

two ANDR molecules defined by the atomic coordinates of Tables 1 and 3 are similar enough with the exception of ring *A*, it is reasonable to suppose that the geometry found for this ring is substantially correct.

In conclusion the determination of the ANDR crystal structure, in spite of the unfavourable molecular model chosen for the energy computation, leads us to believe that the coupling of the potential energy calculation with the minimum residual analysis (Damiani, Giglio, Liquori & Ripamonti, 1967) is a useful tool in solving the crystal structures of complicated compounds without heavy atoms. This method is particularly useful when the replacement of a light atom with a heavy one (to solve the phase problem) changes the molecular geometry.

The authors are indebted to Dr M. S. D'Angelo for help and advice and to Mr G. Iaquaniello for technical assistance. The financial support of the Consiglio Nazionale delle Ricerche is gratefully acknowledged.

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Structure Determination of 2,6-Anhydro- β -D-fructofuranose

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(Received 20 November 1972; accepted 27 February 1973)

2,6-Anhydro- β -D-fructofuranose crystallizes in space group $P2_12_12_1$ with lattice constants $a = 21.445$, $b = 10.732$ and $c = 5.874$ Å with two molecules in the asymmetric unit. The phase problem was solved by a multiresolution method. Because of the remarkable influence of extinction, the last refinement included an isotropic extinction parameter. The residual, R , is 2.8% and the standard deviations in heavy-atom bond lengths are 0.003 Å. The molecular shape can be described by two five-membered rings with three common atoms and a boat-shaped six-membered ring. The furanosyl ring can be described by an E_c -conformation. The torsional angle between the two hydroxyl groups is about 123°. Each OH group takes part in two hydrogen bonds, one as a donor, the other as an acceptor, yielding a total of six intermolecular hydrogen bonds.

Introduction

2,6-Anhydro- β -D-fructofuranose, $C_6O_5H_{10}$, hereinafter called fructose anhydride, is a decomposition product of sucrose on dry heating (Bollmann, 1964). This monomeric fructose anhydride was first described by Goldschmid & Perlin (1960). The conventional form of the structural formula is shown in Fig. 1(a), and a different form in Fig. 1(b). In the latter, two five-membered

rings can clearly be detected having three common atoms. Hence, one six-membered ring is formed which must have a boat form because of the oxygen bridge. This conformation has already been suggested (Goldschmid & Perlin, 1960). To prove this proposal, a three-dimensional X-ray structure analysis was carried out. Crystals of fructose anhydride were supplied by the Institut für Zuckerindustrie der Technischen Universität Berlin.

Experimental

From oscillation and Weissenberg photographs the approximate lattice constants were determined. From the orthorhombic symmetry and the systematically absent reflexions $h00$, $0k0$ and $00l$ for odd orders the space group was assumed to be $P2_12_12_1$. The dimensions of the unit cell and the experimentally measured density indicated eight molecules per unit cell, hence two per asymmetric unit.

With an automatic single-crystal diffractometer (Siemens AED) precise lattice constants were determined and intensities of 1526 reflexions with $4.5^\circ < \theta < 71^\circ$ were measured with Ni-filtered Cu $K\alpha$ radiation. 61 reflexions had an intensity less than twice the statistical error and

Table 1. *Crystallographic data*

Fructose anhydride, $C_6O_5H_{10}$
$M = 162$
$a = 21.445 (3) \text{ \AA}$
$b = 10.732 (2)$
$c = 5.874 (2)$
$V = 1352 \text{ \AA}^3$
Experimental density, $\rho_{\text{exp}} = 1.56 \text{ g cm}^{-3}$
X-ray density, $\rho_x = 1.58 \text{ g cm}^{-3}$
8 Molecules/unit cell
Space group: $P2_12_12_1$

were coded as 'less-thans'. The most important crystallographic data are given in Table 1.

Structure determination

To solve the phase problem, the tangent formula (Karle & Hauptman, 1956) was used taking three variable reflexions in addition to the four reflexions for defining the origin and fixing the enantiomorph. We used

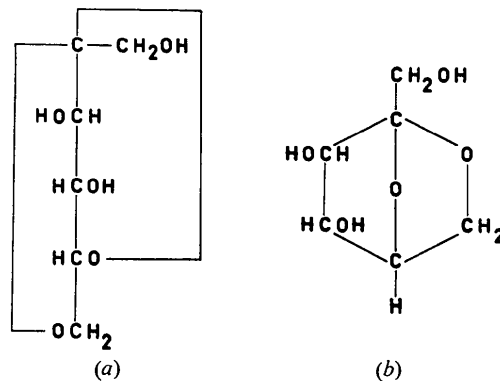


Fig. 1. (a) Conventional structure formula of fructose anhydride. (b) Formula indicating the correct molecular arrangement.

