The Refinement of the Crystal Structure of α-Rhamnose Monohydrate

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The crystal structure of α-rhamnose monohydrate has been refined with three-dimensional data, obtained on an automatic computer-controlled Siemens four-circle diffractometer using Cu $K\alpha$ radiation. Refinement was by the least-squares method using an absolute weighting scheme. The initial coordinates were those of McGeachin & Beevers [*Acta Cryst.* (1957). **10**, 227]. Except for small, insignificant changes in bond angles and bond lengths, the earlier results have been confirmed. A final R index of 0·039 was obtained with a value of $\sum_h w(h)|\Delta(h)|^2/(m-n)$ of 1·01.

Introduction

The crystal structure of α-rhamnose monohydrate was determined by McGeachin & Beevers (1957). Recently, the refinement of other pyranose structures (Rogers & Hough, 1968; Chu & Jeffrey, 1968) has been reported and, in order to compare the bond distances and angles with the structures, α-rhamnose monohydrate has been further investigated.

In the original work, refinement had been carried out on data from two projections and the isotropic thermal parameters quoted were given no absolute significance; also, the observed intensity data had been corrected for extinction and it was therefore felt that a more accurate refinement could be obtained using full three-dimensional data and least-squares refinement applying anisotropic temperature factors to the carbon and oxygen atoms. It was further intended to refine the structure using an absolute weighting scheme (Killean & Lawrence, 1969).

Experimental

The crystallographic data for α-rhamnose monohydrate ($C_6O_5H_{12}.H_2O$) were:

	This work	McGeachin & Beevers
$a=$	$7·906 \pm 0·002$ Å	$a = 7·910 \pm 0·005$ Å
$b=$	$7·921 \pm 0·002$	$b = 7·914 \pm 0·004$
$c=$	$6·673 \pm 0·002$	$c = 6·674 \pm 0·004$
$\beta=$	$95·59 \pm 0·05°$	$\beta = 95·52 \pm 0·10°$
$V=$	$415·87$ Å^3	$V = 415·88$ Å^3
$D_x=$	$1·457 \pm 0·002$ g.cm^{-3}	$D_x = 1·457 \pm 0·005$ g.cm^{-3}

Space group $P2_1$

Single crystals of α-rhamnose monohydrate were obtained by slow evaporation of a solution of α-rhamnose in 90% methyl alcohol and 10% water and an approximately cylindrical crystal of length 0·03 cm and diameter 0·02 cm chosen.

The intensities were measured on a Siemens four-circle diffractometer, controlled on-line by an IBM 1130 computer. Cu $K\alpha$ radiation ($\lambda=1·5418$ Å) was used with a β-filter. The moving-crystal, moving-counter method was employed (θ-2θ scan) with a 2θ scan range of 1·2° and each reflexion was measured for a total period of three minutes, including background. To reduce lost counts, one of a set of six attenuators was placed in the main beam during the measurement of each reflexion. By measuring the intensity of the peak for 0·25 sec the attenuator which would give maximum intensity but keep the number of lost counts down to one per million was chosen.

All reflexions with $\theta < 70°$ were measured, four reflexions being rejected since their peak was indistinguishable from the background and thus the integrated intensities of 833 reflexions were obtained.

Refinement

The refinement was carried out by a full-matrix least-squares program on an IBM 360 computer. The initial positional parameters of the carbon and oxygen atoms were those given by McGeachin & Beevers (1957) and all atoms were given an isotropic temperature factor of 1·5 Å^2. The atomic scattering factors used were those given in *International Tables for X-ray Crystallography* (1962) and all structure factors were initially given unit weight. After five cycles refining positional parameters and isotropic temperature factors the R index was 0·089 and four further cycles with anisotropic temperature factors reduced the R index to 0·054. All fourteen hydrogen atoms were clearly visible from a difference Fourier synthesis and in all further refinement these atoms were included with temperature factors of 1·5 Å^2 but their parameters were not refined.

Individual weights $w(\mathbf{h})$ were then assigned to each structure factor $F(\mathbf{h})$ as described by Killean & Lawrence (1969).

$$[w(\mathbf{h})]^{-1} = \sigma^2(\mathbf{h}) = \sigma_1^2(\mathbf{h}) + c^2|F(\mathbf{h})|^2 + k^2\langle|F(\mathbf{h})|^2\rangle$$

where $\sigma^2(\mathbf{h})$ is the variance of $F(\mathbf{h})$, $\sigma_1^2(\mathbf{h})$ is the contribution to the variance of $F(\mathbf{h})$ due to counting statistics and c and k are constants.

