

feature of the internal motion is that the angles which are altered are those which are already distorted from the ideal configuration, and particularly C(5)–C(6)–C(11). This is consistent with the well known lability of the cyclopentane ring system, compared with that of cyclohexane. In the former the bond angles are considerably greater than the ideal tetrahedral value. Since in such distorted configurations steric forces must be acting in opposition to those resulting from the less than ideal orbital overlap some degree of lability is not unexpected.

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## The Crystal Structure of Methyl $\alpha$ -D-Glucopyranoside

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The crystal structure of methyl  $\alpha$ -D-glucopyranoside,  $C_7H_{14}O_6$ , has been determined by application of the sign correlation procedure to the  $hk0$  projection data and by inspection of the three-dimensional  $E^2 - 1$  Patterson synthesis. The space group is  $P2_12_12_1$ , with four molecules in a unit cell of dimensions  $a = 11.304 \pm 0.010$ ,  $b = 14.785 \pm 0.015$  and  $c = 5.282 \pm 0.005$  Å. The molecule is in the *trans* C1 chair conformation. None of the C–C or C–OH bond lengths differ significantly from their respective means. The C(1)–O(1) bond is slightly shortened and there is a significant difference between the carbon oxygen bond lengths in the pyranose ring.

### Introduction

Methyl  $\alpha$ -D-glucopyranoside,  $C_7H_{14}O_6$ , is the more stable of the two glycosidic anomers obtained when glucose is heated with acidic methanol. This is contrary to the expectation that the more equatorially substituted  $\beta$ -anomer would be the configuration of least non-bonding interaction and the 'anomeric effect' has been postulated to account for this (Lemieux & Chü, 1958; Edward, 1955).

The results of previous crystal structure determinations have suggested that the hemiacetal group (*cf.* Robertson & Sheldrick, 1965; Kim & Jeffrey, 1967), which is that part of the molecule directly involved in anomerization and mutarotation, exhibits bond length variations dependent on whether the molecule is a free pyranose sugar or a glycoside. In particular, it has been proposed that the free hydroxyl of an  $\alpha$  anomer will have a short C(1)–O(1) bond length, whereas the corresponding bond in a glycoside will be normal, but that the differences then appear between the C–O ring links (*cf.* Berman, Chu & Jeffrey, 1967). This structure determination of the methyl glucoside was undertaken

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to obtain further data relating to this problem and to the study of hydrogen bonding in simple carbohydrates.

### Crystal data

The cell dimensions were measured on a Picker automatic four-angle diffractometer.

Methyl  $\alpha$ -glucopyranoside,  $C_7H_{14}O_6$ , M.W. 194.18, m.p. 165°.

Space group  $P2_12_12_1$ , from absences

$$\begin{aligned} h00, h &= 2n + 1 \\ 0k0, k &= 2n + 1 \\ 00l, l &= 2n + 1 \\ a &= 11.304 \pm 0.010 \text{ \AA} \\ b &= 14.785 \pm 0.015 \\ c &= 5.282 \pm 0.005 \\ D_x &= 1.461 \text{ g.cm}^{-3} \\ D_m &= 1.456 \\ \mu_{Cu K\alpha} &= 11.23 \text{ cm}^{-1}. \end{aligned}$$

The cell dimensions determined by Cox & Goodwin (1933) are  $a = 11.21$ ,  $b = 14.58$  and  $c = 5.29$  \AA.

### Experimental

Prismatic crystals with forms  $\{110\}$ ,  $\{120\}$ ,  $\{010\}$ ,  $\{101\}$ ,  $\{011\}$  (Groth, 1910) were grown from methanol solution. Visually estimated Weissenberg  $hk0$  data taken with Cu  $K\alpha$  radiation were used to solve the structure in projection.

A set of three-dimensional data were then taken on the Picker four-angle automatic diffractometer with Cu  $K\alpha$  radiation and a crystal cut to an approximate cube of dimensions  $0.3 \times 0.3 \times 0.3$  mm<sup>3</sup>. The 840 available data, of which 786 were observed above background, were collected in thirty hours with  $2\theta$  scan of 2° and 10 second background counts on each side. The data were reduced with use of a series of programs written for the IBM 1620 computer by Chu & Craven (1967). No absorption corrections were applied.

### Determination and refinement of the structure

The structure was solved by a straightforward but cautious application of the IBM 1620 sign correlation procedure of Beurskens (1963) to the  $hk0$  data. Four sets of signs were obtained and an  $E$  synthesis was calculated for each set. The thirteen highest peaks on one of the maps corresponded to the thirteen atoms of the structure and the first set of  $hk0$  structure factors using these coordinates gave an  $R$  value of 0.26. The other three maps had very uneven distribution of peak heights.

An  $E^2 - 1$  Patterson function was calculated with the three-dimensional data and the  $z$  coordinates were determined from an interpretation of the Harker sections, which were consistent with the molecular model and reasonable hydrogen bonding considerations. The first general structure factor calculation gave an  $R$  value of 0.40, with good agreement for most of the

Table 1. Fractional atomic coordinates and anisotropic thermal parameters in methyl  $\alpha$ -D-glucopyranoside

Key to atomic numbering is given in Fig. 1. The temperature factor expression used was  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$  and the estimated standard deviations are in parentheses.

