

THE DETERMINATION AND REFINEMENT OF
THE STRUCTURES OF SOME CHLORINATED CARBOHYDRATES

by

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ABSTRACT

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The crystal and molecular structures of three chlorinated carbohydrates whose formal nomenclatures are

methyl 2-chloro-2-deoxy- α -D-galactopyranoside
methyl 4,6-dichloro-4,6-dideoxy- α -D-glucopyranoside,
and
methyl 4,6-dichloro-4,6-dideoxy- α -D-galactopyranoside

have been determined by X-ray diffraction using various methods. A scintillation counter was used in each case to collect the data: for the first, $\text{CuK}\alpha$ radiation was used; for the second and third, $\text{MoK}\alpha$ radiation was used.

The structure of the 2-chloro-galactoside was solved by a combination of the Patterson method and trial and error methods. Two possible positions of the chlorine atom found from the Patterson function were differentiated by minimizing R (using $h\ k\ 0$ projection data only) in rotation of a model of the molecule about each chlorine position. A model was used to go from the solved two dimensional structure to three dimensions. Successive Fourier summations and block diagonal least squares refinement established the crystal to be composed of a mixture of the α and β anomers of methyl 2-chloro-2-deoxy-D-galactopyranoside in the approximate ratio of $2\alpha : 1\beta$. Both the α and β anomers are in their expected

C-1 (chair) conformations. Hydrogen bonding involving O(3), O(4) and O(6) links molecules together into infinite sheets, two molecules thick and perpendicular to the x-axis. Mean bond distances are: C-C = 1.53 Å, C-O = 1.42 Å and C-Cl = 1.75 Å.

The structure of the 4,6-dichloro-glucoside was solved by a combination of the Patterson method (to locate the two chlorines), successive Fourier summations (to locate the carbons and oxygens), block diagonal least squares refinement, and a difference synthesis (to locate eight of the hydrogens). The absolute configuration was determined by the anomalous dispersion method (CuK α radiation). The molecule is in the expected C-1 conformation. Hydrogen bonding, involving O(2) and O(3), links molecules together into infinite chains parallel to the y-axis; the mean planes of the molecules are approximately perpendicular to the direction of these chains. Mean bond distances are C-C = 1.52 Å, C-O = 1.42 Å and C-Cl = 1.78 Å.

The structure of the 4,6-dichloro-galactoside was solved by direct methods applied to the two dimensional data of two centrosymmetric projections. A series of programs, employing the Vand-Pepinsky method of phasing reflexions contained in Sayre relationships, was written to do this. After refinement using block diagonal least squares, the two solutions were combined into the three

dimensional solution, which was further refined. A difference Fourier summation revealed the position of six hydrogens. The molecule is again in the expected C-1 conformation. Hydrogen bonding involved O(1), O(2), and O(3) in a complicated network which includes a bifurcated hydrogen bond. As in the 2-chloro-galactoside, molecules are linked by hydrogen bonds into infinite sheets, two molecules thick and perpendicular to the x-axis, but whereas in that structure the basic symmetry elements propagating the networks of bonding were unit cell translations and two-fold rotation axes, the basic elements propagating the networks in 4,6-dichloro-galactoside are unit cell translations and two-fold screw axes. Mean bond distances in this structure are: C-C = 1.53 Å, C-O = 1.45 Å, and C-Cl = 1.80 Å.

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GENERAL INTRODUCTION

Since 1913, when Bragg used it to determine the first crystal structure, X-ray diffraction has been used to solve many thousands of structures. The theory and standard techniques of the science of X-ray crystallography, culminating in a representation of a crystal in terms of its electron density (the "Fourier") may be found in any of many standard reference books on the field,¹⁻⁵ and will not be described here. Standard techniques now include not only "trial and error" methods and the Patterson method but also direct methods.⁶⁻⁹ Although they have been successfully applied to structure determinations in non-centrosymmetric space groups,⁷ direct methods are by far easiest to apply to (and have in the majority of cases been applied to) structure determinations in centrosymmetric space (and plane) groups.

The series of three compounds which were studied for this thesis were chosen because they lend themselves to a variety of methods of solution. The two pertinent features of these compounds are that

1. although the structures of all three belong to non-centrosymmetric space groups (as a necessary consequence of the fact that they are optically active non-racemates), they each belong to space groups having projections as centrosymmetric plane groups, and that

2. the structure of each has one short axis (of circa 5 Å) of projection along which it can be assumed to have no overlap and to be easily recognizable.

This thesis is thus mainly concerned with the procedures of structure determination (of which the most important part is that employing direct methods). Secondary emphasis is put on the actual crystal and molecular structures of the compounds analysed. The most important feature of the crystal structures of the chlorinated carbohydrates is the hydrogen bonding they contain. Replacement of a hydroxyl group with a chlorine should not alter the shape of the molecule (because of the similarity of the size of Cl and OH). Were efficient packing the only consideration in determining the crystal structure, a chlorinated carbohydrate would be expected to have the same structure as a non-chlorinated one. However, because of hydrogen bonding, replacement of a hydroxyl group removes one possible donor to a hydrogen bond with resultant alteration of the crystal structure (e.g. methyl 4,6-dichloro-4,6-dideoxy- α -D-glucopyranoside belongs to space C2,¹⁰ while methyl α -D-glucopyranoside belongs to P2₁2₁2₁¹¹).

This thesis is divided into two parts. The first describes the structure analysis of the three chlorinated carbohydrates studied, which are (respectively)

methyl 2-chloro-2-deoxy- α -D-galactopyranoside,
methyl 4,6-dichloro-4,6-dideoxy- α -D-glucopyranoside,
and, methyl 4,6-dichloro-4,6-dideoxy- α -D-galactopyranoside.
The second part describes the main programs written for
special purposes in these analyses. These include a
collection of four programs for generating solutions by
direct methods, completely general for the primitive
centrosymmetric plane groups of the oblique and rectangular
systems. Also included is the trial and error program
used for the methyl 2-chloro-galactoside and a general
program for contouring the electron density grids produced
by the Fourier summation program used by the X-ray
Crystallography group.

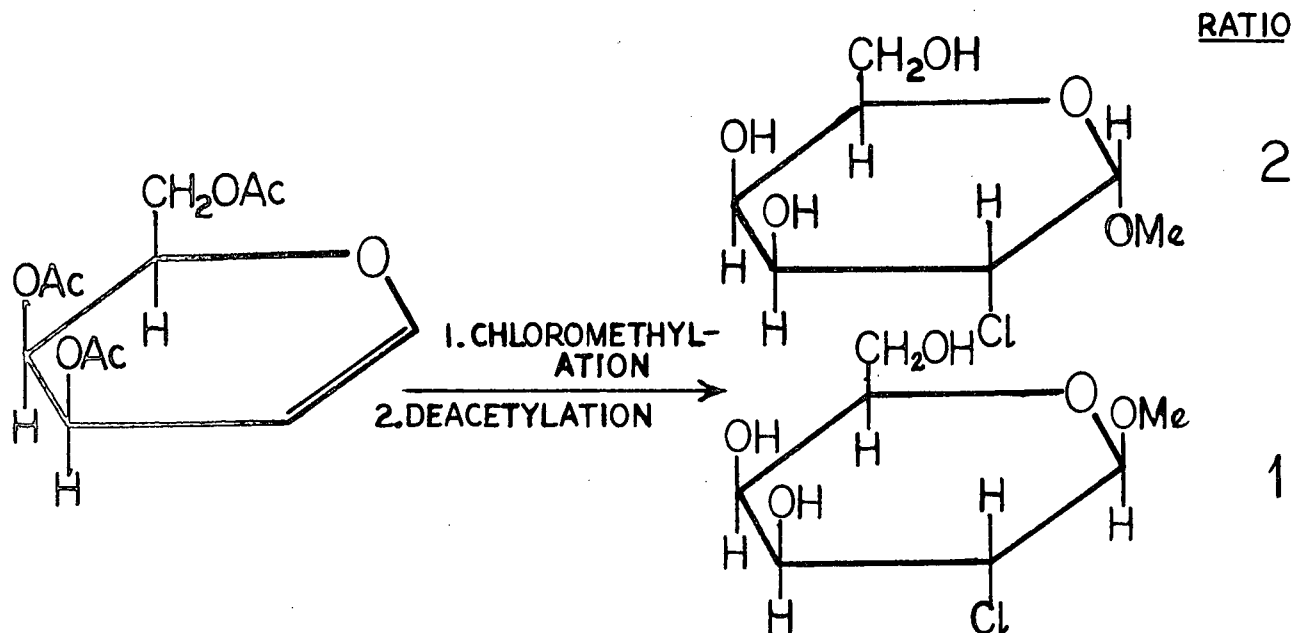
PART I

**THE STRUCTURE OF
THREE CHLORINATED CARBOHYDRATES**

1. THE STRUCTURE OF METHYL 2-CHLORO-2-DEOXY- α -D-GALACTOPYRANOSIDE

Introduction

The compound analysed below was prepared by chloromethylation of a 3,4,6 tri-O- acetyl-hexal.¹² The hexal used was a sample of D-glucal which can yield four possible products: the α and β anomers of methyl 2-chloro-2-deoxy-D-glucopyranoside and the α and β anomers of methyl 2-chloro-2-deoxy-D-mannopyranoside. A crystal of the product is below, however, shown to be composed predominantly of methyl 2-chloro-2-deoxy- α -D-galactopyranoside (although the β anomer is also present). The reaction performed on the hexal should not invert the configuration at C(4) (the only difference between a glucoside and a galactoside). Only if the starting material is D-galactal (possibly present as an impurity in the D-glucal sample) can the results be explained. The proposed reaction is



Experimental

Crystals are colourless plates elongated along b. The crystal chosen had dimensions 1.0 x 0.5 x 0.1 mm. Unit cell and space group data were determined from rotation and Weissenberg photographs ($\text{CuK}\alpha$).