Table 1. *Observed and calculated structure factors*

Columns are h, k, $10F_o$, $10F_c$.

In this case, $\sigma_I^2(\mathbf{h})$ was negligible for most reflexions owing to the large number of counts accumulated during intensity measurement. A relationship between c^2 and k^2 was obtained using the G^2-factor (Kitaigorodskii, 1957).

$$G^2 = \frac{\sum_h |\Delta(\mathbf{h})|^2}{\sum_h |F(\mathbf{h})|^2} = \frac{\sum_h \sigma^2(\mathbf{h})}{\sum_h |F(\mathbf{h})|^2}$$

$$= S^2 + c^2 + k^2$$

$$\therefore c^2 + k^2 = G^2 - S^2$$

At this point of refinement, $G^2 = 0.0033$ and $S^2 = 0.0000$

$$\therefore c^2 + k^2 = 0.0033 \ .$$

Subject to this condition, the individual values of c^2 and k^2 were taken to be those for which $M = \sum_h w(\mathbf{h})$ $|\Delta(\mathbf{h})|^2/(m-n)$ was a minimum where m and n are the numbers of reflexions and parameters respectively. The minimum value of M was 1·21 when $k^2 = 0.0033$ and $c^2 = 0.0000$.

Individual weights were then calculated for all reflexions and three more cycles of refinement carried out. This reduced R to 0·047 and gave a value of M of 0·83, different from the expected value of 1·0 due to the overestimation of the $\sigma^2(\mathbf{h})$ values. $c^2 + k^2$ were recalculated and the values obtained were $c^2 = 0.0000$ and $k^2 = 0.0019$. Further refinement then gave a final R index of 0·039 and a final M value of 1·01. The value obtained

from c^2, which has been considered to be a measure of the accuracy of the intensity measurements, suggests that the observed structure factors have been determined very accurately. The value obtained for k^2, 0·0019, suggests about a 4% error in the scattering curves due to bonding (Killean & Lawrence, 1969).

A check on the validity of the weighting scheme was made by computing the distribution of $|\Delta(\mathbf{h})|/\sigma(\mathbf{h})$ which was found to have the approximately Gaussian form

$$N = 70.0 \exp\left\{-\left(\frac{0.92}{2}\right)(\Delta(\mathbf{h})/\sigma(\mathbf{h}))^2\right\} .$$

65·9% of the reflexions have a value of $|\Delta(\mathbf{h})|/\sigma(\mathbf{h})$ less than 1·0 and, for 96·9%, this value is less than 2·0. For one reflexion, 1,01, $|\Delta(\mathbf{h})|/\sigma(\mathbf{h})$ is 5·1 showing it to be affected by systematic error.

The observed and calculated structure factors are shown in Table 1, the final positional parameters in Table 2 and the thermal parameters in Table 3.

Table 2. *Final coordinates and standard deviations*

	x/a	y/b	z/c
C(1)	0.0883 (3)	−0.1330	0.0789 (3)
C(2)	0.0083 (3)	−0.0909 (3)	0.2716 (3)
C(3)	0.1425 (3)	−0.0285 (3)	0.4330 (3)
C(4)	0.2333 (3)	0.1221 (3)	0.3511 (3)
C(5)	0.3145 (3)	0.0678 (3)	0.1601 (3)
C(6)	0.4023 (4)	0.2111 (5)	0.0609 (5)
O(1)	0.1898 (2)	−0.2771 (2)	0.1120 (2)

Table 2 (cont.)

	x/a	y/b	z/c
O(2)	−0·1187 (2)	0·0346 (3)	0·2244 (2)
O(3)	0·0576 (2)	0·0104 (2)	0·6052 (2)
O(4)	0·3602 (2)	0·1811 (3)	0·5012 (3)
O(5)	0·1820 (2)	0·0065 (2)	0·0139 (2)
O(6)	0·3266 (2)	0·5297 (3)	0·4624 (3)
H(1)	0·000	−0·140	−0·040
H(2)	−0·050	−0·185	0·320
H(3)	0·220	−0·113	0·460
H(9)	0·140	0·213	0·330
H(5)	0·3£0	−0·013	0·200
H(6)	0·460	0·135	−0·040
H(7)	0·320	0·313	0·010
H(£)	0·500	0·250	0·170
H(9)	C·140	0·035	0·705
H(10)	0·350	0·288	0·510
H(11)	0·405	0·585	0·455
H(12)	0·180	−0·325	0·020
H(13)	0·260	0·585	0·375
H(14)	−0·190	0·038	0·320