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	0.5509 (3)	0.3749 (2)	0.4421 (6)	0.0061 (2)	0.0026 (1)	0.0258 (11)	0.0003 (1)	0.0013 (4)	0.0001 (3)
C(2)	0.4310 (3)	0.4107 (2)	0.3553 (6)	0.0063 (2)	0.0025 (1)	0.0215 (10)	0.0006 (1)	-0.0010 (5)	-0.0008 (3)
C(3)	0.3403 (2)	0.3964 (2)	0.5611 (6)	0.0056 (2)	0.0026 (1)	0.0234 (11)	0.0006 (1)	-0.0020 (5)	-0.0013 (3)
C(4)	0.3374 (3)	0.2962 (2)	0.6328 (7)	0.0047 (2)	0.0030 (1)	0.0314 (11)	0.0001 (1)	0.0018 (5)	-0.0001 (4)
C(5)	0.4606 (2)	0.2626 (2)	0.7034 (6)	0.0050 (2)	0.0024 (1)	0.0282 (11)	0.0002 (1)	0.0020 (4)	-0.0007 (3)
C(6)	0.4627 (2)	0.1620 (2)	0.7489 (7)	0.0046 (2)	0.0026 (1)	0.0402 (13)	0.0003 (1)	0.0001 (5)	0.0012 (4)
C(7)	0.7024 (3)	0.4069 (2)	0.7391 (9)	0.0063 (2)	0.0043 (2)	0.0466 (17)	-0.0002 (2)	-0.0044 (6)	-0.0009 (5)
O(1)	0.5865 (2)	0.4286 (1)	0.6495 (5)	0.0053 (2)	0.0030 (1)	0.0324 (9)	0.0004 (1)	-0.0015 (4)	-0.0014 (3)
O(2)	0.4390 (2)	0.5021 (1)	0.2742 (4)	0.0080 (2)	0.0027 (1)	0.0234 (8)	0.0004 (1)	-0.0009 (4)	0.0004 (2)
O(3)	0.2277 (2)	0.4247 (1)	0.4701 (5)	0.0052 (2)	0.0045 (1)	0.0293 (9)	0.0015 (1)	-0.0015 (3)	-0.0012 (3)
O(4)	0.2644 (2)	0.2805 (2)	0.8472 (6)	0.0059 (2)	0.0047 (1)	0.0479 (12)	0.0010 (1)	0.0053 (4)	0.0046 (3)
O(5)	0.5427 (2)	0.2821 (1)	0.5039 (4)	0.0053 (2)	0.0023 (1)	0.0261 (7)	0.0005 (1)	0.0031 (3)	-0.0012 (2)
O(6)	0.5690 (2)	0.1352 (1)	0.8761 (4)	0.0056 (2)	0.0032 (1)	0.0319 (8)	0.0005 (1)	-0.0009 (3)	0.0022 (3)
H(C1)	0.610	0.380	0.280						
H(C2)	0.410	0.370	0.190						
H(C3)	0.370	0.430	0.730						
H(C4)	0.300	0.250	0.490						
H(C5)	0.500	0.300	0.870						
H(C6)	0.460	0.120	0.575						
H(C6')	0.390	0.140	0.830						
H(C7)	0.590	0.340	0.820						
H(C7')	0.710	0.450	0.870						
H(C7'')	0.780	0.420	0.650						
H(O2)	0.440	0.540	0.400						
H(O3)	0.170	0.440	0.600						
H(O4)	0.180	0.310	0.820						
H(O6)	0.640	0.110	0.750						

strong reflections. However, one weak reflection, 021, gave particularly poor agreement, which was corrected by shifting the  $z$  coordinates of the whole molecule by 0.05. The  $R$  index was then 0.27. Several cycles of isotropic refinement and one cycle of anisotropic refinement, using the Busing, Martin & Levy (1962) least-squares program as modified by Shiono (1966) and the Cruickshank (1961) weighting scheme, reduced  $R$  to 0.09. The difference synthesis with  $\sin \theta \leq 0.7$  then

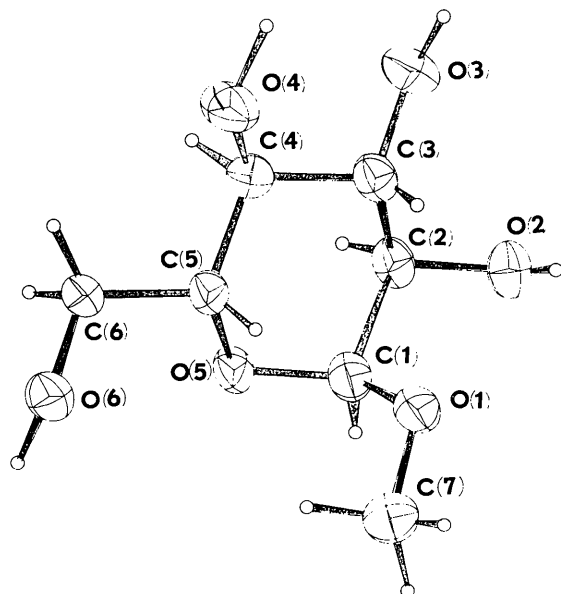


Fig. 1. Identification and numbering of the atoms in methyl  $\alpha$ -D-glucopyranoside.

showed many minor peaks including some at reasonable positions for the hydrogen atoms. A malfunction in the electronics which did not enable the scaler to count beyond 4000 c.p.s. was then discovered. After correction, the strong reflections and an equal number of moderate reflections were remeasured, scaled, and included in the refinement. The new difference synthesis then showed hydrogens at likely positions with no spurious peaks. With these coordinates included, several refinement cycles of positional and thermal parameters of the heavier atoms gave a final  $R$  value of 0.041. The final positional and anisotropic thermal parameters are given in Table 1 and the corresponding r.m.s. displacements in Table 2. The structure factors are given in Table 3; the unobserved and seven strong low order reflections were not included in the refinement and are so indicated.

### Description of the structure

The formal nomenclature for  $\alpha$ -methyl glucoside is methyl  $\alpha$ -D-glucopyranoside. The configuration and atomic numbering are given in Fig. 1. The molecule is in the conventional  $1C_4$  *trans* chair conformation with the conformation angles around the pyranose ring ranging from 54.2 to 60.2°, as compared with 55.8 → 61.7° for an ideal\* pyranose ring and 51.3 → 62.2°, 54.8 → 56.0°, and 56.2 → 60.5° for glucose (Brown & Levy, 1965), sucrose (Brown & Levy, 1963), and  $\beta$ -methyl maltoside (Chu & Jeffrey, 1967), respectively.

\* Hypothetical pyranose ring with C-C 1.525, C=O 1.430 Å, valence angle on carbon atoms 109.5° and that on ring oxygen atoms 113.3°.

Table 2. Principal axes of thermal ellipsoids

The root mean square displacement  $U_i$  corresponds to the  $i$ th principal axis of the ellipsoid and  $\theta_{ia}, \theta_{ib}, \theta_{ic}$  are angles between the  $i$ th axis and the crystallographic axes,  $a, b, c$ .

