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The Crystal and Molecular Structure of Cellobiose

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The structure of β-cellobiose has been determined by three-dimensional Patterson superposition techniques, in which an improved sharpening procedure based on the gradient of the electron density function was used to increase resolution.

The 1:4 linking of the two 'chair' β-glucopyranose residues is confirmed. The molecule has an internal hydrogen bond, $O_3'\text{–}H \cdots O_5$ of length 2·80 Å, and C–O–C angles within the rings of 117° 115°, significantly greater than the tetrahedral angle. It is of interest in connection with the proposed structures of forms of cellulose that the molecule has the bent conformation with the glucose residues somewhat twisted relative to one another, and that the isolated molecule would not have a two-fold axis. All OH hydrogens seem to be involved in the hydrogen bonding scheme in the crystal.

Introduction

Of the several different modifications of cellulose, natural cellulose I and regenerated cellulose II are most commonly studied, although other forms are known (Ellefsen, Gjønnes & Norman, 1959; Marrinan & Mann, 1956). Cellulose II, obtained from cellulose I by esterification and then saponification, are different forms of polymers of cellobiose. These two forms of cellulose differ both in the mutual arrangement of chains and, quite probably, in the relative spacial arrangements of glucose residues in the chain (Petitpas & Méring, 1956). Owing to the method of preparation of cellobiose as a degradation product of cellulose I under fairly drastic conditions it seems certain that cellobiose is most closely related in structural detail to cellulose II, but it may also be of interest in connection with the structure of natural cellulose itself (Liang & Marchessault, 1959).

Some of the different structure models for cellulose II have been summarized by Bjørnhaug, Ellefson & Tønnesen (1953). Model 1 is the 'straight' or extended model proposed (Meyer & Misch, 1937) on the basis of X-ray fiber diagrams for cellulose I but criticized on the basis of infrared studies (Liang & Marchessault, 1959). Model 2 is a 'straight' model proposed by Pierce (1946) for cellulose II. Model 3 is also a straight model intermediate between 1 and 2, but with a reasonable bond angle of about 120° at the glucosidic oxygen (Bjørnhaug *et al.*, 1953). Model 4 has the boat form of the pyranose ring and is eliminated by our study. Models 5, 6, and 7 are all somewhat bent chains first proposed by Hermans (1949) and by Hermans, de Booys & Maan (1943), and used by Carslstrom (1957) for the structure of chitin, but they differ in whether there is a minor rotation (5), a medium rotation (6), or a maximum rotation (7) as one goes from one glucose unit to the next. All of these seven models preserve the 10·3 Å repeat of the fiber patterns of the various forms of cellulose. The structure of cellobiose, as described below, is perhaps between models 5 and 6, with an angle of very roughly 26° between the mean planes of the two six-membered rings. As will be shown later this configuration is determined to a large extent by the intramolecular hydrogen bond. The nearly perpendicular mutual orientation of the mean planes of the glucose rings as suggested by Bjørnhaug *et al.* (1953) for cellulose II is not present in cellobiose, but our results do suggest that the somewhat bent conformation rather than the extended or straight conformation for the chain is more likely.

The method of solution of this structure, which contains no heavy atom, is an example of the power of superposition techniques in three dimensions when carried out with the aid of a computer. An important feature is the increase in resolution of the Patterson function by the use of the gradient of the electron density function. This method provides a physical basis for the $\sin^2 \theta$ type of sharpening function as used by Schomaker & Shoemaker (Lipson & Cochran, 1953), but, more important, allows one to obtain sharper peaks without spurious background when an appropriate sum of the gradient Patterson function and the ordinary sharpened Patterson function is taken. A brief note of this study of the cellobiose

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structure has appeared (Jacobson, Wunderlich & Lipscomb, 1959).

Experimental

Truncated square pyramidal crystals of only moderately good quality were obtained by slow evaporation of a solution of cellobiose in an equal-volume mixture of water and ethylene chlorohydrin. Many other solvents and mixtures gave twinned crystals or small masses of crystals. Weissenberg photographs of 968 observed reflections, 83% of the recorded part of the reciprocal lattice, were taken with the use of the Cu K radiation. A sample of powdered Al was superimposed for calibration of the unit cell dimensions. The 'angular lag' method (Buerger, 1942) on higher levels about a or c indicated that $\beta=90°$ within $\pm 0{\cdot}5°$ or less. Intensities, measured by visual comparison with a standard scale, were corrected graphically for Lorentz and polarization factors (Lu, 1943), but corrections for absorption and extinction were not made. The density of the crystals was measured by flotation in a mixture of benzene and methylene iodide, the refractive index of which was measured and correlated with the density of the solution (Midgley, 1951).

Crystallographic data are listed as follows:

cellobiose, $C_{12}O_{11}H_{22}$, monoclinic,

$$a=10{\cdot}94\pm0{\cdot}02,\ b=13{\cdot}05\pm0{\cdot}05,$$
$$c=5{\cdot}11\pm0{\cdot}02\ \text{Å},\ \beta=90°\pm0{\cdot}5°,$$
$$V=730\pm7\ \text{Å}^3,\ D_m=1{\cdot}55\ \text{g.cm.}^{-3},$$
$$Z=2,\ D_x=1{\cdot}556\ \text{g.cm.}^{-3},$$

$F(000)=364$, $\mu=13{\cdot}8$ cm.$^{-1}$ for Cu $K\alpha$ radiation. Systematic extinctions were observed only for $0k0$ when k is odd. Since the natural cellobiose is optically active and the unit cell contains only two molecules, the space group is $P2_1$ (C_2^2).

Structure determination

Preliminary study

The general molecular orientation and a decision in favor of the bent (Hermans, 1949) conformation instead of the extended (Meyer & Misch, 1937) conformation resulted from a study of the three-dimensional Patterson function carried out at the Institut de Recherches Chimiques Appliquées in Paris, France, (Wunderlich, 1955). Trial and error methods, and the graphical superposition method of obtaining the three-dimensional minimum function (Buerger, 1951) failed to yield the structure. Hence the problem was set aside until, at the University of Minnesota, high speed computer techniques were developed specifically for repeated calculation of the minimum function in three dimensions (Rossmann, Jacobson, Hirshfeld & Lipscomb, 1959). Even so, the usual sharpening procedure in which the expression $\exp(-4\pi^2\sin^2\theta/\lambda^2p)/\hat{f}^2$ was used failed to yield sufficient resolution for the successful use of the minimum function. Excluding H, there are 46 atoms of C and O, producing some 2070 vectors, an average density of some 2·8 peaks/Å^3, ignoring accidental or symmetry induced coincidences. Further sharpening by the use of this exponential function promised to introduce false minima. Hence, we investigated a procedure which would remove much of the false minima, and yet leave the peaks highly sharpened.

The gradient Patterson function

As a one-dimensional example, let us represent the electron density $\varrho(x)$ by the curve in Fig. 1(a). The Patterson function, $P(u)=a\int_0^1\varrho(x)\varrho(x+u)dx$ from two such atoms is shown in Fig. 1(c). Various modification functions such as the exponential function are usually employed to sharpen the Patterson function. However, our approach is to consider other functions of x which change more rapidly than does $\varrho(x)$ as x changes. One such function is $a^{-1}d\varrho(x)/dx$, the gradient of the electron density shown in Fig. 1(b). The gradient Patterson function is

$$Q(u)=a^{-1}\int_0^1\frac{d\varrho(x)}{dx}\frac{d\varrho(x+u)}{dx}dx$$

as shown in Fig. 1(c). This function in itself is of little greater value than a highly sharpened Patterson peak.