Table 2. *Starting set reflexions for tangent refinement*

	<i>E</i> -value	Relative height	Indices	Starting phases
Origin fixing	2.64	4	9 2 0	270°
	2.40	15	13, 7, 0	270
	1.84	55	5 0 7	270
Enantiomorph fixing	2.57	6	0 5 5	90
	2.59	5	4 8 0	0, 180*
Variable	2.57	7	2,11,3	45, 135*, 225, 315
	2.11	31	7 8 1	45, 135, 225*, 315

Table 3. *Bond distances before and after extinction correction*

Bond	Before extinction correction		Difference if $\geq 3\sigma$	After extinction correction		Difference if $\geq 3\sigma$
	Mol. I	Mol. II		Mol. I	Mol. II	
C(1)-O(1)	1.420 (6)	1.435 (6)		1.416 (3)	1.420 (4)	
C(1)-C(2)	1.486 (5)	1.498 (7)		1.497 (3)	1.500 (3)	
C(1)-H(0)	1.20 (5)	1.46 (6)	0.26	1.00 (3)	0.97 (3)	
C(1)-H(1)	1.24 (4)	1.23 (7)		1.01 (3)	0.97 (3)	
O(1)-H(2)	1.16 (6)	0.99 (6)		0.87 (4)	0.89 (5)	
C(2)-C(3)	1.562 (5)	1.510 (7)	0.052	1.554 (3)	1.525 (4)	0.029
C(2)-O(6)	1.439 (5)	1.439 (4)		1.427 (3)	1.430 (3)	
C(2)-O(2)	1.425 (5)	1.427 (6)		1.425 (3)	1.411 (3)	0.014
C(3)-O(3)	1.407 (6)	1.439 (6)	0.032	1.412 (3)	1.421 (4)	
C(3)-C(4)	1.548 (5)	1.553 (4)		1.544 (3)	1.551 (3)	
C(3)-H(3)	1.04 (5)	0.83 (4)	0.21	1.01 (2)	1.00 (3)	
O(3)-H(4)	0.90 (6)	1.07 (6)		0.85 (4)	0.83 (5)	
C(4)-O(4)	1.428 (6)	1.410 (6)	0.018	1.419 (3)	1.425 (4)	
C(4)-H(5)	1.11 (3)	0.93 (4)	0.18	0.99 (3)	0.96 (3)	
O(4)-H(6)	0.73 (6)	1.03 (6)	0.30	0.85 (4)	0.91 (4)	
C(5)-C(4)	1.524 (7)	1.503 (8)		1.528 (3)	1.512 (5)	0.016
C(5)-C(6)	1.526 (7)	1.495 (7)	0.031	1.515 (4)	1.519 (5)	
C(5)-O(2)	1.453 (4)	1.417 (5)	0.019	1.446 (3)	1.454 (4)	
C(5)-H(7)	1.08 (4)	1.14 (7)		1.04 (3)	0.97 (3)	
C(6)-O(6)	1.443 (5)	1.456 (7)		1.452 (4)	1.448 (5)	
C(6)-H(8)	0.87 (4)	1.03 (6)	0.15	1.00 (3)	0.95 (3)	
C(6)-H(9)	1.07 (5)	1.07 (4)		0.99 (3)	0.91 (4)	

the programs *NORMSF*, *SIGMA* and *TANGEN* of the *X-RAY* 70 program system (1970).

Several attempts to determine phases with different origin reflexions were unsuccessful. We found later that this resulted from the choice of the starting set for tangent refinement. In all the unsuccessful attempts, the reflexion with the highest E value (18,0,2) was used in the starting set. This reflexion occurred in a false Σ_2 relationship with two reflexions of very high E values. Therefore, a considerable number of reflexions had incorrect phases at the beginning of the refinement. The phase determination was successful only when the 18,0,2 reflexion was eliminated from the starting set. The set for this attempt is given in Table 2, where an asterisk denotes the correct phase for the variable reflexions. 31 of the 32 possible combinations led to R_E values (Karle & Karle, 1966) greater than 27%; the correct combination including 293 reflexions with $E > 1.2$, yielded $R_E = 19\%$.

In the E map calculated with these 293 reflexions, the 22 highest maxima matched the 10 oxygen and 12 carbon atoms.

Refinement

First, an isotropic refinement was carried out with the least-squares program *ORFLS*. After introduction of anisotropic temperature parameters, R decreased to 7.8%. By means of a difference synthesis, 20 hydrogen atoms were located and included in further refinements with isotropic thermal parameters. Unit weights were used throughout the refinement. After some additional refinement cycles, the marked effects of secondary extinction were evident. Therefore the ten strongest reflexions were eliminated from the data set, and R was 4.9%. The standard deviations of bond lengths between oxygen and carbon atoms had values from 0.005 to 0.008 Å, and for C–H and O–H bond lengths 0.04 to 0.06 Å. The large differences between equivalent bond lengths in the two independent molecules were substantially higher than the significance limit (Table 3).

Obviously, the influence of extinction could not be removed by elimination of the ten strongest reflexions. Therefore, we found it useful to carry out further refinements with the inclusion of an extinction parameter. First, the transmission coefficients and the mean path lengths $\bar{x} = -\partial \ln A / \partial \mu$ necessary for the extinction corrections, were computed for each reflexion with a modified absorption correction program (Burnham, 1966). Refinement was then carried out with the program *LINUS* (Hamilton & Coppens, 1969) in a version with 300 variables and 1121 parameters. After convergence, the isotropic extinction parameter was $g = (2.41 \pm 0.06) \cdot 10^4$ corresponding to a mean mosaic angle spread of 2.4'' or to a mean particle size of $3.7 \cdot 10^{-4}$ cm, respectively (Zachariasen, 1967).