CRYSTAL DATA (λ , $\text{CuK}\alpha = 1.5418 \text{ \AA}$)

Methyl 2-chloro-2-deoxy- α -D-galactopyranoside

$\text{C}_7\text{H}_{13}\text{O}_5\text{Cl}$, $M = 212.7$

Orthorhombic : $a = 29.57 \pm 0.05$, $b = 6.92 \pm 0.03$,
 $c = 4.69 \pm 0.02 \text{ \AA}$.

$U = 959.7 \text{ \AA}^3$

$D_m = 1.45 \text{ gm/cc}$ (flotation in carbon tetrachloride-benzene).

$Z = 4$, $D_c = 1.470 \text{ gm/cc}$.

Absorption coefficient for X-rays, $\mu(\text{CuK}\alpha) = 35.1 \text{ cm}^{-1}$

$F(000) = 448$

Absent spectra $h \ 0 \ 0$ when $h = 2n + 1$
 $0 \ k \ 0$ when $k = 2n + 1$

Space group is $P2_1 \ 2_1 \ 2 \ (D_2^3)$

The intensities of the reflexions were measured on a General Electric XRD - 5 manually operated spectrogoniometer with a scintillation counter. $\text{CuK}\alpha$ radiation was used together with a Ni-filter and pulse-height analyser. Of 662 reflexions with $2\theta(\text{CuK}\alpha) \leq 119.48$ (minimum interplanar spacing 0.89 \AA), 278 whose net intensities (corrected for background) were less than 50 counts, (maximum counts 56470 for $(1 \ 0 \ 1)$) were classified as "unobserved" and were included in the analysis with $F_o = 0.6 F$ (threshold). The crystal was mounted with b parallel to the ϕ -axis of the goniostat. A general background correction was made

for each reflexion (scanned for $\Delta(2\theta) = 2^\circ$) with special treatment given to reflexions occurring on streaks of lower order reflexions. Lorentz and polarization factors were applied, and the structure amplitudes derived.

Structure Analysis

a. Two Dimensional (xy) solution and refinement

The three-dimensional Patterson function presents two possible chlorine atom positions, one at (0.05,0,0), and the other at (0.167,0,0.10), each appearing to be equally likely positions. Due to the shortness of the z-axis, the mean plane of the molecule can be expected to lie approximately perpendicular to z. A model of methyl 2-chloro-2-deoxy- α -D-mannopyranoside, the proposed constituent of the crystal investigated, was used to calculate approximate relative positions in projection, of at least 11 of the 13 atoms. Radial coordinates (r, θ) of the 6 carbons and 4 oxygens in the model used (a rough diagram of which follows) were calculated using chlorine as the origin, assigning C(2) a θ value close to 0.0, and assigning the clockwise direction to increasing values of θ . The radial coordinates of the eleven atoms are:

<u>atom</u>	<u>r(A)</u>	<u>θ(radians)</u>
O(1)	3.0	+1.005
O(3)	2.7	-0.930
O(4)	4.9	-0.459
O(5)	3.94	+0.302
O(1)	2.64	+0.482
C(2)	1.70	-0.026
C(3)	2.66	-0.457
C(4)	4.10	-0.300
C(5)	4.5	+0.017
C(6)	5.8	-0.026

A program (ROT; see Appendix) was written which would rotate the non-chlorine atoms about a given fixed position for a chlorine, starting with Θ at 0 with the Cl(2) - C(2) bond parallel to the y-axis. This program uses the projection data, $F(h\ k\ 0)$, to calculate the discrepancy value, R , for different values of Θ , as the model is rotated clockwise about the chlorine by small increments through 2π radians. The meaning of the various parameters referred to above is best illustrated by a diagram (Figure 1) which follows.

The results, on 76 reflexions of highest intensity, for the two possible chlorine atom positions are shown in Figure 2, as plotted by the program.

The minimum value of R , 0.480, with Cl at (0.05, 0.0) occurred for Θ equal to 0.855 (angles between π and $3\pi/2$ need not be considered as for those values, the molecule lies on a two-fold axis). Seven cycles of refinement by the method of least squares on all two dimensional data resulted in the following reductions in the R -value: 0.594 (initial), 0.526, 0.483, 0.461, 0.446, 0.433, 0.412, and 0.391. As O(3), O(4), C(3) and C(5) still had large positive shifts (~ 5.0) indicated to already large values of thermal parameters ($B \approx 7.0$), these atoms were deleted from a Fourier summation. The peaks on the Fourier map, apart from those corresponding to the atoms used in the phasing, bore no recognizable relation to a carbohydrate molecule.

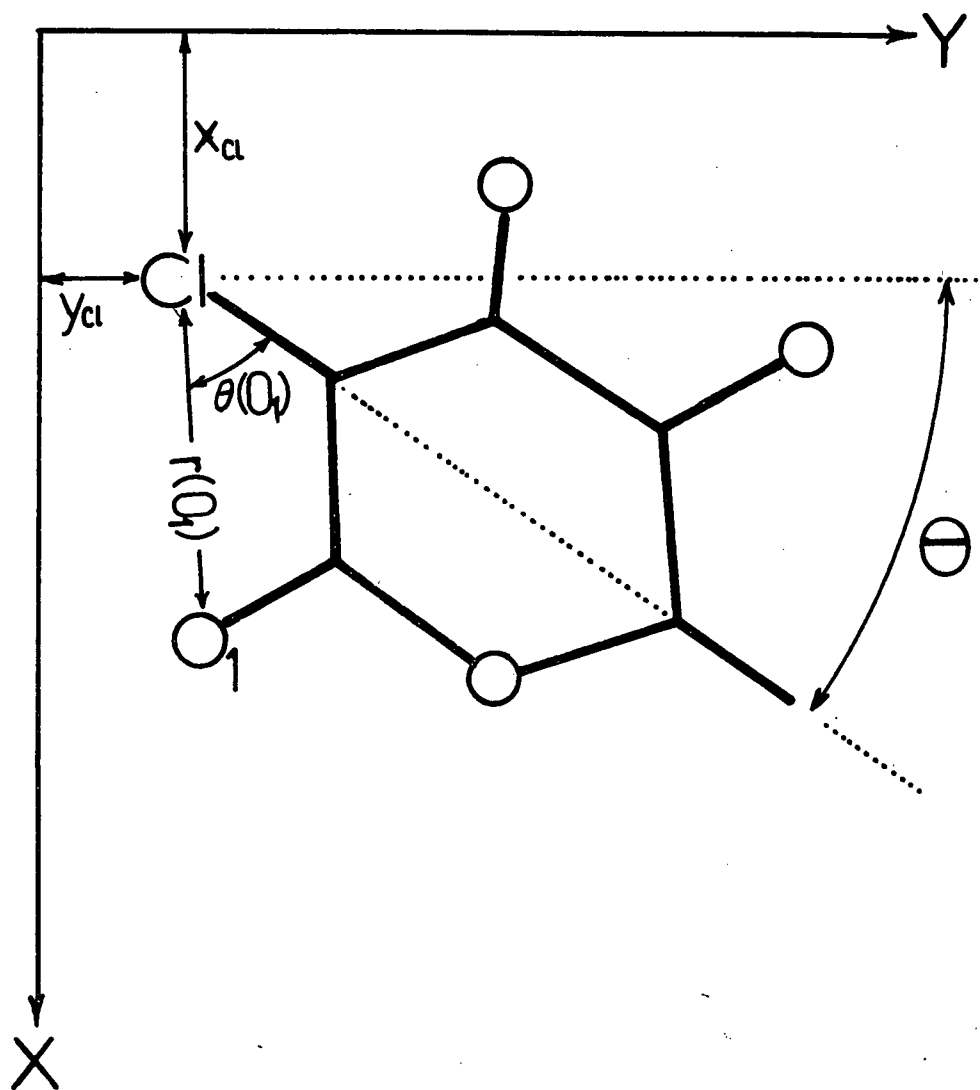


Figure 1. Approximate representation of model used for rotation program (ROT).