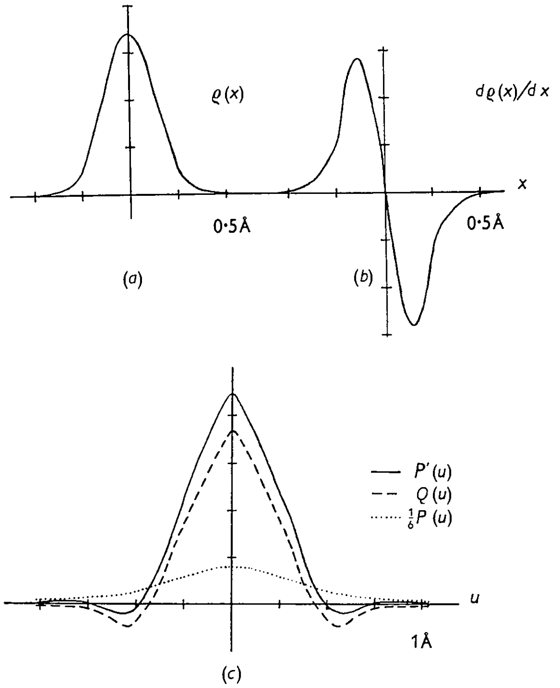

Fig. 1. (Curve a) The electron density function $\varrho(x)$; (Curve b) The sharpened Patterson peak $P(u)$ corresponding to $\varrho(x)$; (Curve c) The derivative function $d\varrho(x)/dx$; (Curve d) The gradient Patterson peak $Q(u)$ (see equation (2)); (Curve e) The scaled sum of $P(u)$ and $Q(u)$.

Indeed, in three dimensions it is the result of the already familiar ($\sin^2\theta/\lambda^2$) sharpening function on an ordinary Patterson peak. Where $Q(u)$ has negative regions $P(u)$ can be made to have positive regions approximately equal in magnitude, if an appropriate relative scaling is chosen. Hence the weighted sum of $P(u)$ and $Q(u)$ can be made into the very sharp peak shown in Fig. 1(c), where very little residual regions occur around the sharp peaks. This rather simple modification made possible the solution of the cellobiose problem because of the increased resolution obtained thereby, and because of the accuracy required in the location of peaks if a number of consecutive superpositions are to be carried out successfully.

The extension to three dimensions in a non-orthogonal coordinate system is straightforward. The function $Q(u, v, w)$ is

$$Q(u, v, w)$$
$$= V\int_0^1\int_0^1\int_0^1 \nabla\varrho(x, y, z) . \nabla\varrho(x+u, y+v, z+w)\,dxdydz\,,$$

where (Condon & Odishaw, 1958) the gradient operator is $\nabla = \mathbf{a}^*\partial/\partial x + \mathbf{b}^*\partial/\partial y + \mathbf{c}^*\partial/\partial z$. The usual expression for $\varrho(x, y, z)$ in terms of F_{hkl} then reduces $Q(u, v, w)$ to

$$Q(u, v, w) = 16\pi^2/V \sum_h \sum_k \sum_l (\sin\theta/\lambda)^2 |F_{hkl}|^2 \cos 2\pi\mathbf{H}.\mathbf{r}\,,$$

where

$$\mathbf{H}.\mathbf{r} = hu+kv+lw \text{ and } 4\sin^2\theta/\lambda^2 = h^2\mathbf{a}^*.\mathbf{a}^* + k^2\mathbf{b}^*.\mathbf{b}^* + l^2\mathbf{c}^*.\mathbf{c}^* + 2hl\mathbf{a}^*.\mathbf{c}^* + 2kl\mathbf{b}^*.\mathbf{c}^* + 2hk\mathbf{a}^*.\mathbf{b}^*$$

in an intermediate step. The function $P'(u, v, w)$ is simply

$$P'(u, v, w) = kP(u, v, w) + Q(u, v, w)$$
$$= 16\pi^2/V \sum_h \sum_k \sum_l [k' + (\sin\theta/\lambda)^2] |F_{hkl}|^2 \cos 2\pi\mathbf{H}.\mathbf{r}\,,$$

where $k' = k/16\pi^2$ is chosen empirically to be about $\frac{1}{6}$ when the $|F_{hkl}|^2$ were modified by

$$\exp\,(-4\pi^2\sin^2\theta/\lambda^2 p)/\hat{f}^2.$$

More important than the neglect of anomalous scattering is the assumption that the same k' will apply equally well to Patterson peaks due to atoms of different shapes.

It may be added parenthetically that the modification of $|F_{hkl}|^2$ in the calculation of $P'(u, v, w)$ has added advantages in giving low weight to low order reflections susceptible to extinction and absorption, and in enhancing, relatively, interactions between heavy atoms at the expense of interactions between heavy atoms and light atoms, and especially light atom-light atom interactions. This effect is due to sharpening both by $1/\hat{f}^2$ and by $(\sin\theta/\lambda)^2$. It is based on the relatively smaller decrease of the atomic scattering factor for heavy atoms as $\sin\theta$ increases. Of course the increased resolution of clusters of light atom interactions also makes this effect more apparent. The $P'(u, v, w)$ function was used by Spencer & Lipscomb (1961) partly as a device for the location of $P \cdots P$ vectors in the presence of numerous $P \cdots C$ or $P \cdots F$ vectors and even more numerous $C \cdots C$, $F \cdots F$, and $C \cdots F$ vectors.

Analysis of the gradient Patterson function

The superposition procedure was not greatly different from the usual graphical methods, except that several series of three-dimensional superpositions were carried out on the UNIVAC SCIENTIFIC 1103 computer before a recognizable structure emerged. We are by no means sure why the several false starts failed to yield a structure, but suspect that there are types of ambiguities well worth further investigation. In general, the choice of a Harker peak for the first superposition has the advantages (a) that it is a vector between symmetry related atoms and hence of known height if resolved, (b) that only one or two coordinates need to be found, and, most important, (c) the position of a symmetry element is simultaneously fixed. Subsequent superpositions may then be carried out on groups of symmetry-related atoms. Because numerous three-dimensional superpositions can be tried in a relatively short time, very complex structures can be solved by this method in spite of the difficulty in location of Harker peaks, which are frequently obscured by larger non-Harker peaks. The distribution of 1·5 Å vectors around the origin indicated that some bonds were roughly parallel to b while others made angles of about 30° with a. A choice was then made of a group of three small peaks, representing bonded atoms, such as A, B, and C of Fig. 2(a) (see also Fig. 2(b)) in order to identify a Harker peak, A. Further superpositions were made on peak B and its symmetry related atom, and then on peak C and its symmetry related atom. Thus each series consisted of five superpositions in each of which the three-dimensional minimum function was computed. The series just described is the only one which gave a recognizable puckered six-membered ring with some of the attached hydroxyl oxygen atoms.

As criteria in recognizing part of the molecule from the other peaks and fragments of peaks left by chance after five superpositions and from other parts of the molecule, spheres of 1·5 Å and 2·5 Å representing nearest neighbor and next nearest neighbor distances respectively, were drawn. One ring and its attached groups were easily located by noting those peaks occurring at the intersection of two spheres. A glance at the final structure will suggest the many places where six-membered rings almost occur, but perhaps only those who have solved other carbohydrate structures will sympathize fully with the problems of ambiguities.