	$i$	$U_i$	$\theta_{ia}$	$\theta_{ib}$	$\theta_{ic}$		$i$	$U_i$	$\theta_{ia}$	$\theta_{ib}$	$\theta_{ic}$
C(1)	1	0.1669 Å	104.48°	15.32°	85.10°	O(1)	1	0.1728 Å	122.59°	33.76°	82.12°
	2	0.1841	121.40	102.02	34.13		2	0.1836	140.54	114.96	118.36
	3	0.2059	35.31	80.64	56.31		3	0.2232	70.29	68.79	150.36
C(2)	1	0.1578	102.50	27.43	66.00	O(2)	1	0.1682	99.73	27.34	115.28
	2	0.1734	113.44	72.53	150.10		2	0.1836	93.29	116.20	153.55
	3	0.2103	26.92	69.54	106.74		3	0.2287	10.28	82.71	97.22
C(3)	1	0.1601	101.23	28.67	63.99	O(3)	1	0.1623	28.12	116.97	82.62
	2	0.1689	133.14	78.52	134.58		2	0.1983	92.76	110.94	158.85
	3	0.2117	45.32	64.10	124.13		3	0.2431	62.03	35.27	109.69
C(4)	1	0.1674	22.93	103.33	108.30	O(4)	1	0.1769	22.41	93.05	112.18
	2	0.1839	102.74	166.65	86.12		3	0.2011	81.45	149.50	60.97
	3	0.2150	71.26	90.40	18.74		3	0.2939	69.43	59.69	37.93
C(5)	1	0.1570	114.57	31.34	71.78	O(5)	1	0.1393	120.11	43.00	62.47
	2	0.1755	141.30	120.76	68.94		2	0.1799	124.33	132.96	62.21
	3	0.2082	62.17	95.42	28.43		3	0.2127	49.01	91.53	41.02
C(6)	1	0.1639	128.74	39.56	96.76	O(6)	1	0.1672	119.51	42.11	117.06
	2	0.1769	141.22	127.91	83.04		2	0.1982	150.46	115.51	76.12
	3	0.2402	88.80	80.34	9.72		3	0.2243	91.04	59.07	30.94
C(7)	1	0.1853	26.80	78.00	66.40						
	2	0.2185	76.21	166.12	91.54						
	3	0.2683	112.51	96.86	23.86						

These results indicate that the range of angles becomes narrower as the ring is more heavily substituted at the O(1) position. The conformation of the C(5)-C(6) bond is plus synclinal (*Psc*) (+73.5°) and thus falls into the range most commonly found in pyranose sugars (Sundaralingam, 1967). The distortion from the idealized 60° is possibly caused by the participation of O(6) in three hydrogen bonds.

As shown in Table 4, the C-C distances vary from 1.506 to 1.531 Å, with an average of 1.519 Å. This spread is not significantly reduced by applying the thermal corrections assuming a riding motion (Busing & Levy, 1964). The carbon valence angles interior to the pyranose ring (109.1 → 110.8°) show a narrower range of values than the exterior angles (106.4 → 113.1°). The oxygen valence angles, 114.0° within the

Table 3. *Observed and calculated structure factors*Columns are Index, |F<sub>Obs</sub>|, |F<sub>Calc</sub>|, A<sub>Calc</sub>, B<sub>Calc</sub>.

\* indicates unobserved reflections, + indicates reflections excluded from refinement.