R for the 1481 observed reflexions decreased to 2.8%. Including the 61 less-than reflexions, R was 3.0%. The residual used is $R = (\sum ||F_o| - |eF_c||) / (|F_o|)$,

where e is the individual extinction coefficient. The extinction correction of the most influenced reflexions exceeded 10% of the intensity for 49 reflexions, 50% for three reflexions. The observed and calculated structure factors are listed in Table 4, including the extinction coefficients (the transmission factors belonging to the intensities are the squares of these extinction coefficients). In Table 5 the final atom parameters are given. The standard deviations of the bond lengths decreased to 0.003 Å for C–C and C–O bond lengths and to 0.03 Å for C–H and O–H bond lengths. In addition, a substantially better agreement of the equivalent bond lengths was obtained (Table 3). Before introducing the extinction parameter, the discrepancies between equivalent bond lengths were greater than 3σ in 10 out of 23 cases, while now only 3 significant deviations were obtained (although the significance limit is much lower!).

Table 4. Final $F_o - F_c$ list

The columns are $h, k, l, 10|F_o|, 10|F_c|, \text{phase (deg} \times 10), \text{extinction factor} (\times 10^3)$.

h	k	l	$10 F_o $	$10 F_c $	phase (deg $\times 10$)	extinction factor ($\times 10^3$)
1	0	0	100	100	0	0
2	0	0	200	200	0	0
3	0	0	300	300	0	0
4	0	0	400	400	0	0
5	0	0	500	500	0	0
6	0	0	600	600	0	0
7	0	0	700	700	0	0
8	0	0	800	800	0	0
9	0	0	900	900	0	0
10	0	0	1000	1000	0	0
11	0	0	1100	1100	0	0
12	0	0	1200	1200	0	0
13	0	0	1300	1300	0	0
14	0	0	1400	1400	0	0
15	0	0	1500	1500	0	0
16	0	0	1600	1600	0	0
17	0	0	1700	1700	0	0
18	0	0	1800	1800	0	0
19	0	0	1900	1900	0	0
20	0	0	2000	2000	0	0
21	0	0	2100	2100	0	0
22	0	0	2200	2200	0	0
23	0	0	2300	2300	0	0
24	0	0	2400	2400	0	0
25	0	0	2500	2500	0	0
26	0	0	2600	2600	0	0
27	0	0	2700	2700	0	0
28	0	0	2800	2800	0	0
29	0	0	2900	2900	0	0
30	0	0	3000	3000	0	0
31	0	0	3100	3100	0	0
32	0	0	3200	3200	0	0
33	0	0	3300	3300	0	0
34	0	0	3400	3400	0	0
35	0	0	3500	3500	0	0
36	0	0	3600	3600	0	0
37	0	0	3700	3700	0	0
38	0	0	3800	3800	0	0
39	0	0	3900	3900	0	0
40	0	0	4000	4000	0	0
41	0	0	4100	4100	0	0
42	0	0	4200	4200	0	0
43	0	0	4300	4300	0	0
44	0	0	4400	4400	0	0
45	0	0	4500	4500	0	0
46	0	0	4600	4600	0	0
47	0	0	4700	4700	0	0
48	0	0	4800	4800	0	0
49	0	0	4900	4900	0	0
50	0	0	5000	5000	0	0
51	0	0	5100	5100	0	0
52	0	0	5200	5200	0	0
53	0	0	5300	5300	0	0
54	0	0	5400	5400	0	0
55	0	0	5500	5500	0	0
56	0	0	5600	5600	0	0
57	0	0	5700	5700	0	0
58	0	0	5800	5800	0	0
59	0	0	5900	5900	0	0
60	0	0	6000	6000	0	0
61	0	0	6100	6100	0	0
62	0	0	6200	6200	0	0
63	0	0	6300	6300	0	0
64	0	0	6400	6400	0	0
65	0	0	6500	6500	0	0
66	0	0	6600	6600	0	0
67	0	0	6700	6700	0	0
68	0	0	6800	6800	0	0
69	0	0	6900	6900	0	0
70	0	0	7000	7000	0	0
71	0	0	7100	7100	0	0
72	0	0	7200	7200	0	0
73	0	0	7300	7300	0	0
74	0	0	7400	7400	0	0
75	0	0	7500	7500	0	0
76	0	0	7600	7600	0	0
77	0	0	7700	7700	0	0
78	0	0	7800	7800	0	0
79	0	0	7900	7900	0	0
80	0	0	8000	8000	0	0
81	0	0	8100	8100	0	0
82	0	0	8200	8200	0	0
83	0	0	8300	8300	0	0
84	0	0	8400	8400	0	0
85	0	0	8500	8500	0	0
86	0	0	8600	8600	0	0
87	0	0	8700	8700	0	0
88	0	0	8800	8800	0	0
89	0	0	8900	8900	0	0
90	0	0	9000	9000	0	0
91	0	0	9100	9100	0	0
92	0	0	9200	9200	0	0
93	0	0	9300	9300	0	0
94	0	0	9400	9400	0	0
95	0	0	9500	9500	0	0
96	0	0	9600	9600	0	0
97	0	0	9700	9700	0	0
98	0	0	9800	9800	0	0
99	0	0	9900	9900	0	0
100	0	0	10000	10000	0	0