When one ring and its attached groups were located, these atoms, only about half of those in the molecule, were used to compute the phases for the projection along [001] (Fig. 3). The second ring was located

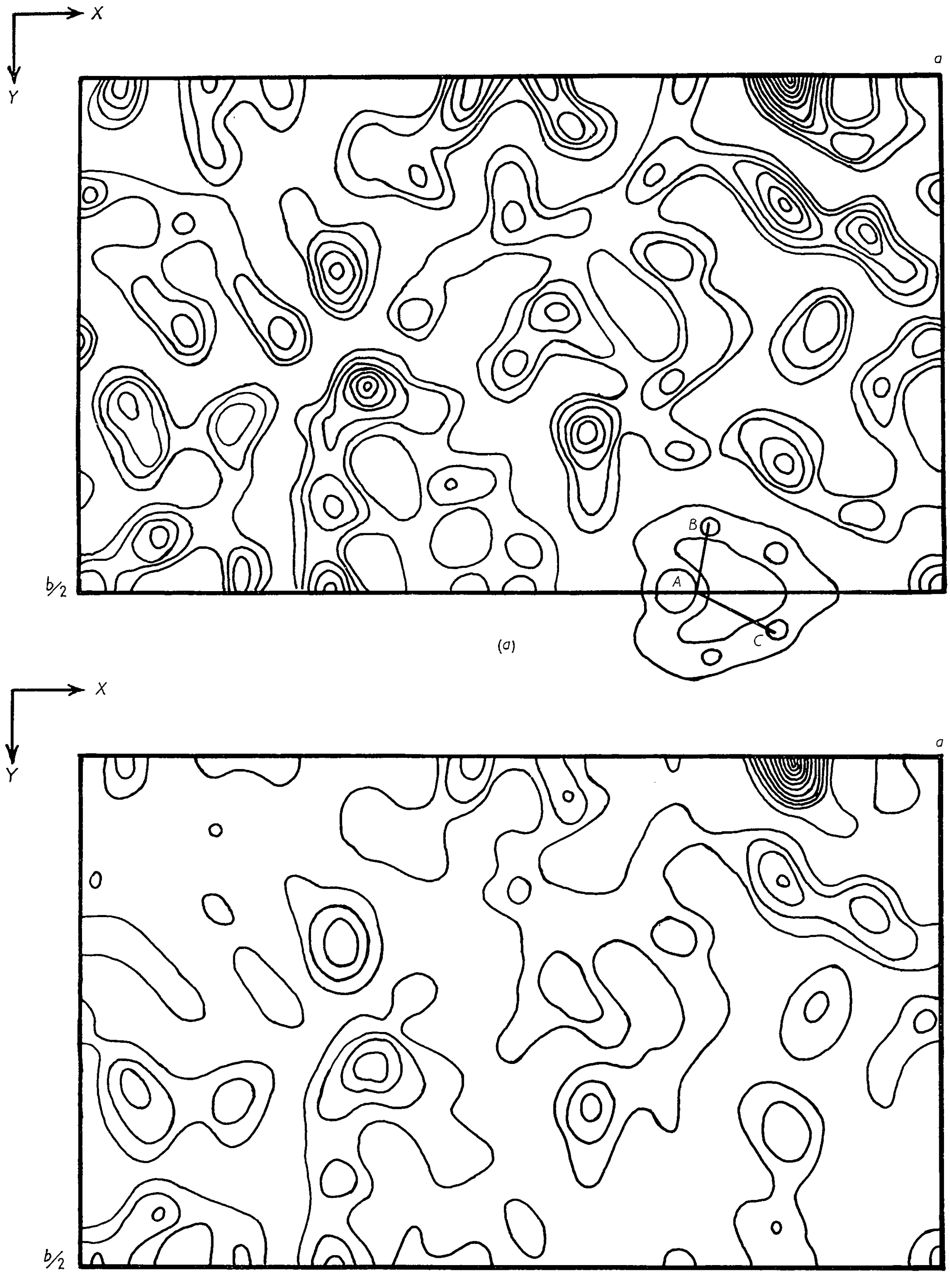

Fig. 2. (*a*) The function $P'(u, v, 12/30)$ for cellobiose; (*b*) The usual sharpened Patterson section $P(u, v, 12/30)$ for cellobiose. The contours in both figures are drawn at intervals of 10 arbitrary units, the lowest contour being 10 units.

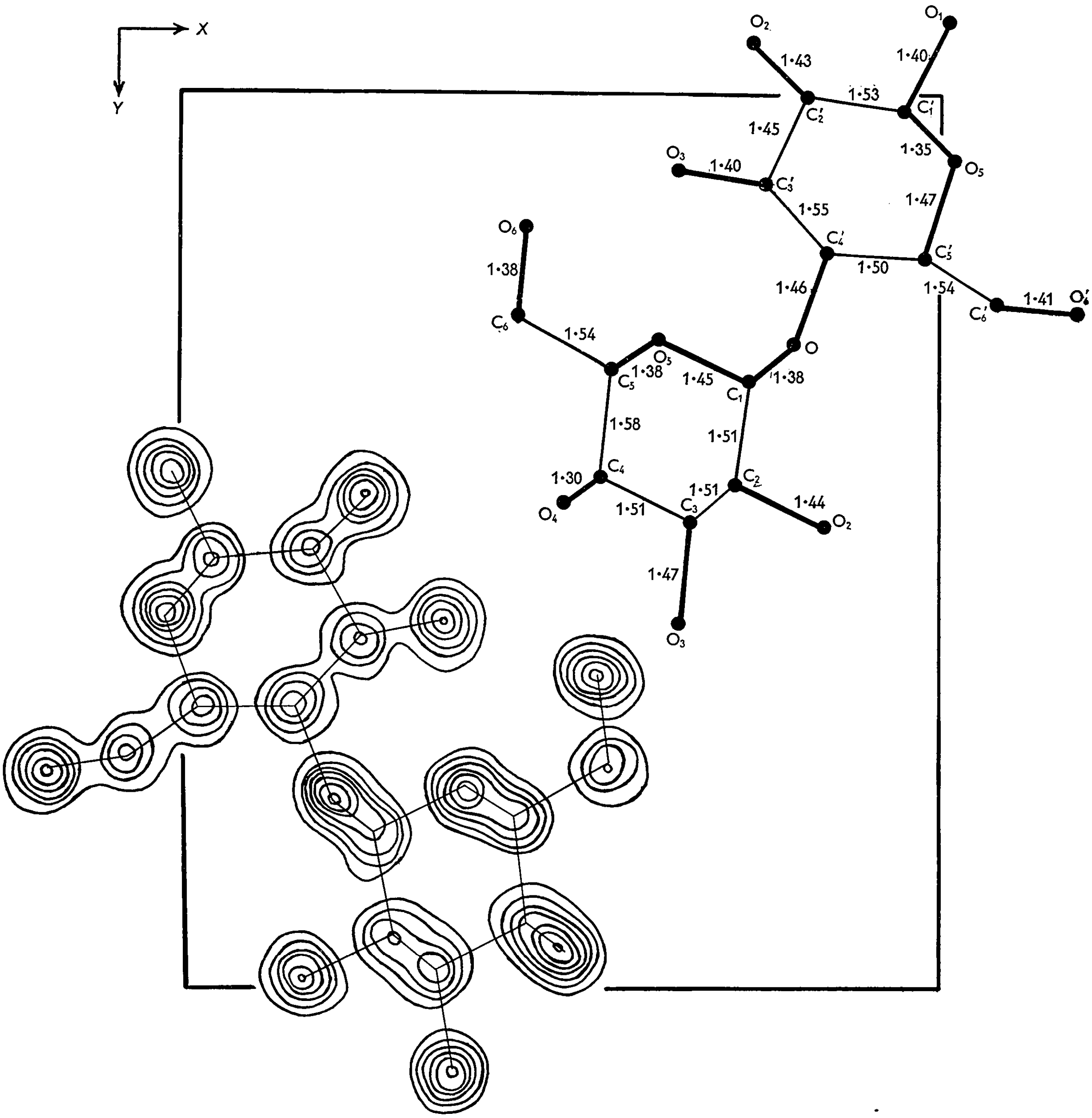

Fig. 3. Projection of the electron density along z, computed after solution of the three-dimensional problem, showing the bond lengths.