K=0 H=0	0	0	335 394	0	394	4 45 51 51	0	3 158 148 0	148-	3 219 216 0	216-	
2 190 202 202	0	0	510 * 625	592-	199-	5 41 41 0	41-	4 102 107 107	0	4 147 147 0	0	
4 39 35 35	0	2	214 233 36	230-	0	15 20 20	0	5 36 36 0	36-	5 25 25 0	25	
6 24 25 25	0	3	230 228 223	49	1 384 413 341-	234-	0	0 31 29 0	29-	0 307 318 318-	0	
1 567 * 667 0	667-	4	69 65 64-	10-	2 156 152 150-	22-	1	1 154 156 109-	111-	1 296 305 305-	8-	
2 91 86 0	86-	5	24 22 7-	21-	3 202 203 195 55	2	2	3 371 376 150	345	2 403 412 351-	215	
3 233 208 0	208-	6	38 37 37	2-	4 52 44 44-	24-	3	130 137 8-	134-	3 180 177 31	172-	
4 15 20 0	20	7	396 * 452	0	452	5 90 92 46	80-	4	81 82 79-	20	4 108 108 93	55
5 91 89 0	89-	8	479 * 541 159-	517-	0	77 78 78	0	5	134 134 30-	130	5 52 54 5	54-
6 61 59 0	59	9	2 158 168 74	151	1 494 542 542	13-	0	0 298 274	0	0 289 309 309-	0	
0 168 166 166	0	3	216 215 159-	145	2 313 315 290-	12-	2	478 503 447	229-	1 200 199 39	195	
1 5 * 2 4 8-	0	4	22 22 8-	20-	3 116 114 33	109	2	386 390 338	193	2 354 351 93	338	
2 126 125 125-	0	5	33 34 5-	34-	4 195 195 160-	111-	3	143 145 75	125	3 148 147 92	115	
3 89 88 88	0	6	156 156 0	156	5 33 36 3	36	4	168 167 165-	27	4 27 21 4	21-	
4 26 29 29	0	7	628 * 710 371	685-	0	396 427 420-	392	5	70 72 2-	72-	5 66 73 55	48
5 30 30 30	0	8	133 133 131-	22	1 486 509 325-	392	0	0 280 304 0	304-	0 87 95 95	0	
6 42 46 46-	0	9	83 77 76	9-	2 190 204 180	97	1	96 93 27	89-	1 191 191 179-	66-	
1 433 455 0	455-	4	153 153 25	151-	3 148 140 98-	100	2	187 175 144-	99	2 164 152 88	124-	
2 160 149 0	149	5	77 79 36-	71	4 111 112 63	92	3	80 77 73	11	3 24 19 17	17	
3 97 93 0	93	6	215 198 0	198	5 90 93 6	93	4	147 152 43-	146	4 78 82 82	4	
4 45 41 0	41-	7	373 389 301-	247-	0	6 * 4 4-	0	5	137 141 14	140	5 23 25 24	5-
5 42 36 0	36	8	2 295 293 156	248-	1 230 231 197-	122-	0	0 39 42 0	42	0 260 254 254	0	
0 262 291 291-	0	3	161 168 142-	89	2 183 189 31-	186	1	164 163 162	20	1 135 121 97	72-	
1 111 100 100-	0	4	96 92 27	80-	3 88 89 78-	83	2	90 87 71	51-	2 136 134 26	131	
2 103 168 168-	0	5	38 36 24-	26-	4 220 229 205	103-	3	106 98 80-	57	3 110 113 104	43-	
3 134 128 128	0	6	223 206 0	206-	5 62 57 2-	57	4	115 118 92	74-	4 28 26 18-	19-	
4 124 124 124	0	7	73 63 60	17	1 95 16 16-	0	5	58 56 9	56	5 38 36 1	36	
5 50 46 46-	0	8	438 461 296	354	2 72 68 36	80-	0	64 56 3	56	0 64 63 63	0	
1 396 414 0	414-	3	135 126 120-	38-	2 19 19 10-	68-	1	96 92 49-	77-	1 196 196 196-	15-	
2 135 133 0	133	4	74 60 14-	59	3 192 184 14	184	2	79 83 80	22	2 54 54 48	24	
3 79 76 0	76	5	108 110 100-	47-	4 50 51 50-	6-	3	71 73 69-	22	3 172 172 107	136-	
4 80 78 0	78-	6	352 359 0	359	5 128 133 132-	19-	4	74 76 76	1	4 77 80 44-	67-	
5 42 44 0	44-	7	192 107 20	196-	0	336 344 344	0	5	52 51 47-	20	5 64 65 53-	38-
0 505 572 572-	0	2	168 165 165-	2	1 171 156 128-	90	0	118 111 0	111	0 99 96 96-	0	
1 544 565 565-	0	3	88 83 9-	83	2 71 77 62-	47-	1	87 90 40-	81	1 55 50 16-	47	
2 224 211 211-	0	4	34 30 16	25-	3 83 74 56-	48-	2	86 94 68-	66	2 93 85 69-	50-	
3 136 136 136-	0	5	47 4 50-	4	4 144 137 122	64	3	153 148 142	41	3 10 * 4 4-	2	
4 37 39 39	0	6	207 190 0	190	5 64 60 60-	22	4	87 89 4-	89	4 48 52 43-	30	
5 90 90 90	0	7	149 141 117	78	0 10 * 6 6-	0	5	54 53 43	32	5 20 19 17-	8-	
1 263 255 0	255	2	145 138 70	119	1 79 61 10	60	0	499 519 0	519	0 8 * 7 H = 4	0	
2 8 * 7 0	21-	3	120 114 42-	107	2 120 114 42-	107	1	87 85 60	60	1 68 73 70	19	
3 35 36 0	36	4	30 27 9	26-	3 135 137 125	57-	2	77 76 36	67-	2 194 187 115	147-	
4 59 59 0	59-	5	58 56 48	29-	4 22 27 27	6-	3	100 92 92	0	3 276 288 288	13-	
5 29 30 0	30	6	586 614 0	614-	5 59 62 57-	25	4	79 75 75	1	4 144 13 12	5-	
0 159 137 137	0	7	163 149 77	128-	0 329 333 333	0	5	70 71 31	54	5 93 91 89-	17	
1 375 379 379	0	8	128 119 117	24	1 131 131 57-	118	0	69 66 0	66-	0 15 * 16 16	0	
2 117 117 117-	0	9	74 71 57	42-	2 26 21 17	13	1	27 22 22	22	1 89 97 91	32	
3 20 * 16 16-	0	10	56 54 52-	14-	3 85 87 87-	81-	2	181 177 175-	23	2 113 112 80-	79-	
4 60 64 64	0	11	47 48 24-	42-	4 69 69 40	57	3	194 197 164	39	3 208 208 85	187-	
5 26 23 23	0	12	216 210 0	210-	5 48 49 44	21	4	74 78 22	75-	4 49 43 35-	25-	
1 293 295 0	295	13	232 229 219-	66	0 79 70 70-	0	5	68 62 36-	51-	0 85 81 81-	0	
2 77 69 0	69	14	163 157 110-	112	1 84 87 86-	30-	6	140 134 0	134-	1 43 42 41	42-	
3 98 96 0	96-	15	64 68 42-	53-	2 58 59 52-	28	7	91 86 86-	86	2 45 43 43-	6-	
4 64 63 0	63-	16	67 67 61-	29	3 135 130 101	82-	8	206 211 82	195	3 99 96 22-	93	
5 15 * 12 0	0	17	62 65 0	65	4 107 104 87	56	9	15 * 15 6-	14-	4 19 18 11	14	
0 231 235 235	0	18	258 259 150	211-	5 40 39 14-	37-	10	31 32 27-	17-	0 45 46 46-	0	
1 29 * 28 28-	0	19	108 106 2	106	0 90 100 100-	0	11	71 65 0	65	1 166 159 139-	70-	
2 16 * 9 9	0	20	91 93 40	84	1 70 71 41	58	12	208 209 22	208-	2 90 86 14	84-	
3 54 57 0	57	21	149 144 50-	135	2 93 92 44	84-	13	63 64 63	12-	3 33 38 11	37-	
4 22 20 20	0	22	166 3 0	3	3 149 153 143	54-	14	52 55 55	3	4 22 23 7	22	
1 13 11 0	11-	23	144 145 104	101	4 78 83 40	26	15	78 83 40	73	0 218 219 219-	0	
2 64 66 0	66	24	120 121 57-	106-	5 58 59 59	0	16	139 142 0	142-	1 185 184 174-	60	
3 104 105 0	105-	25	136 137 75	115	1 204 204 185-	86-	17	101 105 104	6-	2 52 52 41-	33-	
4 61 60 0	60-	26	35 41 21	35-	2 134 133 129	130	18	82 86 78-	35	3 42 40 40-	21	
0 63 72 72	0	27	30 32 0	32-	3 128 124 36	119-	19	43 48 16-	45-	4 45 49 44-	2	
1 24 20 20	0	28	82 80 20-	20-	4 111 112 84-	74-	20	43 48 16-	45-	0 17 * 22 22	0	
2 189 204 204-	0	29	93 88 87	9	5 34 25 25	0	21	119 123 0	123-	1 115 113 18	112	
3 44 39 39-	0	30	49 48 12-	42-	6 30 31 27	39	22	121 121 117-	30	2 45 43 43-	6-	
4 84 86 86	0	31	39 42 2-	42-	7 213 219 199-	92-	23	151 149 144	39	3 228 228 85	26	
1 10 * 4 0	4	32	32 32 0	32-	8 49 43 14	40	24	28 30 24	34	4 4 * 13 H = 4	0	
2 10 12 0	12	33	62 59 41-	42-	9 49 48 37-	30	25	48 49 34-	35-	0 241 251 251	0	
3 86 81 0	81	34	62 59 41-	42-	10 37 41 141	30	26	37 31 0	31	1 94 96 92-	26	
0 250 236 236	0	35	74 71 68	18	1 137 138 125-	57	27	124 127 81-	98	2 21 10 14-	12	
1 47 41 41-	0	36	31 31 0	31	2 104 99 60	79-	28	59 59 23	57	3 68 67 20	64	
2 10 * 13 13	0	37	34 29 27-	9	3 66 66 11-	66	29	26 24 13	20-	0 45 44 44-	0	
3 6 * 1 0	0	38	30 28 27	7-	4 61 64 64	0	30	26 24 13	20-	1 35 35 35-	1	
0 54 48 0	48-	39	76 76 22-	73	5 61 67 14	66-	31	78 79 69-	39-	2 71 71 8	71	
2 36 40 0	40-	40	30 30 0	30-	6 62 61 51-	34-	32	20 20 7-	19	0 6 * 3 3-	0	
0 36 30 30-	0	41	43 40 38-	13-	7 25 24 24	0	33	70 73 67	30	1 45 44 41-	15-	
1 6 * 9 9	0	42	29 26 4-	26	8 25 24 24	0	34	28 27 0	27	2 52 51 11-	50	
0 450 501 0	501	43	16 * 7 0	7-	9 29 31 1-	31-	35	50 54 21-	50-	0 39 38 38-	0	
2 109 114 114	0	44	31 27 3	27-	10 19 23 21-	10-	36	51 53 0	53	1 202 208 0	208	
3 79 76 0	76	45	411 * 485 2	0	11 43 47 47	0	37	13 * 8 0	8-	2 241 236 236	0	
4 78 85 85-	0	46	77 94 0	94	12 28 26 13	22-	38	61 59 59	2	3 92 80 0	80-	
5 52 50 0	50-	47	187 177 177-	0	13 243 249 0	249-	39	376 367 367	0	4 33 33 33-	0	
6 6 * 16 16	0	48	204 205 0	205-	14 281 177 177-	0	40	129 130 0	130-	5 67 69 0	69	
								2 54 58 58	0	0 102 105 0	105-	