Table 5. *Fractional atomic coordinates and anisotropic thermal parameters (all $\times 10^4$)*

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.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(11)	80 (1)	2724 (2)	8353 (5)	16 (1)	48 (2)	215 (8)	1 (1)	-6 (2)	13 (4)
O(11)	-553 (1)	3078 (2)	8129 (4)	17 (0)	63 (2)	424 (10)	2 (1)	-19 (2)	61 (4)
C(12)	122 (1)	1651 (2)	9974 (4)	14 (0)	40 (2)	154 (7)	-3 (1)	-4 (2)	-7 (3)
C(13)	784 (1)	1107 (2)	10387 (4)	14 (0)	41 (2)	143 (7)	-1 (1)	1 (2)	-7 (3)
O(13)	973 (1)	209 (2)	8771 (3)	19 (0)	48 (1)	174 (6)	1 (1)	9 (1)	-4 (3)
C(14)	697 (1)	488 (2)	12739 (4)	14 (1)	60 (2)	131 (7)	-2 (9)	-6 (2)	9 (4)
O(14)	1052 (1)	1079 (2)	14468 (3)	17 (0)	126 (3)	154 (6)	-14 (1)	-8 (1)	13 (3)
C(15)	4 (1)	731 (2)	13145 (4)	15 (1)	50 (2)	171 (8)	-4 (1)	4 (2)	3 (3)
C(16)	-383 (1)	-14 (3)	11471 (5)	16 (1)	64 (2)	213 (9)	-8 (1)	-1 (2)	12 (4)
O(16)	-282 (1)	651 (2)	9350 (3)	16 (0)	52 (1)	178 (6)	-8 (1)	-10 (1)	12 (3)
O(12)	-67 (1)	1973 (2)	12225 (3)	16 (0)	46 (1)	184 (6)	0 (1)	6 (1)	-8 (3)
C(21)	1706 (1)	3870 (3)	7124 (5)	16 (5)	69 (3)	248 (9)	7 (1)	2 (2)	5 (5)
O(21)	1577 (2)	3981 (2)	9486 (4)	24 (1)	74 (2)	262 (7)	1 (1)	21 (2)	-12 (3)
C(22)	2272 (1)	3079 (2)	6725 (5)	14 (1)	53 (2)	224 (9)	-3 (1)	-6 (2)	-3 (4)
C(23)	2503 (1)	3035 (3)	4270 (5)	13 (1)	65 (2)	212 (8)	-4 (1)	-1 (1)	12 (4)
O(23)	2132 (1)	2250 (2)	2870 (4)	20 (0)	120 (3)	176 (7)	-16 (1)	0 (2)	-9 (4)
C(24)	3181 (1)	2572 (3)	4633 (6)	14 (1)	55 (2)	345 (11)	-1 (1)	10 (2)	-2 (5)
O(24)	3610 (1)	3499 (2)	3883 (5)	14 (0)	73 (2)	502 (10)	-2 (1)	30 (2)	11 (4)
C(25)	3197 (1)	2438 (3)	7194 (6)	15 (1)	69 (3)	314 (10)	6 (1)	-14 (2)	2 (5)
C(26)	2788 (2)	1343 (3)	7869 (6)	24 (1)	69 (3)	273 (11)	8 (1)	-1 (3)	22 (5)
O(26)	2167 (1)	1836 (2)	7513 (4)	18 (0)	59 (2)	265 (7)	-2 (1)	6 (2)	17 (3)
O(22)	2808 (1)	3475 (2)	7915 (4)	16 (0)	65 (2)	285 (7)	2 (1)	-18 (2)	-20 (3)

Table 5 (cont.)

Hydrogen atomic coordinates are $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(10)	26 (1)	248 (3)	684 (5)	0.8 (5)
H(11)	34 (1)	341 (3)	905 (5)	0.8 (5)
H(12)	-57 (1)	381 (3)	747 (6)	2.2 (7)
H(13)	108 (1)	184 (2)	1047 (4)	0.1 (5)
H(14)	106 (2)	55 (3)	751 (7)	2.7 (8)
H(15)	77 (1)	-42 (2)	1265 (5)	0.1 (5)
H(16)	141 (2)	133 (3)	1401 (7)	2.9 (8)
H(17)	-13 (1)	69 (3)	1484 (5)	0.4 (5)
H(18)	-23 (1)	-90 (3)	1136 (5)	0.8 (5)
H(19)	-83 (1)	1 (2)	1187 (5)	0.8 (5)
H(20)	180 (1)	469 (3)	651 (5)	0.9 (6)
H(21)	135 (1)	345 (3)	647 (5)	1.0 (6)
H(22)	154 (2)	481 (4)	963 (8)	4.5 (11)
H(23)	251 (1)	390 (3)	367 (5)	0.8 (5)
H(24)	206 (2)	261 (4)	164 (8)	4.5 (12)
H(25)	323 (1)	180 (3)	380 (5)	0.7 (5)
H(26)	393 (2)	311 (4)	313 (7)	4.1 (10)
H(27)	360 (1)	246 (3)	794 (5)	1.6 (6)
H(28)	285 (1)	63 (3)	694 (6)	1.9 (7)
H(29)	282 (1)	113 (3)	936 (6)	1.6 (7)