surprisingly easily, and then least-squares refinement of the $hk0$ data led to $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0{\cdot}22$ at this stage. The z coordinates, available from the final superposition map, were then introduced and three-dimensional refinement was carried out by least-squares procedures. After nine successive refinements in the diagonal approximation, during which R_{hkl} fell from 0·39 to 0·27, R_{hk0} fell from 0·22 to 0·16, and $r_{hkl}=\Sigma w(|F_o|^2=|F_c|^2)^2/\Sigma w|F_o|^4$ decreased from 0·43 to 0·12, a three-dimensional difference map was computed. Many small shifts in coordinates of C and O were indicated, but 17 of the 22 H atoms were also located. Inclusion of the 12 most clearly indicated H atoms reduced R_{hkl} to 0·20. Four cycles of three-dimensional refinement on the I.B.M. 704 with the use of the full matrix in the program written by Busing & Levy (1959a) then reduced R_{hkl} to 0·175 and r_{hkl} to 0·077. A final three-dimensional difference map, computed with the aid of the program by Shoemaker & Sly (1959) fixed the positions of 12 of the 14 H atoms attached to C, and 7 of the 8 H atoms in hydrogen bonds, the latter being somewhat less well defined. Final values are $R_{hkl}=0{\cdot}17$, $R_{hk0}=0{\cdot}13$ and $r_{hkl}=0{\cdot}074$, for the final parameters including 14 H atoms most

Table 2. *Observed and calculated structure factors*

Upper limits of absent reflections are starred.