Table 3 (cont.)

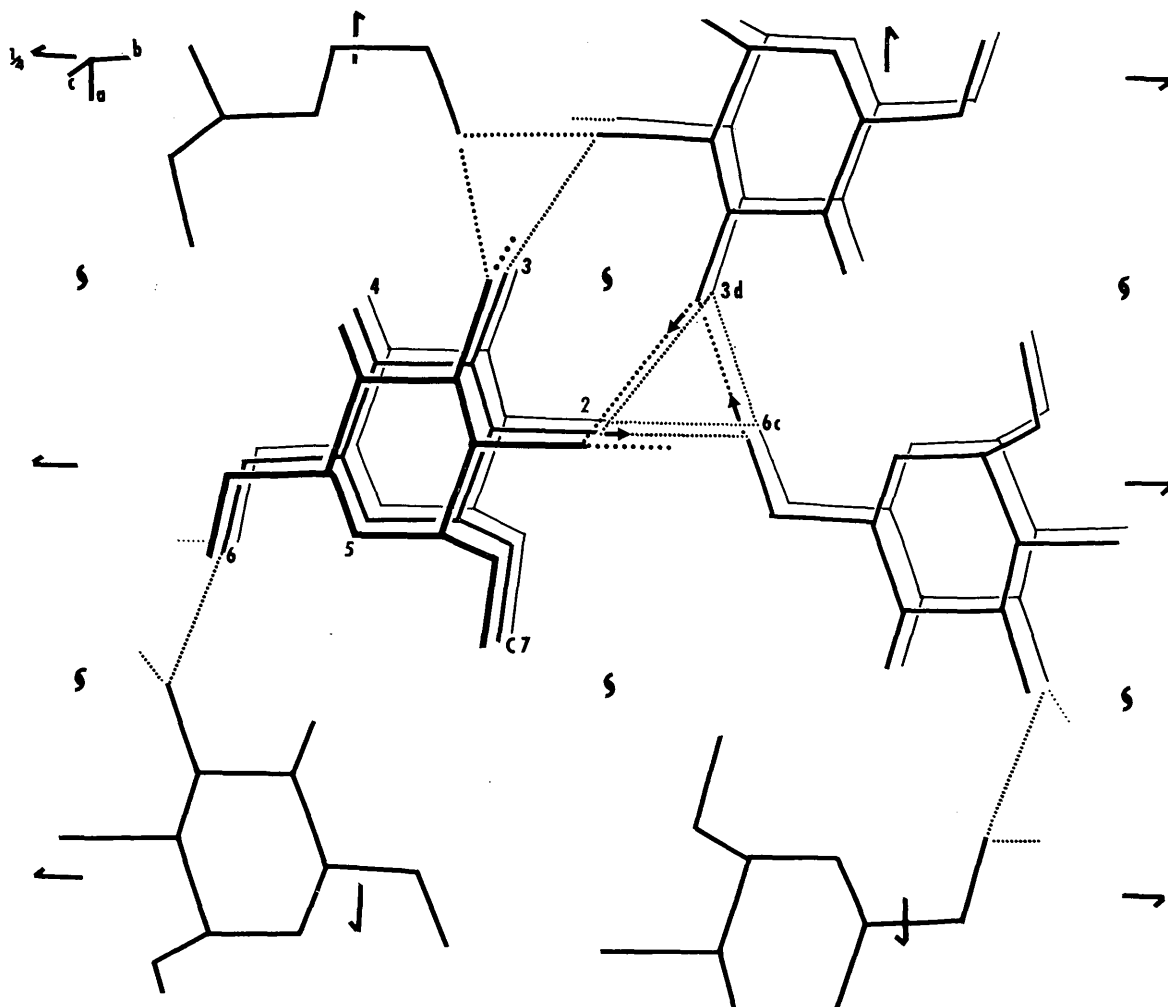
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2	108	104	33	99	2	75	65	48	46	0	115	112	15-	111	0	134	133	133-	0	2	83	88	82-	32
3	197	191	96-	165-	3	128	132	132-	11	1	146	148	6	148	1	87	90	17-	89-	3	28	27	12-	24-
4	20	11	11	-	4	57	58	1-	58-	2	83	91	44-	79-	2	102	104	7-	104	0	64	56	56-	10
5	47	42	10	5	4	270	261	261-	0	3	125	123	87	87	3	13	13	5	12	0	64	56	56-	10
0	24	0	0	25-	0	234	231	261-	0	0	45	43	0	43	0	97	86	86-	0	2	41	38	37-	12-
1	329	323	315	70-	1	194	191	72-	177	0	166	27	27-	3-	1	76	78	63	46-	3	21	30	2-	30
2	61	60	40	46-	2	72	68	65	21	0	134	131	113-	68	2	50	48	47-	11	0	65	62	62-	10
3	59	56	48-	28-	3	127	132	51-	121-	2	148	159	158	19	3	68	66	7-	66	0	65	62	62-	10
4	31	28	26-	7-	4	25	27	24-	12	4	25	27	27-	5-	0	80	72	72-	0	2	128	122	82	91-
5	62	63	36-	52	5	26	26	0	26	4	89	84	0	84-	1	56	60	40-	44	3	22	22	15-	16-
0	313	322	0	322-	0	42	32	32	0	0	112	113	10-	113	2	37	39	22	33-	1	52	57	56-	10
1	347	325	4	325-	1	45	46	36	24-	1	112	113	10-	113	3	54	55	35-	3-	0	52	57	56-	10
2	38	31	31	2	2	83	80	63	48-	2	103	105	103	18-	3	33	18	0	16-	1	7*	7	5	4
3	55	53	18	50-	3	12*	7	7-	1-	3	151	153	135	73-	4	48	45	25-	38	0	124	120	120-	0
4	155	157	54	148-	4	90	90	82-	37-	4	62	61	21	58	3	82	82	17	80-	0	28	25	25-	46
5	43	40	23	33	5	71	70	62-	33	0	33	35	0	35-	2	82	82	17	80-	0	28	25	25-	46
0	327	324	0	324-	0	6*	10	10	0	1	113	111	105	35	2	98	105	62-	85-	0	9*	24	24-	0
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2	166	163	133	94-	1	108	104	42-	95-	4	76	75	26-	71-	2	105	108	107	10	3	52	55	5	55
3	37	37	32-	19	2	108	104	42-	95-	4	76	75	26-	71-	2	105	108	107	10	3	52	55	5	55
4	89	83	47	83	3	45	43	20-	38-	0	117	123	115	115	0	117	123	115	115	0	117	123	115	115
5	46	42	12-	41-	4	144	151	98	119	0	117	123	115	115	0	117	123	115	115	0	117	123	115	115
0	45	43	0	43-	0	113	110	110	0	2	82	85	7	85-	1	33	35	0	35	0	110	108	108	10
1	151	144	142-	25	0	113	110	110	0	3	124	126	125-	14-	1	33	35	0	35	0	110	108	108	10
2	208	204	129	161	1	179	173	137	106	4	40	41	6-	40-	2	60	57	57-	0	0	96	95	95-	0
3	25	27	14	23-	2	22	18	13-	12-	0	18*	4	0	4-	4	30	30	30	0	2	25	26	20	17-
4	28	29	16	25-	3	99	103	65	80	1	22	21	7	20	0	56	38	0	38-	0	110	108	108	10
5	58	55	6-	55-	4	74	75	65-	36	1	22	21	7	20	0	56	38	0	38-	0	110	108	108	10
0	27	25	0	25-	0	87	86	84	0	2	89	96	29	92	0	128	293	190	223	1	48	45	42	15-
1	10	8	6	5-	1	82	82	74-	23	0	58	62	20	57-	2	90	86	46-	2	2	31	20	16	26
2	140	143	143-	14	2	116	118	43	104	0	28	26	0	26	3	20	19	11	16-	0	10	10	10	10
3	47	38	24-	30-	3	84	82	78	26	1	109	111	46	102	4	25	26	26	6	0	29	30	30-	0
4	70	68	67-	12	4	48	47	44	18	2	86	87	19-	85-	0	105	97	0	97-	0	87	88	74	48-