Discussion

The following discussion is based on the parameters after extinction refinement. Fig. 2 shows a stereoscopic pair for molecule II. The molecule shape is that proposed by Goldschmid & Perlin. The atoms C(2), C(3), C(4), C(5) and O(2), and on the other hand C(2), O(2), C(5), C(6) and O(6) constitute the two five-membered rings, while the boat-shaped six-membered ring is formed by the atoms C(2), C(3), C(4), C(5), C(6) and O(6).

In Fig. 3, the bond lengths and angles are given for both molecules. The mean value for the 10 C-C bond

lengths is 1.525 (19) Å [where the standard deviation of a single bond length given in parentheses is

$\sqrt{\sum_i (\bar{x} - x_i)^2 / n}$]. For the C-O(-C) and the C-O(-H)

bond lengths we obtain mean values of 1.425 (14) and 1.424 (9) Å, respectively. For the bond lengths involving hydrogen atoms, which are always of lower accuracy in X-ray structure analyses, remarkable good agreement between different bonds is realized. The mean C-H bond length is 0.98 (3) Å; while the mean O-H bond length is significantly shorter with 0.87 (3) Å.

The comparison of bond lengths with those found in other structures with furanose components shows a significant lengthening of C(3)-C(4) (mean value of 1.548 compared with 1.528 Å in unstrained furanosyl rings) and C(6)-O(6) (1.450 compared with 1.425 Å) which might be caused by the influence of the oxygen bridge O(2). On the other hand, C(1)-C(2) is about 0.03 Å shorter in this compound (1.499 compared with 1.525 Å).

The bond lengths at O(2) show the same anomeric effect observed in several other carbohydrate structures (Berman, Chu & Jeffrey, 1967; Jeffrey & Park, 1972; Rohrer, 1972; Dreissig & Luger, 1973). The bond lengths C(5)-O(2) in molecule I are 5σ and in molecule II are 10σ larger than the corresponding bond C(2)-O(2). Because of the existence of the anhydride ring, the bond angles are not comparable with those of other compounds containing furanose components. The angles at the carbon atoms in the two five-membered rings are all close to the average value of 101.9°. The angle C(6)-O(6)-C(2) (104°) is close to this value, whereas the bond angles at the oxygen atom O(2) com-

mon to both five-membered rings have much lower values, *i.e.* 95.4 and 95.3° respectively. These values are in good agreement with the angles at the corresponding oxygen atoms in 1,4-epoxy-1,4-dihydronaphthalene (Bordner, Stanford & Dickerson, 1970) where the six-membered rings have a similar conformation.

The furanosyl ring in this molecule has a conformation which has not yet been observed in any structure determination of molecules with furanosyl components. With respect to the plane C(2)–O(2)–C(5), C(3) and C(4) are both displaced on the opposite side of C(6)

(Table 6). Following the notation of Sundaralingam (1965) both C(3) and C(4) are in the *exo* position, in contrast to the furanosyl rings so far investigated, where one of these atoms either occupies the *endo* position, or lies in the plane C(2)–O(2)–C(5) (Brown & Levy, 1963; Berman, 1970; Jeffrey & Park, 1972; Rohrer, 1972; Dreissig & Luger, 1973). This unusual effects occurs because the furanosyl ring is now part of a bicyclic ring system.

The best four-atom least-square plane is given by the atoms C(2), C(3), C(4), C(5) (Table 6) with mean

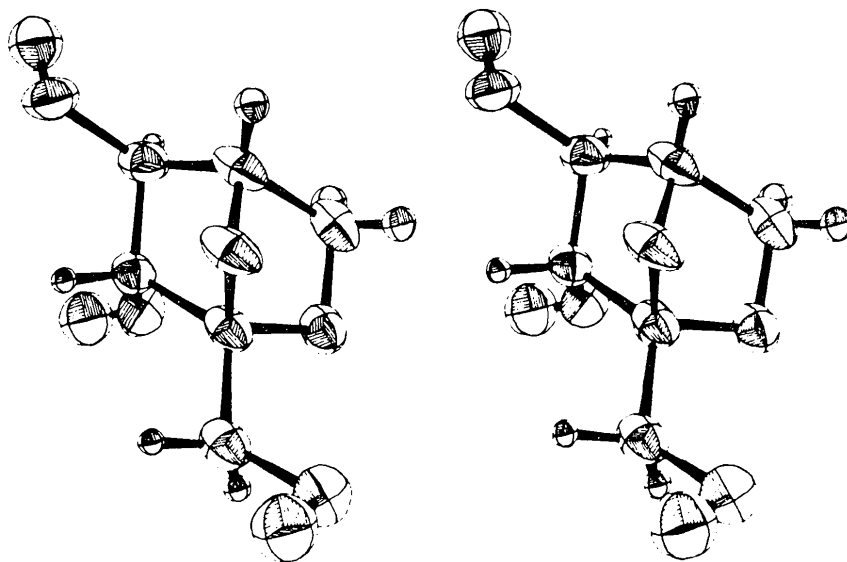


Fig. 2. Stereoscopic pair of drawings of fructose anhydride molecule.