h, k, l	$10F_o$	$10F_c$
0, 0, 0		3640
1.	15*	24
2	76	84
3	39	12
4	351	348
5	387	318
6	481	341
7	69	3
8	37*	16
9	103	82
10	209	201
11	69	92
12	94	64
13	29*	40
1, 1, 0	285	377
2	282	322
3	309	291
4	26*	32
5	132	88
6	251	198
7	197	180
8	37	69
9	137	90
10	32	65
11	32*	30
12	61	71
13	25*	23
0, 2, 0	189	179
1	169	211
2	145	140
3	320	323
4	357	314
5	309	223
6	304	275
7	71	71
8	137	156
9	101	91
10	82	91
11	118	114
12	71	88
13	26*	33
1, 3, 0	150	158
2	220	191
3	69	74
4	158	181
5	319	284
6	169	168
7	82	94
8	69	101
9	99	84
10	71	72
11	68	61
12	26	69
13	26*	29
0, 4, 0	395	426
1	209	139
2	272	256
3	435	426
4	307	308
5	245	225
6	90	80
7	165	181
8	158	162
9	167	174
10	33*	45
11	32*	30
12	26*	28
13	58	79
1, 5, 0	275	248
2	289	288
3	215	176
4	151	149
5	121	100
6	78	66
7	162	165
8	137	154
9	101	91
10	33*	53
11	96	92
12	32*	38
0, 6, 0	717	693
1	414	369
2	203	198
3	350	321
4	111	125
5	108	104
6	58	44
7	165	170
8	58	37
9	101	90
10	32	53
11	94	96
12	26*	25
1, 7, 0	272	239
2	115	107
3	195	190
4	37	36
5	49	59
6	182	173
7	149	162
8	106	109
9	41*	25
10	29	19
11	69	85
12	76	110
0, 8, 0	145	177
1	27*	44
2	148	152
3	226	203
4	205	222
5	170	166
6	82	50
7	115	117
8	143	173
9	66	58
10	37	52
11	71	80
1, 9, 0	142	134
2	47	39
3	58	60
4	182	192
5	192	213
6	84	108
7	31*	30
8	49	34
9	30*	24
0,10, 0	165	136
1	115	96
2	99	84
3,10, 0	132	126
4	187	196
5	104	110
6	205	235
7	45	59
8	28*	24
9	26	47
1,11, 0	156	150
2	74	64
3	76	76
4	52	85
5	45	66
6	58	63
7	92	110
8	26*	16
0,12, 0	205	194
1	114	105
2	88	84
3	71	78
4	33	37
5	82	79
6	66	71
7	84	82
8	82	71
1,13, 0	51	57
2	44	47
4	55	45
5	49	53
6	41	45
8	32	47
0,14, 0	60	93
1	37	53
4	27*	47
5	41	57
6	61	52
1,15, 0	58	53
4	48	46
5	54	68
6	32	67
1,16, 0	35	47
0, 0, 1	36	75
1	178	205
2	942	750
3	97	104
4	278	262
5	59	89
6	68	19
7	48	75
8	42	21
9	70	98
10	43	61
11	42*	17
12	37*	36
0, 1, 1	629	683
1	994	1033
2	643	518
3	688	547
4	111	102
5	63	57
6	322	299
7	251	214
8	61	77
9	49	43
10	45*	43
11	89	76
12	64	76
0, 2, 1	457	506
1	289	327
2	538	462
3	115	154
4	243	232
5	212	210
6	251	256
7	234	229
8	119	150
9	112	103
10	114	85
11	51	79
12	36*	45
0, 3, 1	159	183
1	284	246
2	304	280
3	373	298
4	91	127
5	87	76
6	135	110
7	164	161
8	266	275
9	73	65
10	106	111
11	129	131
12	35*	25
0, 4, 1	272	277
1	257	270
2	135	107
3	335	295
4	246	201
5	135	143
6	54	26
7	57	48
8	234	253
9	131	152
10	67	67
12	83	97
13	42	61
0, 5, 1	291	282
1	305	295
2	170	166
3	333	243
4	60	54
5	68	50
6	191	199
7	141	127
8	77	75
9	106	108
0, 6, 1	81	109
1	49	69
2	233	250
3	312	310
4	206	206
5	114	103
6	44*	23
7	72	25
8	48	14
9	41*	32
0, 7, 1	284	266
1	303	297
2	295	395
3	307	312
4	44*	57
5, 7, 1	77	35
6	45	52
7	197	183
8	117	122
9	84	103
11	72	97
0, 8, 1	62	65
1	234	227
2	240	232
3	137	123
4	151	139
5	128	139
6	100	121
7	145	167
8	70	86
9	67	25
0, 9, 1	175	153
1	150	112
2	100	71
3	168	175
4	59	84
5	77	62
6	157	160
7	153	150
8	47	53
9	72	86
10	57	63
0,10, 1	114	112
1	139	158
2	232	191
3	77	48
4	48*	12
5	48	74
6	135	131
7	48	27
8	46	20
9	21*	36
0,11, 1	260	261
1	124	97
2	77	54
3	71	43
4	66	53
5	108	96
6	108	111
7	48	28
8	42	42
9	59	68
0,12, 1	51	57
1	137	119
2	71	68
3	103	88
4	103	89
5	121	78
6	33*	50
0,13, 1	77	87
1	30*	8
2	62	24
3	48	49
4	84	84
6	29*	32
0,14, 1	40	56
1	106	96
3	72	70
6	41	4
0,15, 1	43	5
3	85	53
1, 0,-1	51	16
2	254	232
3	72	75
4	825	759
5	135	132
6	124	126
7	32*	6
8	54	14
9	39*	9
10	107	82
11	103	107
12	37*	68
1, 1,-1	465	556
2	265	251
3	245	218
4	157	146
5	318	272
6	329	277
7	170	124
8	59	32
9	188	196
10	171	158
11	102	86
1, 2,-1	100	131
2	54	71
3	119	115
4	326	346
5	260	214
6	77	74
7	143	80
8	72	69
9	92	96
10	124	116
11	88	78
1, 3,-1	238	223
2	199	185
3	481	560
4	148	151
5	174	133
6	108	105
7	68	52
8	108	114
9	120	102
10	106	103
11	41*	16
12	43	68
1, 4,-1	147	161
2	31	33
3	135	164
4	246	230
5	51	49
6	53	71
7	175	169
8	111	96
9	57	74
10	43*	46
11	40*	38
1, 5,-1	197	227
2	233	207
3	87	69
4	128	131
5	106	101
6	92	65
7	226	217
8, 5,-1	77	77
9	63	53
10	42*	37
11	38*	50
12	68	45
1, 6,-1	229	227
2	229	226
3	100	59
4	230	232
5	155	124
6	104	81
7	258	257
8	199	173
9	153	148
10	101	98
11	94	97
12	89	87
1, 7,-1	126	99
2	143	131
3	68	75
4	80	28
5	77	49
6	71	37
7	228	221
8	85	83
9	116	115
10	162	160
11	72	44
12	45	10
1, 8,-1	52	78
2	67	32
3	108	94
4	100	86
5	186	167
6	77	33
7	45*	32
8	62	33
9	82	45
10	78	84
1, 9,-1	86	85
2	75	30
3	316	296
4	77	67
5	197	189
6	110	91
7	45*	22
8	72	53
9	68	72
10	40	45
1,10,-1	72	72
2	178	177
3	185	170
4	221	196
5	142	131
6	147	147
7	77	43
8	100	79
9	44	19
10	42	38
1,11,-1	49	58
2	41*	32
3	185	155
4	80	59
5	89	106
6	98	65
7	43*	36
8	54	22
9	64	74
1,12,-1	87	77
2	96	84
3	77	26
5	89	91
6	111	107
7	76	65
8	72	66
1,13,-1	77	72
3	130	93
5	87	81
6	100	103
7	64	48
8	46	32
1,14,-1	55	30
3	72	53
5	55	57
6	81	22
7	64	13
3,15,-1	72	61
0, 0, 2	247	263
1	95	120
2	121	90
3	137	110
4	355	341
5	161	109
6	129	70
7	115	90
8	248	242
9	240	237
10	47*	0
11	75	59
12	37*	34
0, 1, 2	81	147
1	203	181
2	249	249
3	248	253
4	112	119
5	71	70
6	36*	9
7	37*	34
8	140	118
9	76	95
10	127	118
11	43*	38
12	36*	57
0, 2, 2	565	632
1	85	82
2	141	163
3	593	533
4	368	277
5	37*	69
6	118	105
7	152	142
8	241	211
9	170	143
10	57	78
11	42*	40
12	62	36
0, 3, 2	116	141
1	255	249
2	85	90
3	190	201
4, 3, 2	491	404
5	40*	31
6	130	122
7	168	134
8	134	102
9	172	157
10	112	102
11	115	88
12	35*	56
0, 4, 2	293	313
1	145	150
2	138	82
3	296	270
4	270	218
5	117	86
6	161	141
7	66	37
8	121	91
9	59	44
10	137	144
11	41	77
12	89	106
0, 5, 2	72	98
1	67	46
2	88	113
3	115	65
4	99	48
5	149	126
6	106	98
7	80	65
8	56	56
9	92	118
11	67	78
12	36	38
0, 6, 2	105	104
1	45	21
2	112	139
3	170	118
4	158	139
5	161	135
6	83	117
7	58	41
8	180	184
9	61	63
0, 7, 2	105	117
1	32*	33
2	63	40
3	187	162
4	207	204
5	137	113
6	72	54
7	45	41
8	41*	26
9	84	86
0, 8, 2	77	58
1	178	148
2	177	142
3	344	359
4	150	147
5	115	87
6	88	94
7	114	70
8	116	105
9	80	92
0, 9, 2	89	54
1	183	173
2	225	173
3	158	140
4	191	128
5	129	77
6	109	88
7	104	101
8	55	38
9	60	33
0,10, 2	240	200
1	249	224
2	100	86
3	187	158
4	129	100
5	118	51
6	81	85
7	65	52
8	77	80
0,11, 2	64	52
1	80	94
2	165	133
3	77	70
4	49*	62
5	91	66
0,12, 2	111	95
1	115	108
2	41*	37
3	107	77
4	44	26
5	96	61
0,13, 2	47	34
2	84	61
3	93	65
4	120	113
0,14, 2	38	24
3	64	46
4	52	67
0,15, 2	63	62
1, 0,-2	227	281
2	50	67
3	88	49
4	41	88
5	194	191
6	253	267
7	57	53
8	342	356
9	180	194
10	100	77
11	67	62
1, 1,-2	214	239
2	178	144
3	133	143
4	136	152
5	255	237
6	37*	24
7	215	198
8	190	179
9	88	61
10	81	79
11	43*	1
1, 2,-2	185	205
2	44	45
3	326	259
4	363	368
5	167	183
6, 2,-2	111	118
7	86	49
8	172	152
9	46	18
10	81	67
11	43*	10
1, 3,-2	159	187
2	244	221
3	152	157
4	330	321
5	63	94
6	216	197
7	39	103
8	90	80
9	47*	32
10	80	68
11	41*	33
12	42	55
1, 4,-2	173	169
2	217	239
3	76	88
4	134	111
5	102	125
6	64	9
7	188	153
8	137	108
9	79	73
10	45	56
11	59	52
12	69	36
1, 5,-2	41	38
2	107	96
3	172	139
4	92	92
5	116	127
6	207	173
7	90	64
8	246	234
9	116	109
10	77	42
12	72	56
1, 6,-2	65	91
2	108	129
3	38*	50
4	98	96
5	45*	6
6	43*	33
7	179	156
8	246	216
9	131	134
10	103	57
1, 7,-2	110	131
2	154	165
3	63	54
4	95	80
5	47*	30
6	67	47
7	192	147
8	53	51
9	46	32
10	69	91
1, 8,-2	72	86
2	138	144
3	298	276
4	218	189
5	88	79
6	59	53
7	65	46
8	53	48
9	43*	31
1, 9,-2	87	78
2	71	59
3	226	200
4	275	248
5	83	41
6	77	37
7	88	67
8	64	43
9	40	35
1,10,-2	85	95
2	179	176
3	148	126
4	122	107
5	79	68
6	45	54
7	79	57
8	105	57
9	74	43
1,11,-2	112	110
2	68	43
3	109	84
4	90	80
5	88	78
6	42	34
7	133	71
8	80	60
1,12,-2	89	86
2	112	94
3	63	39
4	88	48
5	68	27
6	104	96
7	32*	31
1,13,-2	63	71
2	37*	37
3	77	59
4	40	19
5	94	69
7	90	67
1,14,-2	61	66
2	105	81
3	75	46
4	62	72
5	130	98
3,15,-2	80	82
0, 0, 3	60	79
1	63	0
2	82	93
3	38*	32
4	49*	59
5	191	227
6	76	109
8	33	79
9	50*	33
0, 1, 3	228	241
1	75	102
2	60	85
3	82	84
4	136	131
5	104	64
6, 1, 3	151	162
8	154	129
9	137	128
0, 2, 3	38	109
1	160	165
2	110	133
3	237	274
4	123	153
5	180	189
6	62	84
7	36*	50
8	88	84
9	87	83
0, 3, 3	201	218
1	143	146
2	63	88
3	255	297
4	161	137
5	98	133
6	111	94
7	78	44
8	34*	35
9	78	88
0, 4, 3	102	142
1	145	155
2	144	131
3	44*	109
4	112	121
5	82	79
6	106	133
7	37*	35
8	91	112
9	50*	37
0, 5, 3	89	86
1	58	63
2	44*	42
3	47*	61
4	113	84
5	154	137
6	68	101
7	80	91
8	34	49
9	49	69
0, 6, 3	38	53
1	62	46
2	106	97
3	50*	55
4	111	106
5	87	42
6	40	49
8	33*	39
9	47	51
0, 7, 3	168	173
1	62	45
2	118	98
3	78	82
4	126	106
5	100	105
6	110	109
8	50	6
9	78	93
0, 8, 3	29	34
1	101	111
2	164	168
3	94	73
4	146	129
5	203	186
6	39*	49
8	31*	32
0, 9, 3	189	154
1	154	156
2	116	101
3	144	116
4	51*	41
5	98	129
6	81	78
8	60	41
0,10, 3	33*	49
1	111	111
2	134	124
3	166	179
4	49	72
5	100	88
6	36*	50
0,11, 3	114	120
1	36	16
2	88	68
3	91	68
4	125	95
5	75	53
6	55	68
0,12, 3	26*	58
1	80	58
3	67	52
4	113	106
5	80	83
0,13, 3	55	77
4	86	58
1, 0,-3	46	37
2	33*	33
3	32*	13
4	56*	32
5	54	28
6	175	195
7	260	258
8	57	59
1, 1,-3	134	146
2	256	287
3	84	74
4	75	64
5	245	258
6	130	145
7	191	186
8	33	31
1, 2,-3	285	361
2	148	169
3	65	82
4	291	271
5	45*	40
6	125	145
7	184	135
8	88	81
1, 3,-3	124	152
2	98	137
3	63	78
4	233	239
5	134	141
6	110	122
7	78	85
8	85	80
1, 4,-3	49	49
2	119	129
3	37*	10
4	274	248
5	101	104
6	47*	25
7	209	158
8	122	129
1, 5,-3	46	37
2	91	78
3	71	110
4	58*	36
5	49	68
6	50*	20
7	262	219
8	34*	43
1, 6,-3	32	46
2	44*	48
3	96	128
4	66	48
5	50*	44
6	143	157
7	117	134
8	58	34
1, 7,-3	129	148
2	168	174
3	41*	6
4	171	112
5	100	79
6	118	92
7	79	63
8	32*	51
1, 8,-3	169	224
2	66	61
3	143	191
4	126	97
5	100	75
6	132	128
7	148	110
8	97	74
1, 9,-3	97	120
2	56	63
3	73	103
4	115	84
5	50*	28
6	38*	37
7	59	44
1,10,-3	105	116
2	141	154
3	79	80
4	120	94
5	47	47
6	87	77
1,11,-3	80	59
3	35*	27
4	45*	25
5	92	61
6	96	78
1,12,-3	88	81
3	85	96
4	71	59
5	65	28
6	66	55
1,13,-3	41	48
4	75	55
1,14,-3	59	23
0, 0, 4	269	304
1	63	42
3	156	151
4	50	105
8	33	9
0, 1, 4	113	153
1	152	158
3	78	66
4	220	237
8	80	62
0, 2, 4	52	89
1	140	182
3	147	184
4	130	140
8	56	62
0, 3, 4	102	111
1	60	34
3	46*	67
4	88	72
5	108	77
8	55	57
0, 4, 4	38	55
1	75	92
3	46*	69
4	109	72
8	54	41
0, 5, 4	84	106
1	129	160
3	92	111
4	51*	35
8	29*	17
0, 6, 4	127	148
1	80	82
3	46*	11
4	50*	19
8	60	55
0, 7, 4	123	126
1	39*	51
3	46*	66
4	50	66
8	26*	30
0, 8, 4	101	101
1	149	160
3	44	61
4	47	57
8	63	79
0, 9, 4	50	65
1	51	80
3	42*	45
4	78	43
5	131	109
0,10, 4	27*	44
1	27	37
3	116	79
4	126	74
5	65	70
0,11, 4	60	63
1	73	13
4	85	88
0,12, 4	50	15
1, 0,-4	114	134
2	57	55
3	45*	80
4, 0,-4	181	195
5	50*	25
6	40*	6
7	40	60
8	33	15
1, 1,-4	64	132
2	50	59
3	45*	48
4	159	161
5	88	108
6	99	106
7	79	75
8	56*	10
1, 2,-4	128	180
2	60	117
3	45*	43
4	124	117
5	189	203
6	38	69
7	102	92
8	87	85
1, 3,-4	60	71
2	29*	20
3	46*	45
4	88	45
5	158	164
6	40	41
7	37*	14
8	55	72
1, 4,-4	61	93
2	60	63
3	46*	28
4	161	137
5	49*	44
6	151	158
7	34*	23
8	53	92
1, 5,-4	92	155
2	59	48
3	46*	72
4	125	140
5	88	53
7	97	89
1, 6,-4	62	80
2	65	100
3	110	112
4	88	112
5	125	107
1, 7,-4	66	115
2	45	70
3	96	103
4	106	80
5	102	91
1, 8,-4	59	64
2	60	56
3	44*	44
4	180	159
5	90	69
1, 9,-4	29*	37
2	65	83
3	71	66
4	200	196
1,10,-4	28	52
3	78	77
4	70	39
3,11,-4	58	45
4	60	73
0, 0, 5	49	70
3	78	57
4	103	129
5	99	115
1, 1, 5	89	114
3	146	164
4	103	84
8	23*	13
1, 2, 5	92	121
3	77	50
8	69	89
1, 3, 5	74	89
3	75	9
8	71	110
1, 4, 5	29	71
3	43*	45
1, 5, 5	61	34
3	101	121
1, 6, 5	68	86
3	38*	71
3	64	78
5	86	93
1, 0,-5	112	184
2	75	145
3	45*	31
4	49*	48
5	47*	5
8	41	29
1, 1,-5	31*	36
2	53	100
3	45*	34
4	47*	47
5	45*	38
8	58	72
1, 2,-5	65	101
3	45*	113
4	102	128
5	46	44
3, 3,-5	75	70
4	82	77
5	44*	44
3, 4,-5	43*	11
4	79	96
5	92	56
3, 5,-5	94	106
4	108	104
5	88	86
3, 6,-5	41*	60
4	41*	34
5	39*	2
3, 7,-5	100	155
4	82	81
5	86	52
1, 8,-5	108	42
1, 9,-5	69	29
1, 0,-6	56	94
1, 1,-6	56	118