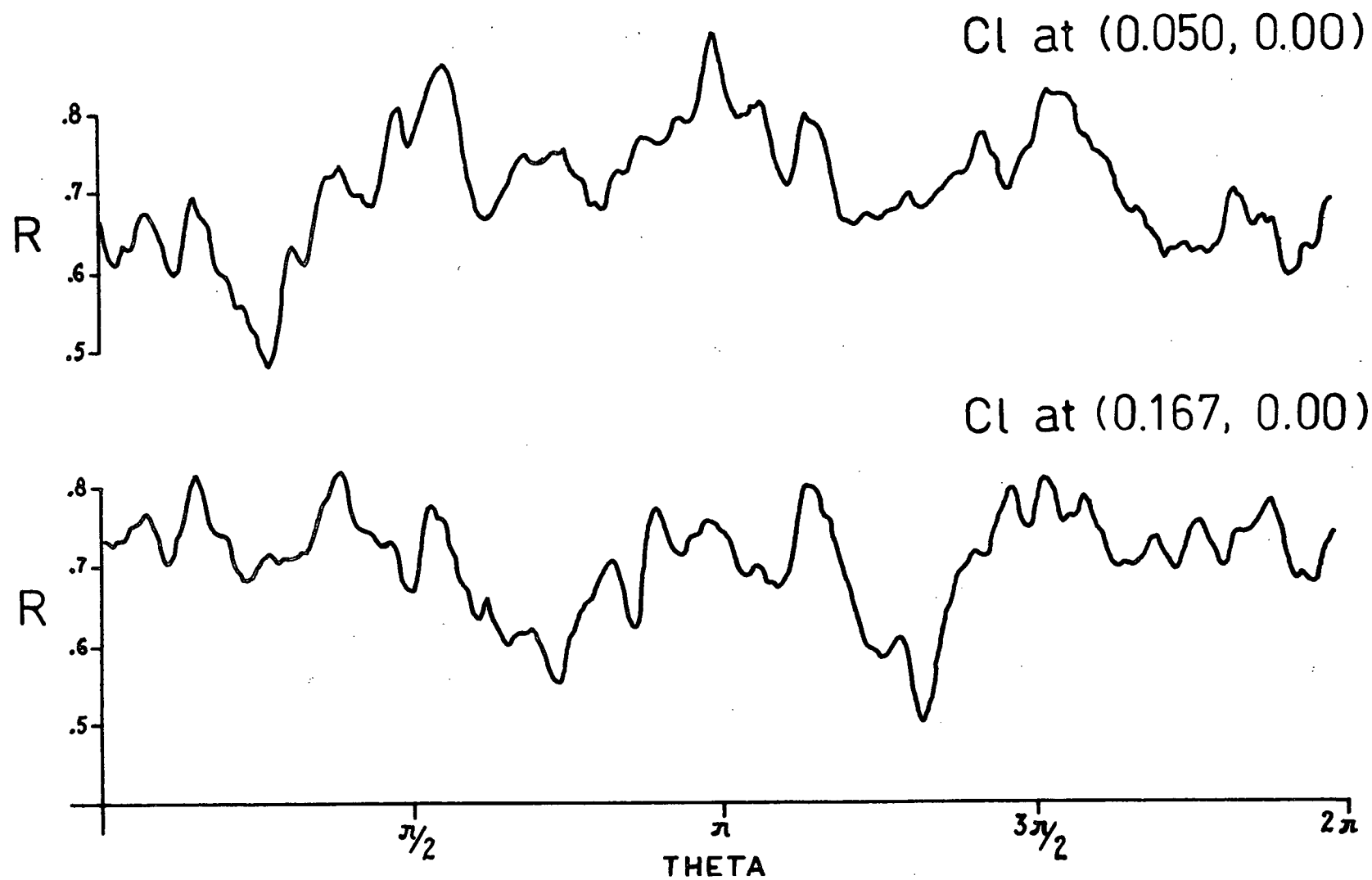


Figure 2. Results for two possible chlorine positions as R versus θ plots.

The minimum value of R , 0.499, with the chlorine atom at (0.167, 0.0) occurred for Θ equal to 4.175. Seven cycles of refinement by least squares, again on all two dimensional data, resulted in the following reductions in the R - value: 0.590 (initial), 0.532, 0.492, 0.467, 0.449, 0.430, 0.415, and 0.402. Now however, only O(4) and O(1) still had large positive shifts (~ 7.0) indicated to large values of thermal parameters ($B \approx 6.0$). A Fourier summation based on the calculated phases of the remaining nine atoms clearly indicated the actual positions of the excluded atoms. The position, in projection, of O(4) needed to be shifted by 0.7 Å, and that of O(1), by 1.3 Å. Further Fourier summations placed all thirteen atoms. (The atom which had previously been labelled O(1) became C(7)). Five cycles of least squares refinement (applying after each cycle only 50% of the indicated shifts) resulted in the following reductions in R : 0.283 (initial), 0.226, 0.203, 0.189, 0.182, 0.176

As the C(4) to C(5) distance in projection was 1.64 Å, an attempt was made to redefine the positions of the two atoms involved by a Fourier summation from which they were excluded. The final four cycles of least squares refinement (each atom was given an initial temperature factor B , of 4.0 Å²; 50% of the calculated shifts applied after each cycle) gave after each cycle, the

following R- values: 0.337 (initial), 0.262, 0.202, and 0.189. The C(4) to C(5) distance was now 1.52 Å, and no other bond was larger in projection than its expected value in three dimensions.

b. Three Dimensional Refinement

The only model which could successfully be fitted onto the two dimensional refined structure was one in which Cl(2) and O(4) were inverted with respect to mannoside proposed as the constituent of the crystal. As the z-coordinate of Cl(2) is known, only two possible solutions exist, which are related by reflexion through the plane $z = z_{Cl}$. Least-squares refinement of the temperature factors, scale, and z-coordinates was carried out for the two possibilities. The first yielded for two cycles, the following values of R : 0.457 (initial), 0.419, and 0.412; the second yielded: 0.290 (initial), 0.243, and 0.222. When all the coordinates were allowed to shift, the R- value for the second possibility was reduced to 0.192 in two further cycles of refinement.

The data had originally been mounted with "minimum observable" intensity as 50 counts (maximum recorded was 56470 for 1 0 1). Any reflexion which has a net intensity of less than 50 would be excluded from the calculation of R. As it was felt that this value excluded too many reflexions, the counter data was again processed reducing

this value to 9, and at the same time adjusting the readings of nine reflexions which on the basis of Weissenberg films appeared to have values very different from those originally estimated from the counter. Of the 662 reflexions recorded, 578 (87%) were now classified as observed with the remaining 84 classified as unobserved. As the solution proposed above (except for the inversion at the two centres) is the enantiomorph of the correct configuration, subsequent work was carried out on the above structure mirrored through $y = 0$. After three cycles of refinement by least squares, the R-value was 0.26. A Fourier summation with phases based on all 13 non-hydrogen atoms, was carried out to try to relocate C(7) and O(1) which had temperature factors (7.7 and 6.8 respectively) higher than was expected. (Also the C(1) - O(1) bond length of 1.16 for the refined structure was very short). In this Fourier map C(7) and O(1) appeared in the refined positions with maximum density of $4.2 \text{ e}/\text{\AA}^3$ and $7.0 \text{ e}/\text{\AA}^3$, respectively. However, O(1) was greatly extended in the z-direction, enough so that two distinct maxima occurred in that direction and that both an α -OMe and a β -OMe group could be postulated as attached to the rest of the pyranose ring. Two O-Me groups (with temperature factors $B = 7.0$ for each atom) were introduced into the structure factor calculation, the oxygens separated in the z-direction by approximately $2/5 \text{ c}$, the carbons by approximately $1/4 \text{ c}$ (the oxygens were also slightly

displaced in y-direction). After one cycle of refinement, the R- value was reduced to 0.218. The temperature factors on the β group were, however, larger than those on the α - group. When each group was tried separately for one cycle (100% of the indicated shifts to the thermal parameters were applied), the results were

α -group: R- values 0.255 (initial), 0.244 (final)
final temperature factors for C and O,
8.9 and 9.4 respectively.

β -group: R- values 0.294 (initial), 0.285 (final)
final temperature factors for C and O,
11.4 and 9.9 respectively.

The α -group gave better agreement but the problem persisted, especially after a Fourier summation with the phases of only ten atoms (deleting C(1), O(1) and C(7)) revealed both the α -group and β -group although the latter was somewhat weaker. The best fit to the data appeared to be a combination of the two structures in the approximate ratio of $2\alpha : 1\beta$. Subsequent refinements were carried out on a postulated structure consisting of $2/3$ O(1) - C(7) in the α position and $1/3$ O(1) - C(7) in the β position. Five cycles of least squares refinement produced the following reductions in the R- value: 0.232 (initial), 0.211, 0.201, 0.189, 0.185, and 0.183. When anisotropic thermal parameters were introduced for the ten atoms excluding O(1) and C(7), and C(1) which was separated into two positions separated by 0.5 Å, and the scale changed slightly, five cycles of block-diagonal least squares refinement on all parameters, except those of

C(1), resulted in these reductions in the R- value: 0.189 (initial), 0.176, 0.168, 0.154, 0.149, and 0.147. The weighting scheme which was used for the refinement of this structure and others in this thesis assigns $\sqrt{w} = 1$ when $|F_o| \leq F^*$, and $\sqrt{w} = F^*/|F_o|$ when $|F_o| > F^*$. For the final stages of the refinement F^* was here given a value of 6.0.

A final difference Fourier synthesis showed only random fluctuations, generally between $0.3 \text{ e}/\text{\AA}^3$ and $-0.3 \text{ e}/\text{\AA}^3$, the maximum value attained being $0.6 \text{ e}/\text{\AA}^3$. One very encouraging sign for the correctness of the above refinement was that reflexion 0 0 1, after the refinement of the structure which included only an α - OMe group, had $|F_o| / |F_c|$ as 52.4/9.7, while after refinement of the final mixed structure, had $|F_o| / |F_c|$ as 43.7/41.2.

Prior to the final computation of structure factors, the intensities of the reflexions with the worst agreement between observed and calculated values of the structure factors were reestimated using films. The following seven reflexions were then included with a revised value of intensity for the recalculation of observed structure factor magnitudes which appear in Table I: 0 2 2, 3 3 4, 1 2 0, 0 1 1, 2 1 1, 2 3 1, and 10 1 2. As these changes are small and few in numbers, they do not alter the previous results or the final R- value. The final positional and thermal parameters are given in Table II, the bond lengths and valency angles in Table III, and the shorter intermolecular distances in Table IV.