5	42	38	36	22-	5	54	52	45	37	3	58	58	45	37	0	105	97	0	97-	0	87	88	74	48-
0	82	92	0	92-	0	30	29	29-	0	0	77	76	0	76-	1	140	135	48-	126	1	30	29	0	29-
1	73	78	73-	26	2	88	86	79	35-	1	79	78	54-	57-	3	44	45	37	26-	3	31	28	0	28
2	61	66	66-	1-	3	52	47	19	43-	2	109	111	42	63-	4	37	32	22	23-	0	154	153	0	159
3	29	29	24	22	4	9*	9	4	7	3	88	91	72-	56	0	77	81	0	81-	0	154	153	0	159
4	10	6	0	6-	0	53	55	55	0	0	16*	11	0	11	1	149	150	135-	66	2	63	57	34	46-
0	34	33	0	33-	1	95	91	32	85-	1	51	50	43-	27	2	151	159	156	28	3	15*	18	14	12-
1	137	132	120	55	2	123	132	21-	130-	2	37	42	40	10	3	26	31	9	30	0	51	55	0	53
2	183	179	168-	62	3	54	61	21-	130-	2	37	42	40	10	3	26	31	9	30	0	51	55	0	53
3	59	64	50-	40-	4	96	91	88	24	0	32	31	0	31	0	4*	51	0	51-	2	49	46	29-	35-
4	49	52	19-	48-	0	63	57	57	0	2	44	42	23-	35	1	101	97	82-	52	3	33	34	5	34-
0	50	45	0	45-	0	192	177	36-	80-	0	43	44	0	44-	0	136	124	5	24-	0	77	80	11	80-
1	154	156	57-	145	2	61	61	61	8	0	43	44	0	44-	3	16*	26	13-	23-	0	77	80	11	80-
2	297	307	41	304	3	25	23	19-	12-	0	364	377	377-	0	4	9*	18	17	4-	1	48	49	36-	34
3	20*	22	17-	14	4	43	42	39-	16	0	155	144	0	144	0	65	63	0	63	3	48	46	39-	24
4	27	28	21-	18	0	129	131	130	0	2	58	62	60	70	1	43	41	19-	36	6	6*	6*	11	11
0	223	225	0	225	0	199	203	167-	114-	3	125	120	0	120-	2	53	54	53-	10	0	131	130	0	130
1	256	258	232	112	2	71	70	36	60-	4	7*	2	2	0	3	69	67	64-	20-	1	31	34	16	30-
2	164	163	162	15	3	65	64	29	57	0	165	148	148	0	0	35	38	0	38-	0	81	81	58-	56
3	58	57	46	33	0	64	65	65-	0	1	135	131	131	108	1	37	35	32	15-	0	8*	0	0	0
4	42	42	27-	33-	1	89	89	62-	63	2	130	128	126-	23	2	73	74	74	4	1	48	56	45	34-
0	21	15	0	15-	2	31	30	28	11	3	55	44	38	22-	3	45	42	21	36-	2	12*	16	4	16-
1	46	48	19	44-	3	26	29	27-	11-	4	22	24	4-	24	0	176	188	0	188	0	24	29	0	29-
2	71	70	43	56-	0	83	88	88	0	0	70	71	71-	0	1	112	113	96-	96-	1	36	35	35	1
3	48	50	15	48	0	36	39	35-	16	1	97	95	51-	80	2	46	99	25-	96-	0	60*	7	11	11
0	26	24	0	24	2	50	46	35	30	2	208	217	141	164-	3	27	24	22-	10-	0	6*	7	0	7-
1	46	43	15	47	0	46	49	51	6	3	136	141	63-	126	6	162	161	0	161	1	52	48	48	4
2	54	56	55	12-	0	141	146	146-	0	4	21	17	16	6	0	162	161	0	161	1	52	48	48	4
3	39	41	19	36-	1	56	57	26	51-	0	250	252	252	0	2	72	71	42	58	0	51	56	0	56
0	141	141	0	141-	0	31	35	33-	0	1	78	75	31	68-	3	40	40	8-	39-	1	54	56	54-	16-
1	80	84	60	84	1	159	158	147	59	2	149	149	121	86-	0	14*	3	0	3	0	15	15	15	0
2	31	31	27	14	1	73	65	0	65-	3	46	46	44-	13-	0	14*	3	0	3	0	15	15	15	0
3	53	55	32-	45-	2	271	278	278-	0	4	52	54	39	37	1	126	120	118	19-	1	11*	12	0	12
0	15*	19	0	19-	4	15*	16	16-	0	0	105	107	107	0	1	74	77	66	39-	0	6*	5	0	5
1	69	64	60-	35-	5	26	30	0	30	2	34	31	21	23	0	6*	5	0	5-	0	6*	2	2	2
2	36	36	33	14-	0	25																		