Table 1(*a*). *Atomic positional and temperature parameters*

(x, y, and z are expressed in fractions of **a**, **b**, and **c** respectively)

	x	y	z	B (Å^2)
C_1	0·748	0·307	0·017	1·44
C_2	0·731	0·433	−0·015	1·94
C_3	0·672	0·474	0·232	2·39
C_4	0·553	0·424	0·304	2·27
C_5	0·563	0·303	0·273	0·89
C_6	0·443	0·244	0·308	2·43
C_1'	0·957	0·011	−0·470	2·35
C_2'	0·827	0·000	−0·365	2·44
C_3'	0·767	0·097	−0·320	2·11
C_4'	0·853	0·175	−0·180	1·06
C_5'	0·979	0·179	−0·291	1·24
C_6'	1·075	0·234	−0·119	2·01
O_2	0·847	0·480	−0·073	2·57
O_3	0·654	0·585	0·212	1·83
O_4	0·503	0·453	0·525	1·84
O_6	0·456	0·143	0·225	1·83
O_5	0·630	0·271	0·057	1·81
O_1'	0·013	−0·084	−0·511	2·63
O_2'	0·753	−0·059	−0·539	2·38
O_3'	0·658	0·080	−0·184	2·90
O_6'	1·183	0·227	−0·267	2·35
O_5'	1·023	0·073	−0·311	1·69
O	0·803	0·278	−0·202	0·97

Table 1(*b*). *Coordinates of the hydrogen atoms which were located from the difference map*

	x	y	z
H_1	0·77	0·31	0·14
H_2	0·67	0·44	−0·20
H_3	0·72	0·48	0·38
H_4	0·51	0·41	0·15
H_5	0·59	0·29	0·37
H_1'	0·97	0·06	−0·65
H_2'	0·83	−0·03	−0·25
H_3'	0·76	0·14	−0·48
H_4'	0·86	0·14	−0·03
H_5'	0·98	0·13	−0·47
$H_6'(1)$	1·07	0·18	0·06
$H_6'(2)$	1·02	0·32	−0·06
H (O_1')	1·08	−0·07	0·35
H (O_3')	0·63	0·14	−0·10
H (O_6')	1·20	0·30	−0·37
H (O_2)	0·84	0·52	0·05
H (O_3)	0·69	0·65	0·16
H (O_4)	0·52	0·52	0·52
H (O_6)	0·42	0·14	0·10

reliably located. Final atomic positions for C and O (Table 1(*a*)) are obtained from this final refinement, but the H atom positions are those obtained from the second three-dimensional difference map. Standard deviations, computed from the full matrix, are

$$\sigma_x = \sigma_y = \sigma_z = 0{\cdot}020 \text{ Å}, \quad \sigma_B = 0{\cdot}4 \text{ Å}^2 \text{ for C},$$

and

$$\sigma_x = \sigma_y = \sigma_z = 0{\cdot}014 \text{ Å}, \quad \sigma_B = 0{\cdot}3 \text{ Å}^2 \text{ for O}.$$

Observed and calculated structure factors are listed in Table 2, and an analysis of R values is listed in Table 3. Atomic scattering curves were those of Hoerni & Ibers (1954) for C and O, and the curve of McWeeny (1951) for H.