Discussion

a. Molecular Structure and Dimensions

The crystal structure investigated has been shown to be a mixture of an α -galactoside and a β -galactoside in the approximate ratio of 2:1. O(1) and C(7) were shown in the refinement to occupy two distinct positions (α and β). In the actual crystal which contains a mixture of the two structures, instead of the rest of the atoms occupying the mean positions indicated by the refinement, they occupy slightly different positions depending upon whether the terminal group is α or β . This group would affect the position of C(1) most (and for this reason, C(1) was separated into C(1) and C(1') and O(3), O(4), and O(6) least (especially as these are hydrogen bonded among themselves).

The conformation of the molecule is shown in Figure 3 in projection along c. The α (C(1)-O(1)-C(7)) group appears with solid lines, the β (C(1')-O(1')-C(7')) group appears with broken lines. Both the α -anomer and the β -anomer have a chair form pyranose ring on which the substituents have conformations (α :1a2e3e4a5e; β :1e2e3e4a5e). The packing of the molecule in the unit cell is shown in Figure 4. The bond length and the valency angles in the molecule are given in Table III. The values for the C(1)-O(1)-C(7) and C(1')-O(1')-C(7') group have been included but will be less accurate than the rest. The range of the carbon-carbon distances (not including those in the terminal

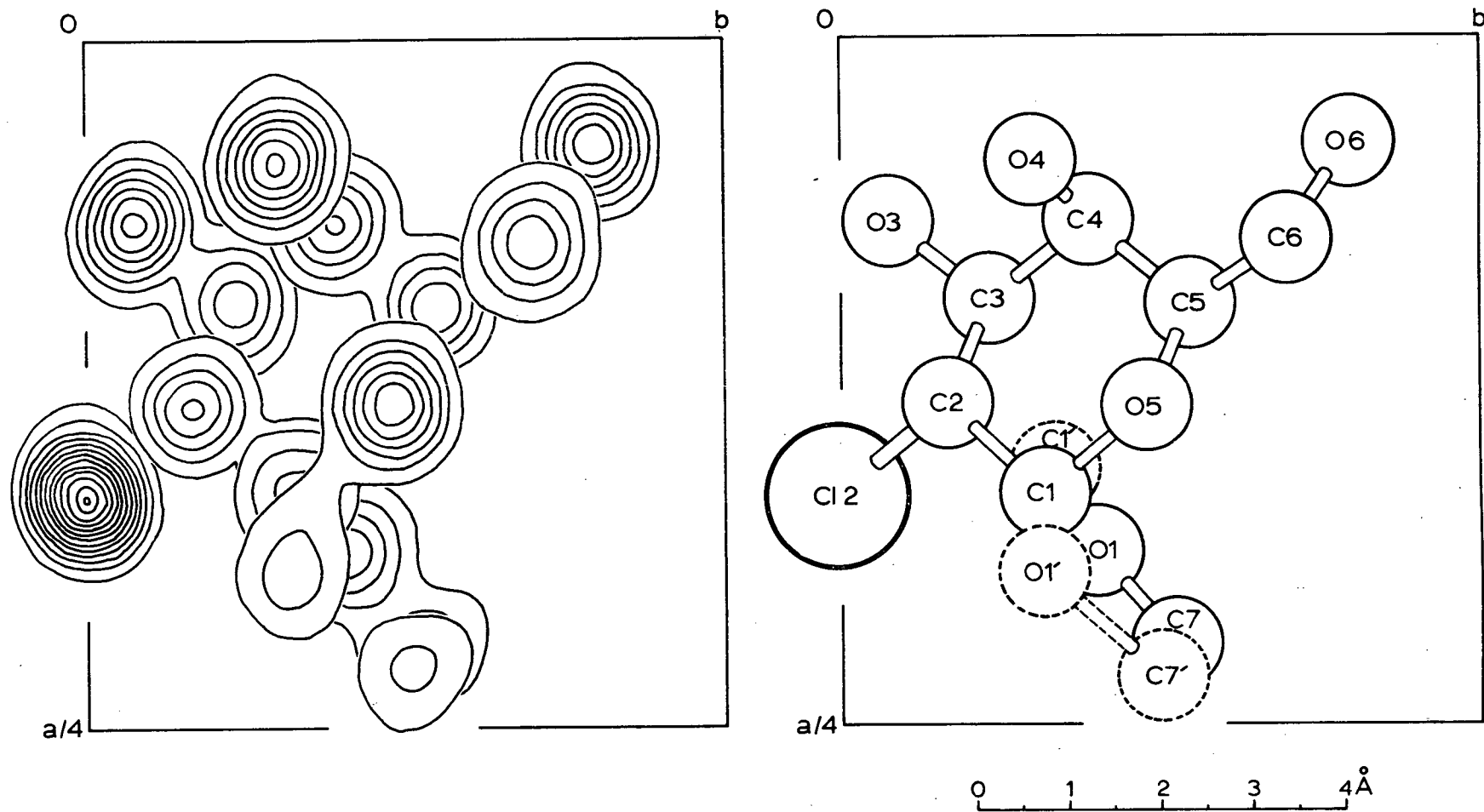


Figure 3. Superimposed sections of electron density distribution (contours at 1,2,3...e/Å³) and a drawing of the molecule.

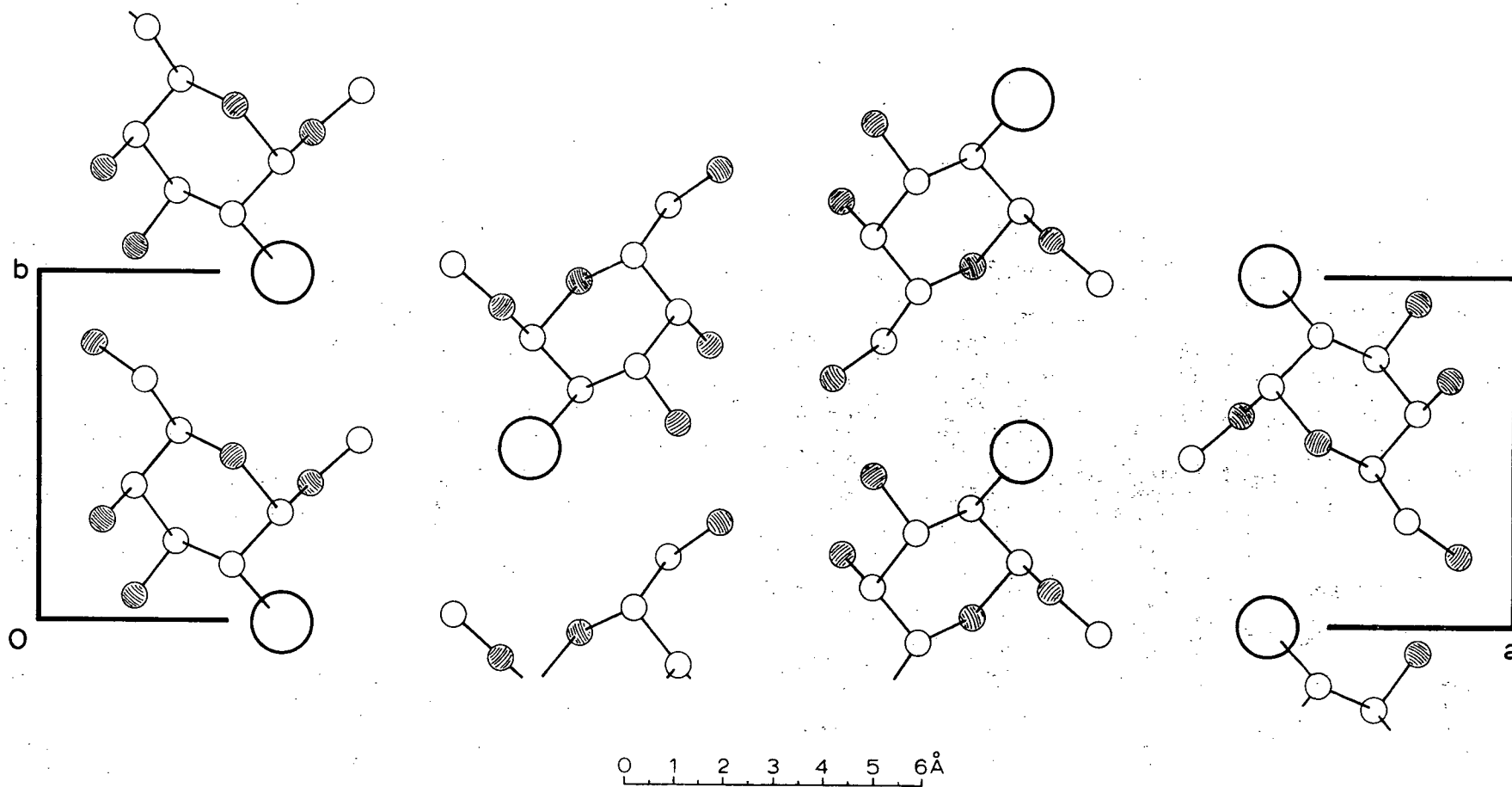


Figure 4. Packing diagram; view along c.

group) is 1.48 - 1.60 Å ($\sigma = 0.02$), with a mean value of 1.52 ($\sigma = 0.01$) while the range for the C-O distances (again excluding those in the terminal group) is 1.40 - 1.45 Å ($\sigma = 0.02$), with a mean value of 1.42 Å ($\sigma = 0.01$). The variation in valency angles (not including those involving atoms of the "terminal" group) is from 104° to 114° ($\sigma = 2^\circ$) with a mean value of 110.5° .