Table 4. Bond lengths and angles in methyl  $\alpha$ -D-glucopyranoside

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

<i>i</i>	<i>j</i>	<i>D</i> ( <i>ij</i> )	<i>D</i> ( <i>ij</i> )*	<i>i</i>	<i>j</i>	<i>k</i>	$\angle$ ( <i>ijk</i> )
C(1)	C(2)	1.526 (4) Å	[1.526] Å	C(1)	C(2)	C(3)	109.8 (2)°
C(2)	C(3)	1.509 (4)	[1.509]	C(2)	C(3)	C(4)	109.1 (2)
C(3)	C(4)	1.531 (4)	[1.533]	C(3)	C(4)	C(5)	110.8 (2)
C(4)	C(5)	1.525 (4)	[1.528]	C(4)	C(5)	C(6)	112.0 (2)
C(5)	C(6)	1.506 (4)	[1.511]	C(4)	C(5)	O(5)	110.2 (2)
C(1)	O(1)	1.411 (4)	[1.414]	C(5)	O(5)	C(1)	114.0 (2)
C(2)	O(2)	1.421 (4)	[1.426]	O(1)	C(1)	C(2)	106.9 (2)
C(3)	O(3)	1.423 (4)	[1.432]	C(1)	C(2)	O(2)	111.3 (2)
C(4)	O(4)	1.420 (4)	[1.435]	C(2)	C(3)	O(3)	108.8 (2)
C(5)	O(5)	1.434 (4)	[1.434]	O(3)	C(3)	C(4)	110.4 (2)
C(1)	O(5)	1.414 (4)	[1.416]	C(3)	C(4)	O(4)	111.6 (2)
C(6)	O(6)	1.433 (4)	[1.434]	O(4)	C(4)	C(5)	106.4 (2)
C(7)	O(1)	1.430 (4)	[1.442]	C(4)	C(5)	O(5)	110.2 (2)
				O(5)	C(1)	C(2)	110.2 (2)
				C(1)	O(1)	C(7)	113.0 (2)
				O(5)	C(1)	O(1)	112.6 (2)
				O(2)	C(2)	C(3)	113.1 (2)
				C(5)	C(6)	O(6)	111.2 (2)
				O(5)	C(5)	C(6)	107.8 (2)

\* Bond lengths corrected assuming 'riding motion' (Busing &amp; Levy, 1964).

Fig. 2. The crystal structure of methyl  $\alpha$ -D-glucopyranoside viewed down the *c* axis, showing the helical arrangement of hydrogen bonds.

the bonds in unsubstituted pyranose sugars, is shortened by  $3\sigma$  from the average C–OH bond in  $\alpha$ -methyl glucoside. They correspond more closely to those of  $\beta$ -methyl maltoside than to sucrose, where there is part of a C–O–C–O–C–O–C conjugated system in the  $\alpha$  link (Sundaralingam, 1967).

The hydrogen bonding scheme, illustrated in Fig. 2, consists of pairs of three-membered helices O(2)–O(6*c*)–O(3*d*)–O(2*a*) related by the *c* screw axis. For every pair of helices spiraling in the +*c* direction, there is another in the –*c* direction. This is a characteristic feature of several carbohydrate crystal structures and similar helices were found in methyl maltoside, sucrose and glucose.

The hydrogen bonding O...O distances involved in this helical arrangement are unusually close to the average value of 2.704 Å (Table 6), and the O–H...O angles are comparable to those observed in carbohydrates where the hydrogen positions have been more precisely determined by neutron diffraction (Brown & Levy, 1963, 1965). The ring and glycosidic oxygens do not participate in the hydrogen bonding scheme, although O(5) has a close intermolecular O...O contact, *i.e.* to O(4), of 3.25 Å. All other O...O contacts are > 3.3 Å.

The hydrogen-bond environment for O(4) is similar to that of the corresponding atom in the glucose unit of sucrose, as shown below:

Methyl $\alpha$ -glucoside	O...O	O–H–O
	O(5)	3.252 Å 113.5°
	O(4)H	
	O(6)	2.927 124.6
Sucrose	O...O	O–H–O
	O(2)	2.835 Å 117.2°
	O(4)H	
	O(6)	3.370 151.5

In both structures, O(4) is in close contact with the oxygen of a CH<sub>2</sub>OH group and a ring oxygen atom. In each, one contact is longer than a hydrogen bonding

Table 6. *Hydrogen bonding distances and angles*

		Symmetry code		
–		<i>x</i>	<i>y</i>	<i>z</i>
<i>a</i>		<i>x</i>	<i>y</i>	1 + <i>z</i>
<i>b</i>		0.5 + <i>x</i>	0.5 – <i>y</i>	1 – <i>z</i>
<i>c</i>		1 – <i>x</i>	0.5 + <i>y</i>	1.5 – <i>z</i>
<i>d</i>		0.5 – <i>x</i>	1 – <i>y</i>	0.5 + <i>z</i>
<i>e</i>		1.5 – <i>x</i>	1 – <i>y</i>	0.5 + <i>z</i>
<i>f</i>		–0.5 + <i>x</i>	0.5 – <i>y</i>	2 – <i>z</i>