Table 3. *Values of* $\Sigma||F_o|-|F_c||/\Sigma|F_o|$ *for different classes of reflections*

	R	Range of $\sin\theta$	R	Number of reflections
All planes	0·171	0·00–0·40	0·123	120
h odd	0·184	0·40–0·50	0·141	107
k odd	0·172	0·50–0·60	0·164	155
l odd	0·166	0·60–0·65	0·164	102
$k+l$ odd	0·176	0·65–0·70	0·170	111
$l+h$ odd	0·174	0·70–0·75	0·161	129
$h+k$ odd	0·181	0·75–0·80	0·210	137
$h+k+l$ odd	0·163	0·80–0·85	0·244	126
		0·85–0·90	0·257	100
		0·90–1·10	0·305	74

Discussion of the structure

The accepted bonding arrangement of the cellobiose molecule is confirmed. There are two 'chair' form β-glucose residues linked by an oxygen bridge in the 1:4 positions. The bond lengths, shown in Table 4, are not particularly satisfactory, perhaps owing to the poor quality of the crystals, and in spite of the low calculated standard deviations of 0·03 Å for C–C, 0·025 Å for C–O and 0·02 for O–O (Busing & Levy, 1959*b*). Thus the C_4–O_4 bond distance of 1·30 Å is five times its standard deviation and the C_1'–O_5' bond distances of 1·35 Å is three times its standard deviation from the more usual C–OH distance of about 1·43 Å. There are no such problems in the corresponding distances in the other β-glucose residue, and yet there are certainly no indications from either the difference maps of the behavior of temperature factors in many cycles of least-squares refinement that these atoms are incorrectly placed. Perhaps it is only that the laws of probability have caught up with us, for we hardly believe that these shortenings are real.

Table 4. *Interatomic distances*

C_1–C_2	1·51 Å	C_1'–C_2'	1·53 Å
C_2–C_3	1·51	C_2'–C_3'	1·45
C_3–C_4	1·51	C_3'–C_4'	1·55
C_4–C_5	1·58	C_4'–C_5'	1·50
C_5–C_6	1·54	C_5'–C_6'	1·54
C_1–O	1·38 Å	C_1'–O_1'	1·40 Å
C_1–O_5	1·45	C_1'–O_5'	1·35
C_2–O_2	1·44	C_2'–O_2'	1·43
C_3–O_3	1·47	C_3'–O_3'	1·40
C_4–O_4	1·30	C_4'–O	1·46
C_5–O_5	1·38	C_5'–O_5'	1·47
C_6–O_6	1·38	C_6'–O_6'	1·41

Intramolecular hydrogen bond

$O_3' \cdots O_5$	2·80 Å

Intermolecular hydrogen bonds

$O_2 \cdots O_5'$	2·71 Å	$O_4 \cdots O_6$	2·85 Å
$O_2 \cdots O_1'$	2·75	$O_4 \cdots O_2'$	2·80
$O_3 \cdots O_6$	2·70	$O_2' \cdots O_6'$	2·78
$O_3 \cdots O_6'$	2·80		

The bond angles, with calculated standard deviations of 1·7°, do not present such a problem. It is especially interesting that the two ring oxygen atoms form bonds at angles of 117·3° and 115·2°, and that the bridge oxygen has a bond angle of 117·5°. Although the angles in the aliphatic ethers (Sutton *et al.*, 1958), in sucrose sodium bromide dihydrate (Beevers & Cochran, 1947), and in α-glucose (McDonald & Beevers, 1952) are closer to the tetrahedral angle, it may be noted that the angle at the ring oxygen atom in α-rhamnose monohydrate is 120° (McGeachin & Beevers, 1957). On the other hand the bridge oxygen atom in sucrose is only 104·7°! Nevertheless, we feel that the bond angles, especially those about O atoms found here for cellobiose are highly relevant to models of cellulose, in view of the fact that previously only tetrahedral angles have been assumed. The length of the cellobiose molecule is highly relevant as an overall criterion of the bond angles and the correspondence between cellobiose and cellulose: the $O_1' \cdots O_4$ distance of 10·27 Å in cellobiose corresponds quite well to the fiber axis of 10·3 Å in all forms of cellulose.

Table 5. *Bond angles*

C_2-C_1-O	108·9°	$C_2'-C_1'-O_1'$	112·1°
$C_2-C_1-O_5$	110·7	$C_2'-C_1'-O_5'$	110·0
$O-C_1-O_5$	109·8	$O_1'-C_1'-O_5'$	112·2
$C_1-C_2-C_3$	108·4	$C_1'-C_2'-C_3'$	113·5
$C_1-C_2-O_2$	109·1	$C_1'-C_2'-O_2'$	111·0
$C_3-C_2-O_2$	113·5	$C_3'-C_2'-O_2'$	108·6
$C_2-C_3-C_4$	114·7	$C_2'-C_3'-C_4'$	111·3
$C_2-C_3-O_3$	110·3	$C_2'-C_3'-O_3'$	109·3
$C_4-C_3-O_3$	109·7	$C_4'-C_3'-O_3'$	113·1
$C_3-C_4-C_5$	110·4	$C_3'-C_4'-C_5'$	114·3
$C_3-C_4-O_4$	116·8	$C_3'-C_4'-O$	109·6
$C_5-C_4-O_4$	113·3	$C_5'-C_4'-O$	106·5
$C_4-C_5-C_6$	115·3	$C_4'-C_5'-C_6'$	115·4
$C_4-C_5-O_5$	114·4	$C_4'-C_5'-O_5'$	107·0
$C_6-C_5-O_5$	113·2	$C_6'-C_5'-O_5'$	105·0
$C_5-C_6-O_6$	110·8	$C_5'-C_6'-O_6'$	109·0

Ring oxygen bond angles

$C_1-O_5-C_5$	117·3	$C_1'-O_5'-C_5'$	115·2

Bridge oxygen bond angle

C_1-O-C_4'	117·5°

Hydrogen bond angles

$C_2-O_2-O_1'$	121·6°	$C_1'-O_1'-O_2$	102·5°
$C_2-O_2-O_5'$	124·9	$C_2'-O_2'-O_4$	121·3
$O_1'-O_2-O_5'$	114·5	$C_2'-O_2'-O_6'$	124·6
$C_3-O_3-O_6$	113·7	$O_4-O_2'-O_6'$	107·9
$C_3-O_3-O_6'$	131·6	$C_3'-O_3'-O_5$	99·9
$O_6-O_3-O_6'$	99·0	$C_6'-O_6'-O_3$	111·7
$C_4-O_4-O_6$	124·5	$C_6'-O_6'-O_2'$	121·8
$C_4-O_4-O_2'$	115·3	$O_3-O_6'-O_2'$	124·1
$O_6-O_4-O_2'$	101·2	$C_5-O_5-O_3'$	132·4
$C_6-O_6-O_3$	109·0	$C_1-O_5-O_3'$	102·6
$C_6-O_6-O_4$	135·3		
$O_3-O_6-O_4$	101·8		