A close inspection of the large observed and calculated structure factors showed that the calculated values were not systematically larger than the observed values and, hence, for the crystal used, no extinction corrections were necessary. A comparison between the obser-
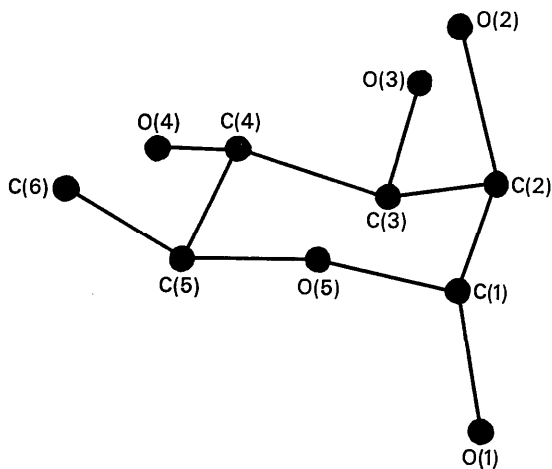
ved structure factors for this work and those of McGeachin & Beevers shows that in the latter work some of the larger structure factors had been underestimated, which probably accounts for the very small temperature factors they obtained.

Discussion

A schematic diagram of the structure, showing the identification of the atoms, is shown in Fig. 1 and the bond lengths and angles with estimated standard deviations are listed in Table 4.

Table 4. Bond lengths and angles with standard deviations

i	j	D(ij)
C(1)	C(2)	1·526 (3) Å
C(2)	C(3)	1·522 (3)
C(3)	C(4)	1·521 (3)
C(4)	C(5)	1·543 (3)
C(5)	C(6)	1·509 (4)
C(1)	O(1)	1·401 (3)
C(2)	O(2)	1·429 (3)
C(3)	O(3)	1·419 (3)
C(4)	O(4)	1·424 (3)
C(5)	O(5)	1·444 (3)
C(1)	O(5)	1·422 (3)

i	j	k	∠ijk
C(1)	C(2)	C(3)	110·5 (3)°
C(2)	C(3)	C(4)	108·9 (3)
C(3)	C(4)	C(5)	109·1 (3)
C(4)	C(5)	O(5)	108·5 (3)
C(5)	O(5)	C(1)	115·0 (3)
O(5)	C(1)	C(2)	110·0 (3)
C(1)	C(2)	O(2)	107·7 (3)
O(2)	C(2)	C(3)	110·9 (3)
C(2)	C(3)	O(3)	106·7 (3)
O(3)	C(3)	C(4)	113·6 (3)
C(3)	C(4)	O(4)	108·9 (3)
O(4)	C(4)	C(5)	110·7 (3)
C(4)	C(5)	C(6)	113·4 (3)
C(6)	C(5)	O(5)	106·8 (3)
O(5)	C(1)	O(1)	111·9 (3)
O(1)	C(1)	C(2)	108·6 (3)

Fig. 1. Schematic diagram of α-rhamnose monohydrate showing the labelling used.

The average C–C bond length is 1·524 ± 0·005 Å with a standard deviation for each bond of 0·012 Å compared with a standard deviation for each bond from the least-squares refinement of about 0·004 Å. The equivalent result for β-D-glucose (Chu & Jeffrey, 1968)

Table 3. Final anisotropic temperature factors × 10⁵ defined as

$$[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hk B_{12} + 2hl B_{13} + 2kl B_{23})]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	981 (33)	1054 (41)	810 (39)	−70 (30)	36 (29)	−132 (32)
C(2)	889 (31)	793 (38)	878 (41)	−95 (29)	135 (28)	23 (31)
C(3)	1078 (35)	696 (38)	747 (39)	121 (28)	45 (32)	14 (30)
C(4)	814 (32)	805 (40)	933 (41)	−12 (27)	−17 (30)	−78 (32)
C(5)	861 (30)	1164 (44)	1093 (43)	−45 (27)	104 (30)	−21 (34)
C(6)	1334 (44)	1804 (64)	1792 (60)	−506 (44)	389 (41)	164 (51)
O(1)	1353 (28)	1011 (29)	1194 (32)	76 (23)	49 (24)	−305 (25)
O(2)	933 (23)	1228 (33)	1077 (31)	137 (25)	125 (21)	245 (28)
O(3)	1255 (29)	1280 (36)	793 (31)	21 (29)	218 (23)	−108 (28)
O(4)	1053 (26)	1025 (33)	1399 (36)	−43 (25)	−266 (25)	−267 (27)
O(5)	1040 (25)	1279 (37)	748 (29)	−200 (26)	81 (21)	46 (28)
O(6)	1042 (25)	1086 (31)	1664 (38)	−105 (25)	71 (24)	−31 (30)

was $1\cdot520 \pm 0\cdot0034$ Å and for α-D-glucose monohydrate (Rogers & Haugh, 1968) $1\cdot524 \pm 0\cdot0034$ Å.