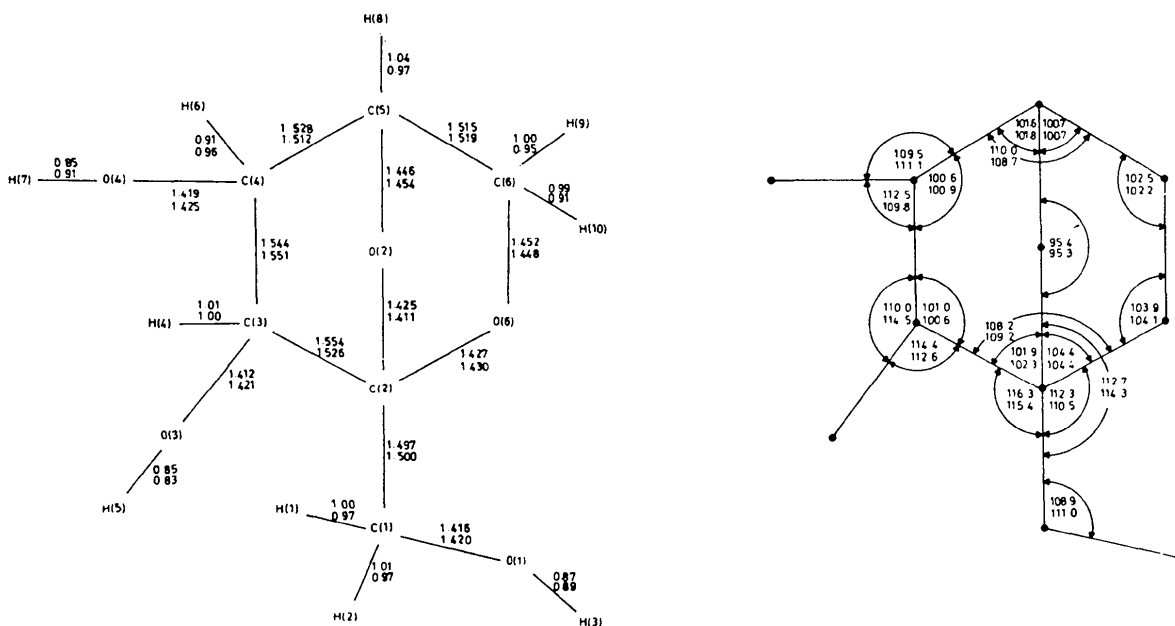


Fig. 3. Bond lengths and angles in both molecules after extinction correction.

Table 6. *Deviations of atoms from the least-squares planes (Å)*

	Plane 1		Plane 2		Plane 3	
	Mol. I	Mol. II	Mol. I	Mol. II	Mol. I	Mol. II
C(1)	0.520	0.444	-0.553	0.530	-0.079	-0.105
C(2)	0.014*	0.001*	-0.002*	0.000*	0.000*	0.000*
C(3)	-0.019*	-0.002*	1.410	-1.386	1.285	1.277
C(4)	0.019*	0.002*	1.377	-1.375	1.302	1.273
C(5)	-0.014*	-0.002*	0.002*	0.000*	0.000*	0.000*
C(6)	-1.351	-1.356	-0.003*	0.000*	-1.183	-1.185
O(6)	-1.284	-1.295	0.003*	0.001*	-1.131	-1.135
O(2)		0.826	-0.784	-0.782	0.000*	0.000*
σ (standard deviation of defining atoms)	0.019	0.002	0.003	0.000	0.000	0.000
	\angle Planes 1, 2		\angle Planes 1, 3		\angle Planes 2, 3	
	Mol. I	Mol. II	Mol. I	Mol. II	Mol. I	Mol. II
	112.8°	112.5°	58.8°	58.6°	54.0°	53.9°

standard deviations of 0.019 and 0.002 Å for the two molecules. Accordingly, the conformation of the furanosyl ring can be described in an envelope form which might be represented by the symbol E_o (oxygen ring atom out-of-plane). The envelope conformation is very distinct in this structure and leads therefore to torsional

angles at O(2)–C(2) and at O(2)–C(5) of up to 60° while in other furanosyl rings maximum values of 40° are obtained (Table 7).

The conformation of the anhydride ring is quite similar to that of the furanosyl ring. It has the envelope form, too, with O(2) as the out-of-plane atom (Table 6). This conformation has already been observed in the anhydro parts of 1,6:2,3-di-anhydro- β -D-glycopyranose (Park, Kim & Jeffrey, 1971). The torsional angles in the anhydro ring are in the range 0–55°, like those in the furanosyl ring (Table 7).