The intramolecular hydrogen bond of 2·80 Å appears to be of great importance in establishing the relative orientations of the two rings, relatively twisted from one another by very roughly 26°. This distance occurs between the hydroxyl group attached to C_3' of one glucose residue and the ring oxygen O_5 of the other residue. In sucrose (Beevers & McDonald, 1952) a similar intramolecular hydrogen bond occurs between the ring oxygen of the furanose residue and the hydroxyl oxygen atom O_4 of the glucose residue. This hydrogen bond has been presumed to exist in chitin (Carslstrom, 1957), in native cellulose (I) (Liang & Marchessault, 1959), and in mercerized cellulose (II) (Marchessault & Liang, 1960; Petitpas & Méring, 1956). Interestingly, the cellobiose molecule is rather close to the 'bent and twisted' conformation considered by Marchessault & Liang (1960) for cellulose II, but rejected by them in favor of the 'bent' form on the basis of a comparison of predicted and observed infrared absorption bonds. Both the 'straight' and 'bent' forms of cellulose, as proposed by most previous workers, have the glucose residues related by a two-fold screw axis. Furthermore, the cylindrically symmetrical distribution function obtained by Fourier inversion of the X-ray diffraction data of cellulose I (Norman, 1954), suggests that the successive β-glucose residues along the fiber axis are indeed related by a two-fold screw axis. Their studies raise the possibility that the units of cellulose II are not really identical to those in cellobiose, but, nevertheless, they may be very closely related. However, re-examination of these data in the light of the structure found here for cellobiose would at least seem desirable.

Intermolecular hydrogen bonds are shown in Table 4. Only the bridge oxygen atom takes no part in the hydrogen bond network, while O_5 and O_5' of the rings are acceptors for intramolecular and intermolecular hydrogen bonds, respectively. Omitting the intramolecular hydrogen bond, there is a three-dimensional network which clearly explains the hardness and brittleness of the crystals, and which accounts for the absence of cleavage planes. The seven intermolecular hydrogen bonds (Fig. 4) use all of the remaining hydroxyl hydrogen atoms, and all are shorter than 2·9 Å. The only two other distances less than 3·25 Å in the structure are $O_4 \cdots O_3' = 2{\cdot}99$ Å, which can be rejected as a possible hydrogen bond because of the acute angles with $O_4 \cdots O_2'$ and $O_4 \cdots O_6$, and $O_1'-O =$ 3·08 Å, which can likewise be rejected because the angle $C_1'-O_1'-O$ would be very large and because of steric interference with one of the H atoms attached to C_6'. One set of hydrogen bonds $O_2 \cdots O_1'$ and $O_2 \cdots O_5'$ joins molecules in successive unit cells along the *c* axis, and a second set forms an infinite helical chain of hydrogen bonds with the helical axis along *b*.

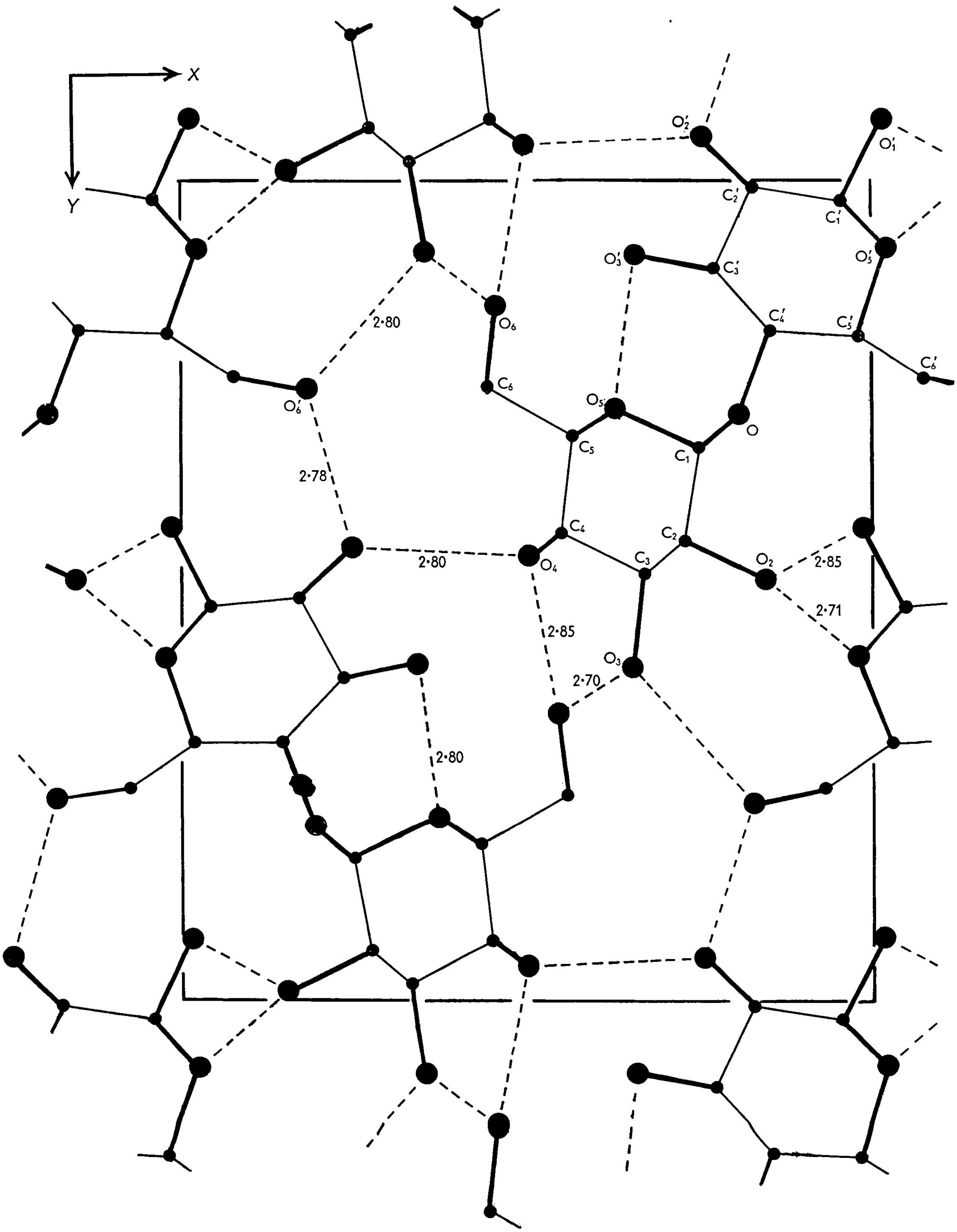

Fig. 4. Projection of the atomic positions along *z*, showing the hydrogen bonds as dotted lines.

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Syntheses for the Deconvolution of the Patterson Function. Part IV. Refinement of the Theory and a General Comparison of the Various Syntheses

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The details of the γ class of syntheses are given in this paper. The theory of the standard syntheses namely, $|F|$, exp $[i\alpha]$, exp $[2i\alpha]$, $1/|F|$ and $1/F$ is refined to the next higher order of approximation. The results are then applied to work out the ratio ϱ of the strength of the peak at the unknown to that at the known atomic positions in the α, β, γ, α', β' and γ' syntheses. Finally a general comparison of the various syntheses is made using the above ratio as the criterion for judging their relative merits.

1. Introduction

In Part I (Ramachandran & Raman, 1959) of this series were outlined the general principles involved in certain classes of syntheses which were proposed for developing a structure from its Patterson function when a part of it is known. The more detailed mathematical aspects of the problem were presented in Part II (Raman, 1959) and the treatment there pertained to the general case of a non-centrosymmetric structure. The extension of the theory to the centrosymmetric case was considered in Part III (Raman, 1961).

Two of the classes, namely α and β were discussed at length in the earlier parts and it was pointed out that the third class, namely the γ, was likely to have properties in between the α and β classes. The existence