The standard deviations quoted above are those estimated from the inverses of the diagonal elements of the matrix of the normal equations used to calculate shifts to parameters in the least squares refinement. A block diagonal matrix is used to approximate the correct full matrix. Estimates of the standard deviations tend to be too low in such an approximation because of the neglect of the interatomic interactions. Also, for a structure which is a mixture, the parameters refined for each atom (except O(1) and C(7) which are separated into distinct positions) give the "average" position of each atom with the possibility that the bond lengths and angles may not correspond to either molecule in particular.

b. Intermolecular distances and hydrogen bonding

All intermolecular distances less than 4.0 Å were calculated and those less than 3.6 Å are included in Table IV. The three shortest approaches that occur correspond to possible H-bonds between the three atoms O(3), O(4) and O(6). Figure 5 shows the arrangement of

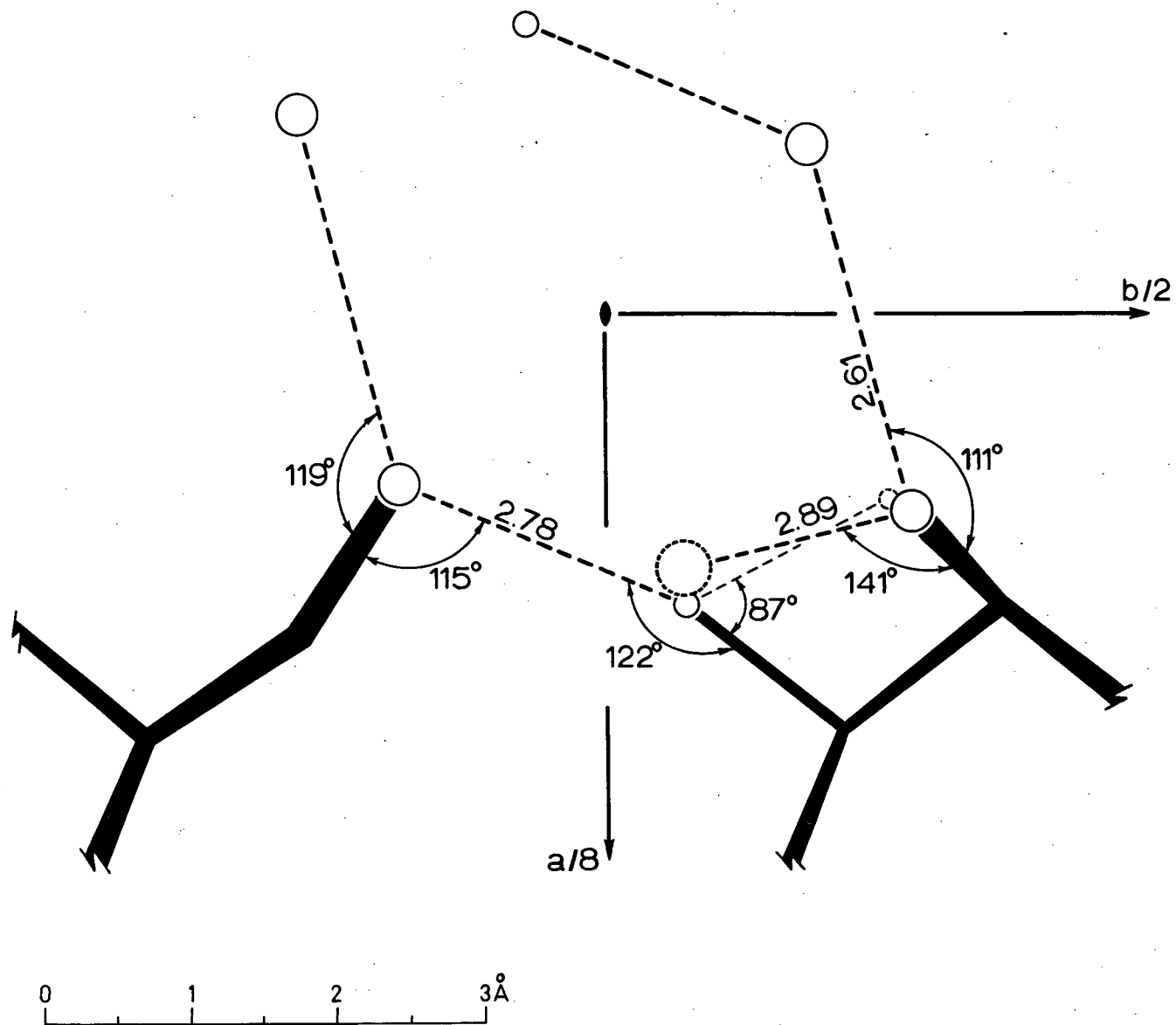


Figure 5. Hydrogen bonding; view along c of near origin region (the dotted O's have been offset for clarity).

atoms around the origin and shows these close approaches. Two hydrogen bonding schemes are possible, both of which correspond to a hydrogen bonding network which spirals along the z-direction. The two are:

1. O(4)-H (lower level)...O(3)-H (level of molecule represented)...O(6)-H...O(4)-H...
O(3)-H (higher level)...etc.
2. O(4)...H-O(3)...H-O(6)...H-O(4)...H-O(3).

If the bonding hydrogens are located between oxygens then the successive H-O-C angles for the two schemes would be

1. $141^\circ - 122^\circ - 119^\circ - 141^\circ - 122^\circ$ etc.
2. - $87^\circ - 115^\circ - 111^\circ - 87^\circ$ etc.

Assuming that these angles tend toward the tetrahedral angle (H-O-H in water is 105° , in ordinary ice O'-O-O" is tetrahedral), the second scheme is the most probable one.

Only two other short approaches occur, C(7')-O(1'), a distance of 3.09 Å and O(4)-C(3), a distance of 3.15 Å. The former separation involves the β -group whose position is poorly defined; the latter arises as a consequence of the hydrogen bond of O(4) to the oxygen attached to C(3) (i.e. O(3)) and corresponds to a van der Waals separation.

TABLE I

Measured and calculated structure amplitudes ($\times 10$).
Unobserved reflexions have $F_0 = -0.6 F$ (threshold).

