D-mannofuranose.

Table 6. *Hydrogen-bonding distances and angles in* 1,6-*anhydro-β*-D-*mannofuranose*

i	*j*	*k*	D_{jk}	D_{ik}	$\angle ijk$
O(2*a*)	H(O2*a*)	O(4*e*)	2·05 Å	2·818 Å	134°
		O(5*e*)	2·29	3·140	146
O(3*a*)	H(O3*a*)	O(1*b*)	2·04	2·859	169
O(5*a*)	H(O5*a*)	O(2*f*)	2·23	2·934	145
		O(3*f*)	2·31	2·997	143

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

O(1*a*)···O(2*a*)	2·832 Å
O(1*a*)···O(4*a*)	2·318
O(1*a*)···O(5*a*)	3·095
O(2*a*)···O(3*a*)	2·650
O(2*a*)···O(5*g*)	2·934
O(4*a*)···O(5*a*)	2·776

Symmetry code

a	x	y	z
b	$-\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$
c	$-\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
d	$-1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
e	$-1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
f	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
g	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
h	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
i	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$

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The Crystal and Molecular Structure of 2,3-Diazanaphthalene

By C. Huiszoon, B. W. van de Waal, A. B. van Egmond and S. Harkema

Chemical Physics Laboratory, Twente University of Technology, P.O. Box 217, *Enschede, The Netherlands*

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The structure of 2,3-diazanaphthalene (phthalazine) has been determined by X-ray methods. Cell constants and intensity data were obtained with a single-crystal diffractometer. The space group is *Pbca*. Cell constants are 13·695, 10·557 and 9·285 Å. There are eight nearly planar molecules in the unit cell.

Introduction

In our laboratory research is carried out on the chemical and physical properties of diazanaphthalenes. Topics included so far are electron spin resonance (van den Ham, du Sart & van der Meer, 1971) and photoelectron spectra (van den Ham & van der Meer, 1972). In the course of these investigations the determination of the structures of the diazanaphthalenes seemed worth while. Moreover the crystal structure may be of interest from a lattice-dynamical point of view.

Of the anhydrous diazanaphthalenes, the crystal and molecular structure of 1,8-diazanaphthalene has been determined by Clearfield, Sims & Singh (1972). The structures of the dihydrates of 1,5-diazanaphthalene (orthorhombic form) and 2,6-diazanaphthalene have been solved by Brufani, Duranti, Giacomello & Zambonelli (1961) and by Brufani, Fedeli, Giacomello, Riccieri & Vaciago (1966) respectively. In the present paper the crystal and molecular structure of 2,3-diazanaphthalene or phthalazine is described.

Experimental

Small single crystals with linear dimensions of about 0·4 mm were grown by slow sublimation in vacuum