<i>i</i>	<i>j</i>	<i>k</i>	<i>D</i> ( <i>jk</i> )	$\angle$ ( <i>ijk</i> )
C(2)	O(2)	O(6 <i>c</i> )	2.700 Å	118.9°
C(3)	O(3)	O(2 <i>d</i> )	2.702	122.6
C(6)	O(6)	O(3 <i>b</i> )	2.710	109.2
C(4)	O(4)	O(6 <i>f</i> )	2.927	140.0
O(2)	H(O2)	O(6 <i>c</i> )	1.84	169
O(3)	H(O3)	O(2 <i>d</i> )	1.76	162
O(6)	H(O6)	O(3 <i>b</i> )	1.61	170
O(4)	H(O4)	O(6 <i>f</i> )	2.19	125

Intermolecular non-bonded O...O distances less than 3.3 Å

O(5)	O(4) <i>b</i>	3.252 Å
------	---------------	---------

Interatomic contacts between CH<sub>3</sub> and CH<sub>2</sub> groups.\*

<i>i</i>	<i>j</i>	<i>D</i> ( <i>ij</i> )
C(7)	C(7) <i>e</i>	3.60 Å
H(C7')	C(7) <i>e</i>	3.04
H(C6')	C(7) <i>f</i>	3.19
H(C7'')	C(6) <i>b</i>	3.19
H(C7''')	H(C6) <i>b</i>	2.43
H(C7')	H(C7'') <i>e</i>	2.43

\* All distances listed are within 0.3 Å of the sum of the van der Waals radii assuming that C = 1.7 Å and H = 1.2 Å.

distance and the other has a reasonable hydrogen bonding distance but an O–H–O angle which shows that the hydrogen is far from the line of centers. In  $\alpha$ -methyl glucoside, the O(4)–O(6) contact has the appropriate hydrogen bonding distance and a rather small angle of 124°. Since O(6) is already involved as a donor and acceptor in the hydrogen bonding scheme, we may classify O(4)–O(6) at best as a weak hydrogen bond. In sucrose, Brown & Levy (1963) have described O(4)–O'(2) (where O(2) is the ring oxygen of the fructose group) as a close contact rather than a hydrogen bond, on the basis of their more precise determination of the hydrogen atom position.

The close packing of the non-polar C(7)H<sub>3</sub> and C(6)H<sub>2</sub> groups around the screw axis parallel to *c* at  $\frac{3}{4}, \frac{1}{2}$  may be as important a structure determinant as the helical hydrogen bonding pairs, as shown in Table 6. There are six pairs of atoms within van der Waals

Table 5. *Summary of bond length variations in glucosidic sugars*

Average C–C†	Average C–O(H)†	$3\sigma$ (10 <sup>–3</sup> Å)	$\Delta$ (10 <sup>–3</sup> Å)*				Compound
			C(5)–O(5)	O(5)–C(1)	C(1)–O(1)	O(1)–R	
1.523 (24) Å	1.417 (12) Å	9	+10	+09	–28	H	$\alpha$ -D-Glucose (Brown & Levy, 1965)
1.519 (25)	1.424 (13)	12	+10	–10	–13	CH <sub>3</sub>	Methyl $\alpha$ -D-glucoside (this work)
1.524 (19)	1.428 (12)	22	+12	–20	–12	gluc.	$\beta$ -Methyl maltoside (Chu & Jeffrey, 1967)
1.525 (14)	1.418 (10)	9	+18	–10	+02	fruc.	Sucrose (Brown & Levy, 1963)
1.519 (18)	1.424 (11)	12	+13	+09	–41	H	$\beta$ -D-Glucose (Chu, 1967)

\*  $\Delta$  refers to deviation from mean carbon hydroxyl length.

† Number in parentheses refers to range of values in 10<sup>–3</sup> Å.

contact distance. The alternation of these types of polar and non-polar regions is also found in  $\beta$ -methyl maltoside (Chu & Jeffrey, 1967) and  $\beta$ -methyl xyloside (Brown, Cox & Llewellyn, 1966).

The thermal ellipsoid parameters given in Table 2 show that the oxygen atoms appear to have higher thermal vibration amplitudes perpendicular to their C-O bonds than along them. This phenomenon was also observed in  $\beta$ -methyl maltoside (Chu & Jeffrey, 1967), sorbose (Kim & Rosenstein, 1967), and arabinose (Kim & Jeffrey, 1967). As in  $\beta$ -methyl maltoside, the methyl group has high thermal motion consistent with its van der Waals environment.

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## The Crystal and Molecular Structure of Trimeric Bis(acetylacetonato) zinc (II)

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Bis(acetylacetonato)zinc(II),  $Zn(AcAc)_2$ , may be sublimed to give white monoclinic crystals containing the trimer,  $[Zn(AcAc)_2]_3$ . The unit cell dimensions are  $a=18.63$ ,  $b=8.437$ ,  $c=12.20$  Å,  $\beta=112.68^\circ$ ; measured density,  $1.41$  g.cm $^{-3}$ ; calculated density for  $Z=2$ ,  $1.45$  g.cm $^{-3}$ . Space group:  $C2$ . The structure was solved, including hydrogen atoms and refined by least squares to a conventional residual of 2.6% using 1835 non-zero reflections measured with a counter diffractometer. The trimer contains a central octahedrally coordinated zinc atom, lying on the crystallographic twofold axis, and two terminal pentacoordinated zinc atoms. The coordination geometry about the terminal zinc atoms is closer to a trigonal bipyramidal than to a square pyramidal arrangement. Both the octahedron and the trigonal bipyramids show considerable distortions from their ideal geometries, with mean angular deviations of  $8.2^\circ$  and  $5.3^\circ$  respectively. Each terminal zinc atom is connected to the central one by two shared oxygen atoms, one at an axial and the other at an equatorial position of the trigonal bipyramid. The absolute configuration of the trimer for the crystal studied was determined by considering the anomalous dispersion of the zinc atoms.

#### Introduction

The fact that bis-( $\beta$ -ketoenolato)metal(II) compounds of the first transition series metals (except copper) are coordinately unsaturated when monomeric, and thus

either oligomerize or add donor ligands, is now well known. For the nickel (Bullen, Mason & Pauling, 1965) and cobalt (Cotton & Elder, 1965, 1966; Cotton & Eiss, 1968) acetylacetonates, there are extensive X-ray crystallographic data available, while for others there