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	
2	0	0	244	279	0	4	0	366	359	8	1	1	304	322	12	5	1	28	43	10	1	2	-92	47	10	1	2	-92	47	
4	0	0	661	907	2	4	0	61	51	9	1	1	321	340	13	5	1	28	31	11	1	2	-15	10	7	2	1	123	89	
6	0	0	86	86	2	4	0	93	85	10	1	1	257	230	14	5	1	40	57	12	1	2	99	97	9	2	3	136	134	
8	0	0	679	847	3	4	0	164	118	11	1	1	135	133	15	5	1	57	67	13	3	2	26	17	10	2	3	75	61	
10	0	0	456	590	4	4	0	191	142	12	1	1	54	54	16	5	1	40	36	14	3	2	73	75	11	2	3	26	31	
12	0	0	89	102	5	4	0	352	305	13	1	1	259	250	17	5	1	49	29	15	3	2	46	53	12	2	3	66	31	
14	0	0	86	90	6	4	0	144	130	14	1	1	141	104	18	5	1	-16	11	16	3	2	47	59	13	2	4	67	69	
16	0	0	29	37	7	4	0	189	216	15	1	1	43	48	19	5	1	-16	13	17	3	2	56	47	14	2	4	27	22	
18	0	0	103	108	8	4	0	70	63	16	1	1	67	79	20	5	1	157	94	18	3	2	56	56	15	2	5	56	56	
20	0	0	78	100	9	4	0	-14	3	17	1	1	141	187	21	5	1	40	56	19	3	2	56	45	16	2	6	-16	29	
22	0	0	99	74	10	4	0	48	58	18	1	1	59	62	22	5	1	54	79	20	3	2	49	42	17	2	7	-16	33	
24	0	0	101	100	11	4	0	-15	5	19	1	1	49	62	23	5	1	63	80	21	3	2	-17	18	18	2	8	48	30	
26	0	0	28	33	12	4	0	81	75	20	1	1	63	57	24	5	1	44	26	22	3	2	40	37	19	2	9	-16	12	
28	0	0	-17	13	13	4	0	26	35	21	1	1	105	108	25	5	1	47	52	23	3	2	147	145	20	2	10	27	32	
30	0	0	125	121	14	4	0	130	115	22	1	1	-16	23	26	5	1	40	73	24	3	2	193	215	21	2	11	94	73	
32	0	0	25	13	15	4	0	60	60	23	1	1	27	26	27	5	1	135	101	25	3	2	194	199	22	2	12	105	89	
1	1	0	164	102	16	4	0	161	175	24	1	1	105	108	28	5	1	75	83	26	3	2	161	145	23	2	13	90	83	
2	1	0	704	695	17	4	0	184	176	25	1	1	-17	23	29	5	1	57	52	27	3	2	147	145	24	2	14	112	79	
3	1	0	40	76	18	4	0	90	78	26	1	1	49	61	30	5	1	-17	23	28	3	2	133	120	25	2	15	122	122	
4	1	0	140	155	19	4	0	40	50	27	1	1	56	68	31	5	1	56	48	29	3	2	87	73	26	2	16	67	56	
5	1	0	114	191	20	4	0	28	18	28	1	1	-16	19	32	5	1	39	53	30	3	2	51	32	27	2	17	146	156	
6	1	0	45	46	21	4	0	24	24	29	1	1	612	551	33	5	1	463	535	31	3	2	159	155	28	2	18	104	89	
7	1	0	247	299	22	4	0	52	33	30	1	1	173	154	34	5	1	125	1	32	3	2	26	23	29	2	19	108	68	
8	1	0	93	79	23	4	0	-17	18	31	1	1	243	176	35	5	1	243	243	33	3	2	75	40	30	2	20	87	92	
9	1	0	475	589	24	4	0	94	86	32	1	1	350	354	36	5	1	371	344	34	3	2	85	75	31	2	21	48	47	
10	1	0	120	164	25	4	0	-16	4	33	1	1	167	157	37	5	1	66	117	35	3	2	33	99	32	2	22	39	47	
11	1	0	177	162	26	4	0	26	23	34	1	1	230	239	38	5	1	166	136	36	3	2	27	29	33	2	23	64	64	
12	1	0	54	74	27	4	0	-26	20	35	1	1	467	429	39	5	1	256	41	37	3	2	121	74	34	2	24	47	47	
13	1	0	114	173	28	4	0	-14	27	36	1	1	230	265	40	5	1	30	54	38	3	2	68	56	35	2	25	-16	22	
14	1	0	150	162	29	4	0	-15	15	37	1	1	595	634	41	5	1	143	167	39	3	2	79	95	36	2	26	56	40	
15	1	0	185	189	30	4	0	36	38	38	1	1	140	121	42	5	1	258	147	40	3	2	95	95	37	2	27	-16	28	
16	1	0	21	21	31	5	0	144	115	39	1	1	411	420	43	5	1	241	151	41	3	2	24	151	38	2	28	-16	14	
17	1	0	93	100	40	5	0	93	80	40	1	1	214	197	44	5	1	226	272	42	3	2	63	57	39	2	29	39	41	
18	1	0	66	59	41	5	0	138	90	41	1	1	141	142	45	5	1	31	27	43	3	2	56	55	40	2	30	63	51	
19	1	0	94	117	42	5	0	-15	71	42	1	1	157	162	46	5	1	37	47	44	3	2	-15	13	41	2	31	99	76	
20	1	0	35	3	43	5	0	125	100	43	1	1	109	132	47	5	1	21	111	45	3	2	113	98	42	2	32	64	76	
21	1	0	204	198	44	5	0	37	10	44	1	1	105	123	48	5	1	-14	24	46	3	2	157	174	43	2	33	75	101	
22	1	0	89	71	45	5	0	97	95	45	1	1	63	73	49	5	1	2	18	47	47	3	2	177	193	44	2	34	40	44
23	1	0	-16	13	46	5	0	27	34	46	1	1	115	98	50	5	1	152	102	48	3	2	75	69	45	2	35	28	14	
24	1	0	74	58	47	5	0	117	118	47	1	1	160	159	51	5	1	37	36	49	3	2	126	17	46	2	36	-17	5	
25	1	0	86	64	48	5	0	-17	20	48	1	1	45	48	52	5	1	26	21	50	3	2	40	47	47	2	37	40	37	
26	1	0	-17	26	49	5	0	-17	20	49	1	1	26	42	53	5	1	27	27	51	3	2	80	41	48	2	38	28	41	
27	1	0	71	53	50	5	0	57	43	50	1	1	54	51	54	5	1	62	75	52	3	2	82	24	49	2	39	63	81	
28	1	0	40	26	51	5	0	116	116	51	1	1	98	98	55	5	1	75	55	53	3	2	58	55	50	2	40	105	85	
29	1	0	49	42	52	5	0	-17	16	52	1	1	28	29	56	5	1	-17	11	54	3	2	48	75	51	2	41	48	50	
30	1	0	27	30	53	5	0	-17	13	53	1	1	120	111	57	5	1	40	54	55	3	2	29	1	52	2	42	38	21	
31	1	0	76	0	54	5	0	28	43	54	1	1	28	26	58	5	1	28	2	56	3	2	63	51	53	2	43	39	16	
32	1	0	25	19	55	5	0	-17	10	55	1	1	40	55	59	5	1	37	36	57	3	2	65	55	54	2	44	55	35	
0	2	0	333	313	20	5	0	137	100	56	1	1	145	145	60	5	1	256	273	58	3	2	50	18	55	2	45	40	19	
1	2	0	198	159	21	5	0	29	32	1	1	61	33	61	5	1	130	108	59	3	2	39	35	1	5	46	3	-17	36	
2	2	0	776	645	22	5	0	-16	6	2	1	133	95	62	5	1	128	144	60	3	2	88	103	2	5	47	2	-17	16	
3	2	0	159	140	23	5	0	-16	22	2	1	166	118	63	5	1	136	120	61	3	2	112	12	1	5	48	2	-17	26	
4	2	0	359	369	24	5	0	25	0	3	1	308	291	64	5	1	258	247	62	3	2	57	47	1	6	49	2	-17	14	
5	2	0	30	11	25	5	0	-14	1	4	3	108	70	65	5	1	173	175	63	3	2	-17	13	5	5	50	2	-17	7	
6	2	0	352	316	26	5	0	94	121	5	3	1	95	34	66	5	1	221	171	64	3	2	24	48	6	5	51	3	28	41
7	2	0	552	571	27	5	0	-17	15	6	3	1	334	291	67	5	1	261	275	65	3	2	24	17	7	0	0	4	114	-114
8	2	0	115	77	28	5	0	115	77	7	3	1	395	314	68	5	1	164	155	66	3	2	47	17	8	0	4	57	65	
9	2	0	147	118	29	5	0	40	35	8	3	1	162	177	69	5	1	137	176	67	3	2	39	67	9	0	4	57	65	
10	2	0	45	3	30																									

TABLE II

FINAL POSITIONAL PARAMETERS (fractional), ISOTROPIC THERMAL
PARAMETERS (\AA^2), AND ANISOTROPIC THERMAL PARAMETERS

$$(\exp -\{b_{11}h^2 + b_{12}hk + b_{13}kl + b_{22}k^2 + b_{23}kl + b_{33}l^2\}),$$

together with estimated standard deviations in parenthesis,
 referring to the last decimal positions of respective values.

Atom	x	y	z	B
Cl(2)	0.1665(2)	-0.0036(7)	0.0952(13)	7.83(15)
C(2)	0.1329(4)	0.169(2)	0.267(4)	4.6(4)
C(3)	0.0948(5)	0.233(2)	0.082(3)	6.1(5)
C(4)	0.0661(5)	0.391(2)	0.253(4)	5.7(4)
C(5)	0.0969(5)	0.548(2)	0.343(4)	4.6(4)
C(6)	0.0739(5)	0.700(2)	0.523(3)	6.0(4)
O(3)	0.0665(3)	0.077(1)	-0.001(2)	5.3(3)
O(4)	0.0448(3)	0.299(1)	0.497(2)	5.1(2)
O(5)	0.1330(4)	0.481(2)	0.516(2)	5.9(3)
O(6)	0.0388(3)	0.797(2)	0.385(3)	6.3(3)
C(7)	0.2192(8)	0.526(5)	0.282(6)	7.4(6)
O(1)	0.1858(4)	0.401(2)	0.185(4)	5.9(3)
C(7 ^a)	0.2315(12)	0.501(6)	0.415(8)	4.6(8)
O(1 ^a)	0.1944(8)	0.314(4)	0.530(6)	5.4(6)
C(1)	0.1650	0.317	0.436	5.0
C(1 ^a)	0.1564	0.336	0.343	5.0

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cl(2)	0.00218(6)	0.0018(5)	0.006(1)	0.032(1)	-0.013(5)	0.126(4)
C(2)	0.0013(1)	-0.0010(12)	0.006(2)	0.019(3)	-0.007(11)	0.074(8)
C(3)	0.0024(2)	-0.0013(14)	-0.002(2)	0.021(3)	-0.042(9)	0.069(8)
C(4)	0.0019(2)	-0.0009(15)	0.007(2)	0.019(3)	-0.009(11)	0.068(9)
C(5)	0.0017(2)	-0.0003(13)	-0.004(2)	0.017(3)	0.025(10)	0.086(9)
C(6)	0.0024(2)	-0.0005(17)	0.002(2)	0.029(4)	-0.001(13)	0.049(7)
O(3)	0.0019(1)	-0.0013(9)	0.006(1)	0.020(2)	0.011(7)	0.069(5)
O(4)	0.0018(1)	-0.0014(9)	0.002(2)	0.024(2)	-0.021(8)	0.063(5)
O(5)	0.0022(1)	-0.0011(11)	-0.003(2)	0.025(2)	-0.006(10)	0.070(5)
O(6)	0.0017(1)	-0.0014(9)	0.004(2)	0.025(3)	-0.005(10)	0.103(7)

TABLE IIIBOND LENGTHS AND VALENCY ANGLES

<u>i</u>	<u>j</u>	<u>D(ij)</u>	<u>i</u>	<u>j</u>	<u>k</u>	<u>Angle</u> <u>(ijk)</u>
C1(2)	C(2)	1.75 A	C(1)	O(1)	C(7)	106.5°
O(1)	C(1)	1.45	C(1')	O(1')	C(7')	102.9
O(1')	C(1')	1.43	C(2)	C(1)	O(1)	96.1
O(1)	C(7)	1.39	C(2)	C(1')	O(1')	117.4
O(1')	C(7')	1.78	O(5)	C(1)	O(1)	99.5
O(3)	C(3)	1.42	O(5)	C(1')	O(1')	96.1
O(4)	C(4)	1.45	O(5)	C(1)	C(2)	103.2
O(5)	C(1)	1.52	O(5)	C(1')	C(2)	118.3
O(5)	C(1')	1.46	C(1)	C(2)	C1(2)	109.2
O(5)	C(5)	1.42	C(3)	C(2)	C1(2)	111.4
O(6)	C(6)	1.40	C(2)	C(3)	O(3)	112.2
C(1)	C(2)	1.61	C(4)	C(3)	O(3)	110.2
C(1')	C(2)	1.40	C(3)	C(4)	O(4)	109.1
C(2)	C(3)	1.49	C(5)	C(4)	C(4)	111.2
C(3)	C(4)	1.60	C(4)	C(5)	C(6)	113.2
C(4)	C(5)	1.48	O(5)	C(5)	O(6)	104.5
C(5)	C(6)	1.51	C(5)	C(6)	C(6)	114.4
			C(1)	O(5)	C(5)	125.0
			C(1')	O(5)	C(5)	105.5
			C(1)	C(2)	C(3)	122.8
			C(1')	C(2)	C(3)	106.2
			C(2)	C(3)	C(4)	108.3
			C(3)	C(4)	C(5)	108.6
			C(4)	C(5)	O(5)	112.6