Another point of interest is the arrangement of the OH groups in relation to the bicyclic ring system. The bonds C(1)–O(1) of the hydroxymethyl groups are nearly parallel to C(3)–C(2) with torsional angles of 178.5 and 172.4°, respectively. This *trans-gauche* position is most favourable in the furanose components so far investigated. Concerning the two hydroxyl groups, we found O(3) in an axial and O(4) in an equatorial position. The torsional angles O(3)–C(3)–O(4) are 125.3 and 122.4° which are quite different from the value of 160° proposed by Sundaralingam (1965) as an explanation for the resistivity to oxidation of bridged bicyclic anhydro-sugars.

As usual in carbohydrate structures the molecules are arranged in a complex system of intermolecular hydro-

Table 7. *Torsional angles (°)*

	Mol. I	Mol. II
(a) Furanosyl ring		
C(3)–C(2)···O(2)–C(5)	57.7	58.9
C(2)–O(2)···C(5)–C(4)	60.4	59.1
O(2)–C(5)···C(4)–C(3)	38.4	35.7
C(5)–C(4)···C(3)–C(2)	3.0	0.3
C(4)–C(3)···C(2)–O(2)	33.7	36.4
(b) Anhydride ring		
O(6)–C(2)···O(2)–C(5)	54.8	55.0
C(2)–O(2)···C(5)–C(6)	52.9	52.7
O(2)–C(5)···C(6)–O(6)	33.9	33.1
C(5)–C(6)···O(6)–C(2)	0.6	0.1
C(6)–O(6)···C(2)–O(2)	34.0	34.9
(c) Six-membered ring		
C(3)–C(2)···O(6)–C(6)	73.9	73.9
C(4)–C(3)···C(2)–O(6)	75.9	74.0
C(2)–C(3)···C(4)–C(5)	3.0	0.3
C(3)–C(4)···C(5)–C(6)	67.6	70.0
C(4)–C(5)···C(6)–O(6)	72.8	73.3
C(5)–C(6)···O(6)–C(2)	0.6	0.1
(d) Hydroxo-methyl group		
O(6)–C(2)···C(1)–O(1)	53.0	63.0
C(3)–C(2)···C(1)–O(1)	178.5	172.4
(e) Hydroxyl groups		
O(3)–C(3)···C(4)–O(4)	125.3	122.4

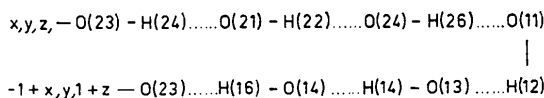


Fig. 4. Hydrogen bonding system.

Table 8. *Hydrogen-bonding system*

Hydrogen bond	O–H	Distances (Å)		Angle O–H···O (°)	Symmetry operation
		H···O	O···O		
O(11)–H(12)···O(15)	0.88	1.89	2.701	154	$-x, \frac{1}{2} + y, \frac{3}{2} - z$
O(13)–H(14)···O(14)	0.85	1.87	2.698	164	$x, y, -1 + z$
O(14)–H(16)···O(23)	0.85	1.96	2.796	167	$x, y, 1 + z$
O(21)–H(22)···O(24)	0.89	1.90	2.755	161	$\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
O(23)–H(24)···O(21)	0.83	2.20	2.972	154	$x, y, -1 + z$
O(24)–H(26)···O(11)	0.91	1.85	2.738	164	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$