On the basis of the t test (Fisher & Yates, 1953), it can be seen that the C(4)–C(5) and C(5)–C(6) bond lengths are significantly different from each other and from all the other C–C bond lengths. In α-D-glucose monohydrate and in β-D-glucose, the C(5)–C(6) bond length is probably significantly smaller than the other C–C bond lengths but C(4)–C(5) is not.

The average C–O bond length, excluding the carbon atoms bonded to the oxygen atom in the ring and C(1)–O(1), is $1\cdot424 \pm 0\cdot003$ Å compared with $1\cdot425 \pm 0\cdot003$ Å for both β-D-glucose and α-D-glucose monohydrate. As with these two sugars, the C(1)–O(1) bond length in α-rhamnose monohydrate, $1\cdot401 \pm 0\cdot003$ Å, was significantly different from the other C–O bond lengths.

The C(5)–O(5) bond length differs significantly from all other C–O bond lengths while C(1)–O(5) does not. It has been noted by Snyder, Rosenstein, Kim & Jeffrey (1970) that in sugars where an oxygen atom is bonded to the C(6) atom in a direction parallel to the C(4)–C(5) bond as in α-D-glucose (Brown & Levy, 1965), no significant difference exists between bond lengths C(5)–O(5) and C(1)–O(5) but when the oxygen atom is bonded in a direction anti-parallel to the C(5)–H(5) bond, as in α-D-glucose monohydrate, a significant difference does exist. This difference can now be seen to exist when only hydrogen atoms are bonded to C(6).

The bond lengths and angles differ insignificantly from those quoted by McGeachin & Beevers, the largest discrepancy being $0\cdot049$ Å in the C(2)–O(2) bond which cannot now be considered significantly different from C(3)–O(3) and C(4)–O(4). The positions of the hydrogen atoms are close to those given by McGeachin & Bee-

vers with the exception of H(6) in the methyl group. The average C–H bond length for the carbon atoms in the ring was $0\cdot96$ Å and for the methyl group was $1\cdot06$ Å. The hydrogen bond distances are listed in Table 5 along with the O–H–O bond angles.

Table 5. *Hydrogen bond lengths and angles*

Symmetry code

a	x,	y,	z+1
b	1−x,	½+y,	1−z
c	−x,	−½+y,	−z
d	x,	1+y,	z
e	−x,	−½+y,	−z+1

i	j	k	D(ij)	D(jk)	ik	ijk
O(3)	H(9)	O(5a)	0·91 Å	2·07 Å	2·81 Å	138
O(4)	H(10)	O(6)	0·85	1·94	2·78	167
O(6)	H(11)	O(4b)	0·83	1·93	2·74	168
O(1)	H(12)	O(2c)	0·89	1·84	2·71	163
O(6)	H(13)	O(1d)	0·87	2·10	2·91	157
O(2)	H(14)	O(6e)	0·89	1·89	2·78	174

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The Crystal and Molecular Structure of the *N,N,N',N'*-Tetramethylbenzidine–Chloranil (2:1) Molecular Complex

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Crystals of the (2:1) complex of *N,N,N',N'*-tetramethylbenzidine (TMBD) and chloranil are monoclinic, space group $P2_1/a$, with $a=16\cdot498$, $b=8\cdot413$, $c=14\cdot149$ Å, $\beta=117\cdot42°$, $Z=2$. The structure was solved directly by the symbolic-addition procedure, and was refined by the block-diagonal least-squares method. In this complex, the crystal structure comprises distinct molecular groups where one chloranil molecule is sandwiched between two TMBD molecules. The chloranil molecule is situated on one of the two benzene rings of TMBD; the other benzene ring is appreciably twisted around the bond connecting the two benzene rings. The dihedral angle between the two benzene rings in TMBD is 30·8°.

Introduction

The electronic spectra of single-crystals of molecular complexes that involve *N,N,N',N'*-tetramethylben-

zidine (TMBD) or benzidine (BD) as electron donor have been studied in our laboratory (Amano, Kuroda & Akamuto, 1969). Results showed that these molecular complexes take a non-ionic structure in the ground