(distances not
involving
O(1'), C(1'), or C(7'))

$$\sigma = .02-0.03$$

(angles not involving
O(1'), C(1'), or C(7'))

$$\sigma = 2^\circ$$

TABLE IVSHORTER INTERMOLECULAR DISTANCES (3.6A)

X^I	Y^I	i	$D(X^I-Y^I)$
O(5)	O(1)	II	3.55 A
C(7')	O(1')	VI	3.09
O(1')	Cl(2)	II	3.54
O(4)	C(3)	II	3.15
O(5)	C(3)	II	3.36
C(4)	O(6)	V	3.42
C(6)	O(3)	IV	3.44
C(6)	O(3)	III	3.59
C(6)	O(4)	V	3.51
O(4)	O(3)	II	2.89
O(6)	O(3)	III	2.78
O(6)	O(3)	IV	3.56
O(6)	O(4)	III	3.52
O(4)	O(6)	V	2.61

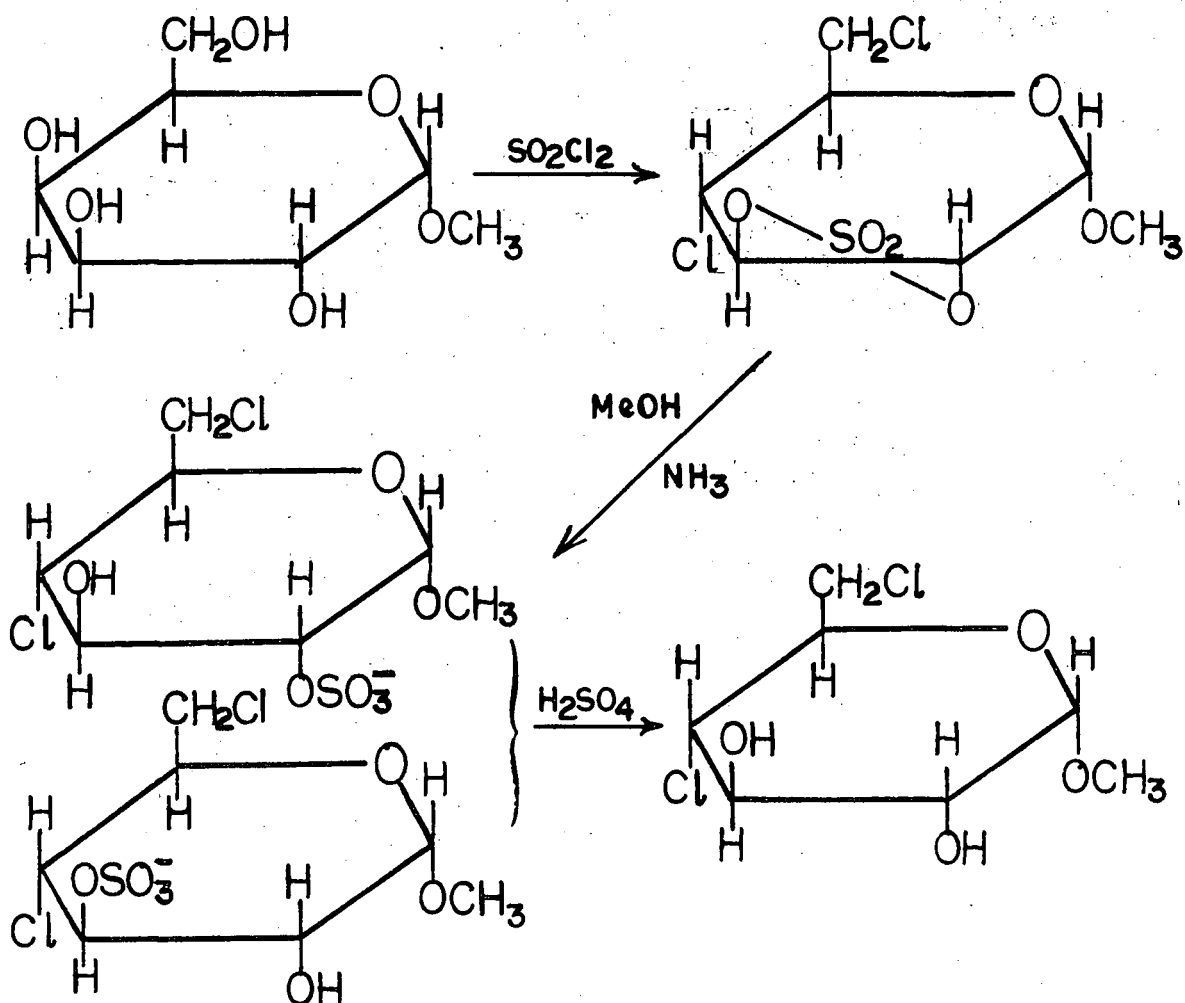
Symmetry Code

I	x	y	z
II	x	y	z + 1
III	x	y + 1	z
IV	x	y + 1	z + 1
V	-x	-y + 1	z
VI	-x + $\frac{1}{2}$	y + $\frac{1}{2}$	-z + 1

2. THE CRYSTAL AND MOLECULAR STRUCTURE OF
METHYL 4,6-DICHLORO-4,6-DIDEOXY- α -D-
GLUCOPYRANOSIDE

Introduction

Methyl 4,6-dichloro-4,6-dideoxy- α -D-glucopyranoside is prepared by reaction of methyl α -D-galactopyranoside with sulphuryl chloride, followed by desulphation.¹³
 The reaction goes as follows:



The present crystal structure investigation of the compound was undertaken with three objects in view: to examine the use of direct methods of crystal structure analysis for non-centrosymmetrical structures; to attempt to measure the absolute configuration using the anomalous scattering of the chlorine atoms ($f'' = 0.7$ for CuK_α radiation); and to obtain further details of the geometry and dimensions of carbohydrate molecules. Since the structure was readily determined from the Patterson function the first object has not been pursued, but the structure and absolute configuration have been determined.

Experimental

Crystals of the compound (from chloroform/petroleum ether) are colourless plates, elongated along b , with (001) developed. Unit cell and space group data were determined from rotation and Weissenberg photographs and on the G.E. spectrogoniometer.

Crystal data

(λ , $\text{CuK}_\alpha = 1.5418 \text{ \AA}$; λ , $\text{MoK}_\alpha = 0.7107 \text{ \AA}$)

Methyl 4,6-dichloro-4,6-dideoxy- α -D-glucopyranoside

$\text{C}_7\text{H}_{12}\text{O}_4\text{Cl}_2$, M. W. = 231.1

m. $119-121^\circ$; $[\alpha]_D = +122^\circ$ (c, 1.9)

Monoclinic, $a = 16.51 \pm 0.03$,

$b = 5.06 \pm 0.01$

$c = 13.16 \pm 0.03 \text{ \AA}$, $\beta = 115.6^\circ \pm 0.1^\circ$

$U = 991 \text{ \AA}^3$

$D_m = 1.54$ (flotation in carbon tetrachloride-acetone)

$$Z = 4, D_c = 1.55 \text{ g.cm.}^{-3}$$

Absorption coefficients for X-rays, $\mu(\text{CuK}_\alpha) = 58 \text{ cm.}^{-1}$

$$\mu(\text{MoK}_\alpha) = 6.4 \text{ cm.}^{-1}$$

$$F(000) = 480$$

Absent spectra: hkl when $h + k = 2n + 1$

Space group is $C2(C_2^3)$ Cm and $C2/m$ being excluded since the compound is optically active.

The intensities of the reflexions were measured on a General Electric XRD 5 Spectrogoniometer, using a scintillation counter, MoK_α radiation (Zr filter and pulse height analyser), and a θ - 2θ scan. Of 810 reflexions with $2\theta(\text{MoK}_\alpha) \leq 47^\circ$ (minimum interplanar spacing, 0.89 Å), 544 had intensities greater than 1.5 times the background. The 266 reflexions with intensities less than 1.5 times the background were classified as unobserved, and were included in the analysis with $|F_o| = 0.6 F(\text{threshold})$. The crystal was mounted with b parallel to the ϕ axis of the goniostat, and had cross-section $0.2 \times 0.05 \text{ mm.}$; no absorption corrections were applied. The intensities were corrected for background (which was approximately a function of θ only), Lorentz and polarization factors were applied, and the structure amplitudes were derived.