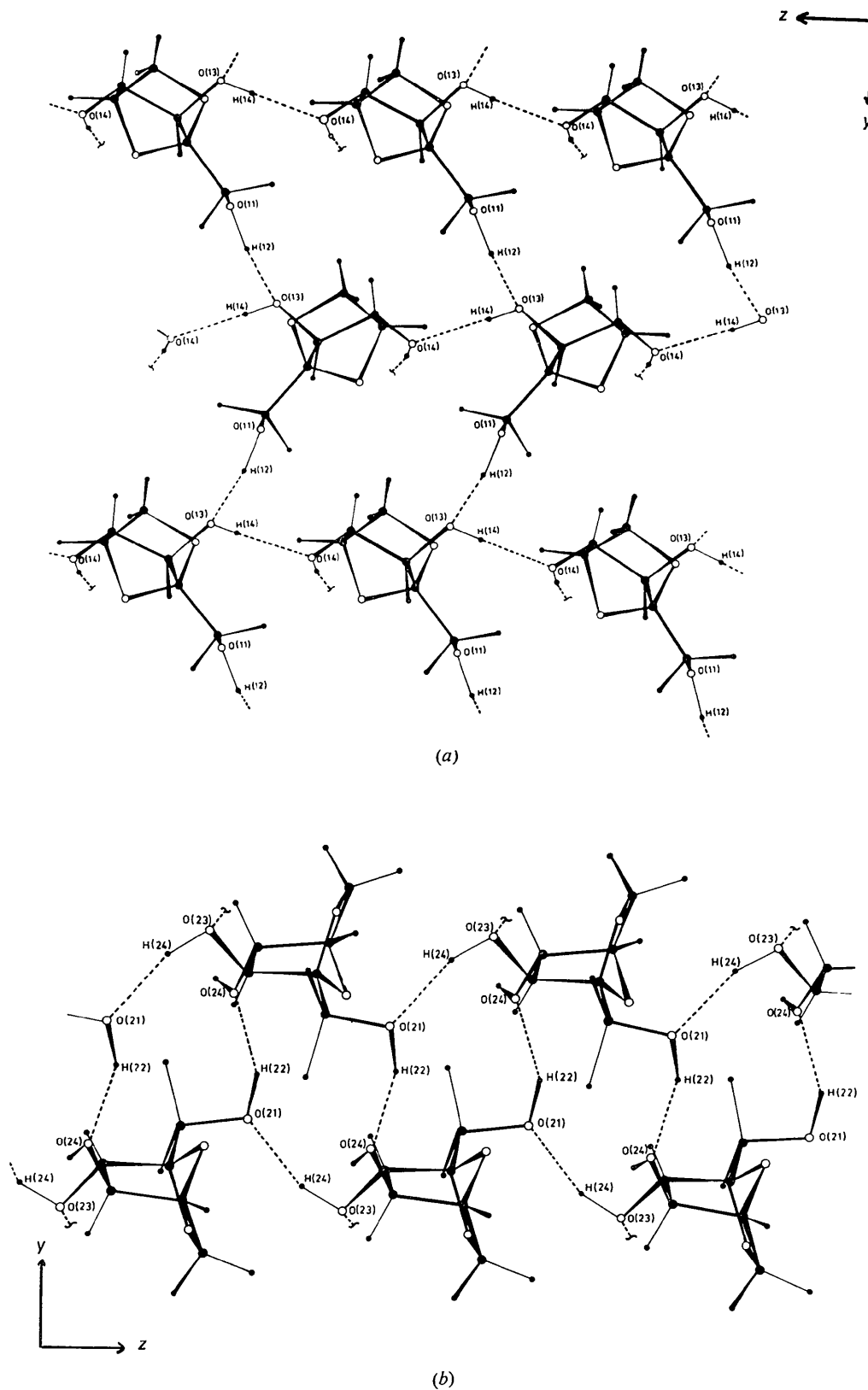


Fig. 5. Hydrogen bonds between (a) molecules I, and (b) molecules II.

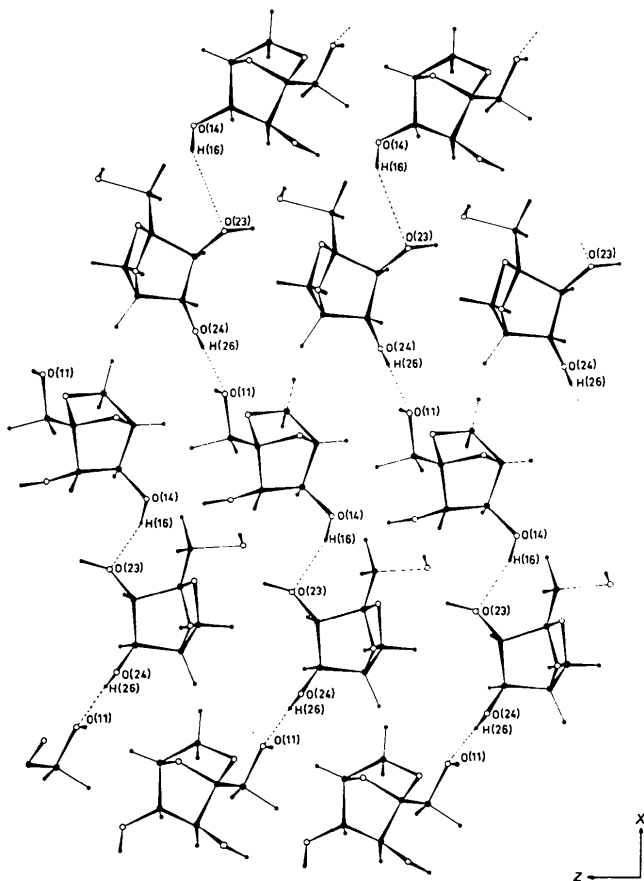


Fig. 5. (cont.) (c) Hydrogen bonds between molecules I and II.

gen bonds. All OH groups take part in two hydrogen bonds, both as donors and acceptors, while the ether atoms O(2) and O(6) are not included in the hydrogen bond system. Of the six different bridges existing in this structure, two are between symmetry related positions of molecule I, two are between molecule II, while the remaining two are between the two molecules. The distances and angles involving the hydrogen bonds are given in Table 8. Except for O(23)–H(24)···O(21), all O···O distances lie between 2.7 and 2.8 Å, the H···O distances between 1.85 and 1.96 Å.

The hydrogen bond scheme is shown in Fig. 4. It consists of an infinite chain containing all six hydrogen bonds.

An illustration of the network formed by hydrogen bondings is shown in Fig. 5(a)–(c).

The hydrogen bonds in molecule I build up a network in the yz plane [Fig. 5(a)] while the bonds connecting molecule II are tilted about the screw axis in the z direction [Fig. 5(b)]. On the other hand, both bonds between molecules I and II establish chains in the x direction [Fig. 5(c)].

We would like to thank Professor Dr K. Plieth and the Deutsche Forschungsgemeinschaft for the use of the diffractometer. We are also grateful to the Institut für Zuckerindustrie der Technischen Universität Berlin for supplying the single crystals, and the Fachbereich Kybernetik der Technischen Universität Berlin for the use of the IBM 360-67 computer.

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