Structure Analysis

The chlorine atom positions were determined from the three-dimensional Patterson function as (0.067, 0, 0.192) and (0.125, 0.5, 0). A three-dimensional electron-density

distribution, computed with phases based on the chlorine atoms ($R = 0.48$) had false mirror planes at $y = 0$ and $\frac{1}{2}$, but the whole molecule was nevertheless clearly indicated, and coordinates were obtained for all non-hydrogen atoms, except C(1) and C(6), which were poorly resolved. A second Fourier summation revealed the positions of these two atoms. The structure was then refined by least-squares methods, with minimization of $\sum w(|F_o| - |F_c|)^2$, with $\sqrt{w} = 1$ when $|F_o| \leq F^*$, and $\sqrt{w} = F^*/|F_o|$ when $|F_o| > F^*$. Analysis of the values of $w(|F_o| - |F_c|)^2$ during the course of the refinement indicated $F^* = 25$ as being appropriate. The scattering factors of the International Tables were used, without correction for anomalous dispersion, since the corrections are negligible for $\text{MoK}\alpha$ radiation. R , initially 0.33, was reduced by five isotropic cycles to 0.13, and by five further anisotropic cycles to 0.11. At this stage, an $(F_o - F_c)$ synthesis revealed the positions of all the hydrogen atoms, except the three methyl hydrogens and the hydrogen bonded to O(2) [in fact the measured O(3) - H(8) distance is about 1.3 Å in an intermolecular O(3)...O(2) hydrogen bond of length 2.70 Å, so that H(8) appears only slightly closer to O(3) than to O(2), and its exact location is doubtful]. Two further cycles of least-squares, in which the hydrogens were included but not refined, completed the refinement, the final R being 0.09 for the 544 observed reflexions.

The measured and final calculated structure factors are listed in Table V. Sections of the final three-dimensional electron-density distribution are shown in Figure 6, together with a drawing of the structure. A final difference map showed maximum fluctuations of $\pm 0.6 \text{ e.}\text{\AA}^{-3}$ near the two-fold axes and the chlorine atoms.

The final positional and thermal parameters are given in Table VI, the bond lengths and valency angles in Table VII, and the shorter intermolecular distances in Table VIII.

Absolute Configuration

As a final step in the analysis the absolute configuration of the molecule was determined by the anomalous dispersion method.¹⁴ Structure factors were calculated for all the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions, using scattering factors for the chlorines of the form:

$$f = (f_{\text{Cl}} + f'_{\text{Cl}}) + i f''_{\text{Cl}}$$

For $\text{CuK}\alpha$ radiation, $f' = 0.3$, $f'' = 0.7$.¹⁵ Thirty-two pairs of reflexions with the largest differences between $F_{\text{O}}(hkl)$ and $F_{\text{O}}(\bar{h}\bar{k}\bar{l})$ were chosen, and the intensities were measured with a scintillation counter and $\text{CuK}\alpha$ radiation. The crystal was mounted about b , so that with a quarter-circle orienter it was necessary to use two mountings to perform the measurements. The intensities of the hkl and $\bar{h}\bar{k}\bar{l}$ reflexions were recorded, the crystal was remounted upside down, and the $h\bar{k}l$ and $\bar{h}k\bar{l}$ intensities were measured.

$I_0(hkl)$ was taken as the average of the first two readings, and $I_0(\bar{h}\bar{k}\bar{l})$ the average of the second set. The results (Table IX) indicate (unambiguously, apart from one reflexion of those measured) that the parameters used to calculate the structure factors (those of Table VI referred to a right-handed set of axes) represent the true absolute configuration. All the diagrams depict the correct absolute configuration of D-glucose.

Discussion

The analysis has established the structure and absolute configuration of methyl 4,6-dichloro-4,6-dideoxy- α -D-glucopyranoside, the molecule having the usual chair conformation (Figure 6). The C-C bond distances (Table VII) are in the range 1.50-1.55 Å ($\sigma = 0.04$ Å), mean 1.52₄ Å ($\sigma = 0.02$ Å), and the range of C-O distances is 1.39-1.44 Å ($\sigma = 0.04$ Å), mean 1.422 Å ($\sigma = 0.02$ Å). The C-Cl distances are 1.75 and 1.81 Å, mean 1.78 Å ($\sigma = 0.03$ Å). None of the individual bond distances differs significantly from the mean lengths. The mean distances are similar to those in other pyranoid sugars.¹⁶ The carbon valency angles within the ring vary from 107° to 110° ($\sigma = 2^\circ$), mean 108.6° ($\sigma = 1^\circ$), and the angle at O(5) is 113°, perhaps slightly larger than the tetrahedral angle, as is commonly found in other sugars.¹⁶ The external angles are in the range 106° to 114° ($\sigma = 2^\circ$).

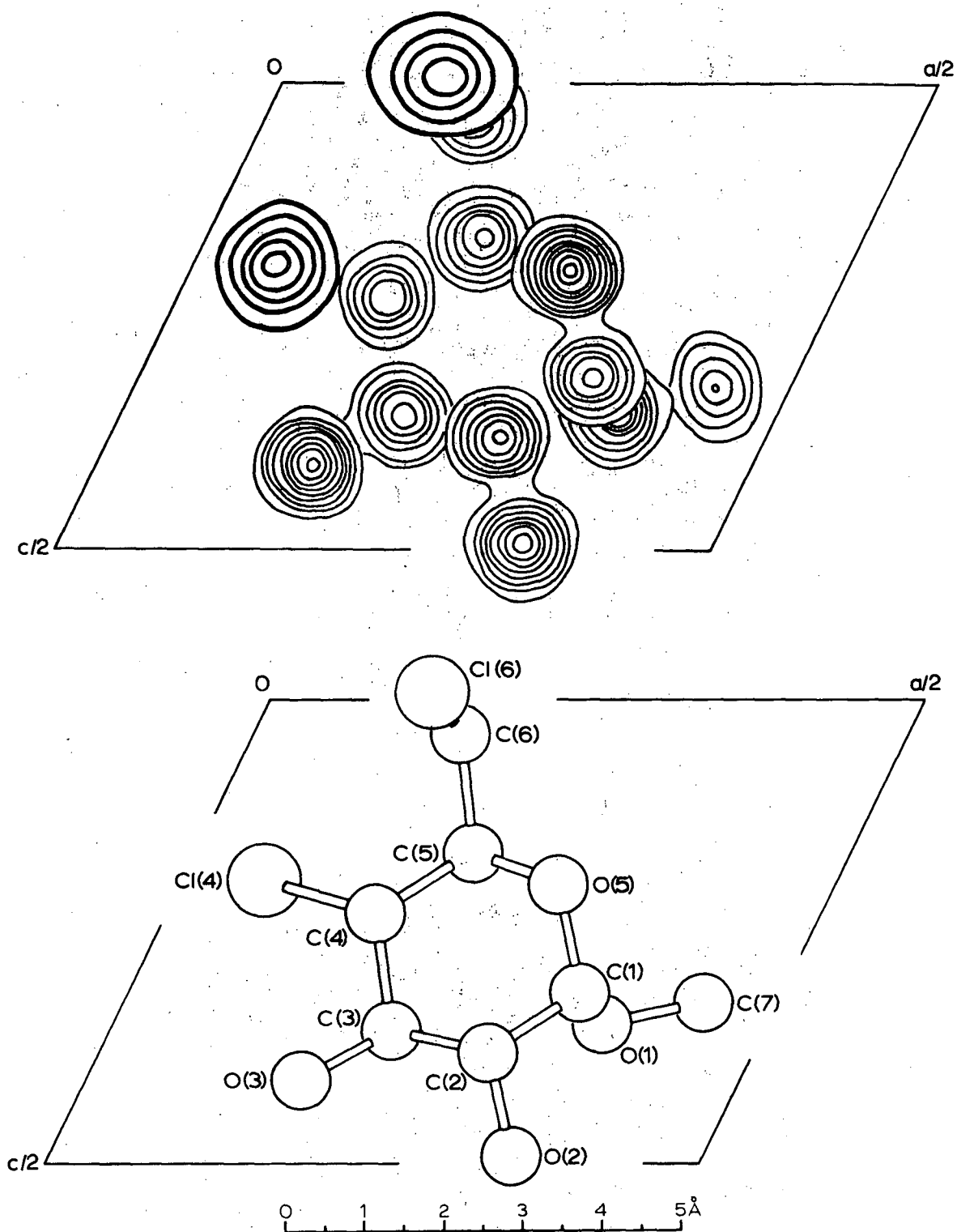


Figure 6. Superimposed sections of electron density distribution (contours at $1, 2, 3 \dots e/\text{\AA}^3$ for C and O; $1, 5, 10 \dots e/\text{\AA}^3$ for Cl) and a drawing of the molecule.

The bond lengths and valency angles involving hydrogen (Table VII) have been determined less precisely, and the methyl hydrogens and the hydrogen bonded to O(2) have not been located. The range for C-H bonds is 0.9-1.3 Å ($\sigma = 0.3$ Å), and for H-C-X angles (X = C, O, or Cl) 92° - 128° ($\sigma = 17^\circ$). The average values are 1.1 Å and 109° , and the differences between individual values are not significant.

The packing of the molecules in the unit cell (Fig.7) and the shorter intermolecular distances (Table IV) indicate the presence of one definite hydrogen bond, $O(3) \cdots O(2^{IV}) = 2.70$ Å, and a second possible bond, $O(2) \cdots O(3^{IV}) = 3.08$ Å. This latter distance is however at the extreme of hydrogen bond distances usually found¹⁶ (2.68-3.04 Å). The angles at O(2) and O(3) (Figure 8) support the assignment of H(8) to O(3), and the hydrogen bonding scheme: $\cdots O(2^{III}) - H \cdots O(3) - H \cdots O(2^{IV}) - H \cdots$. The other intermolecular distances correspond to van der Waals interactions.

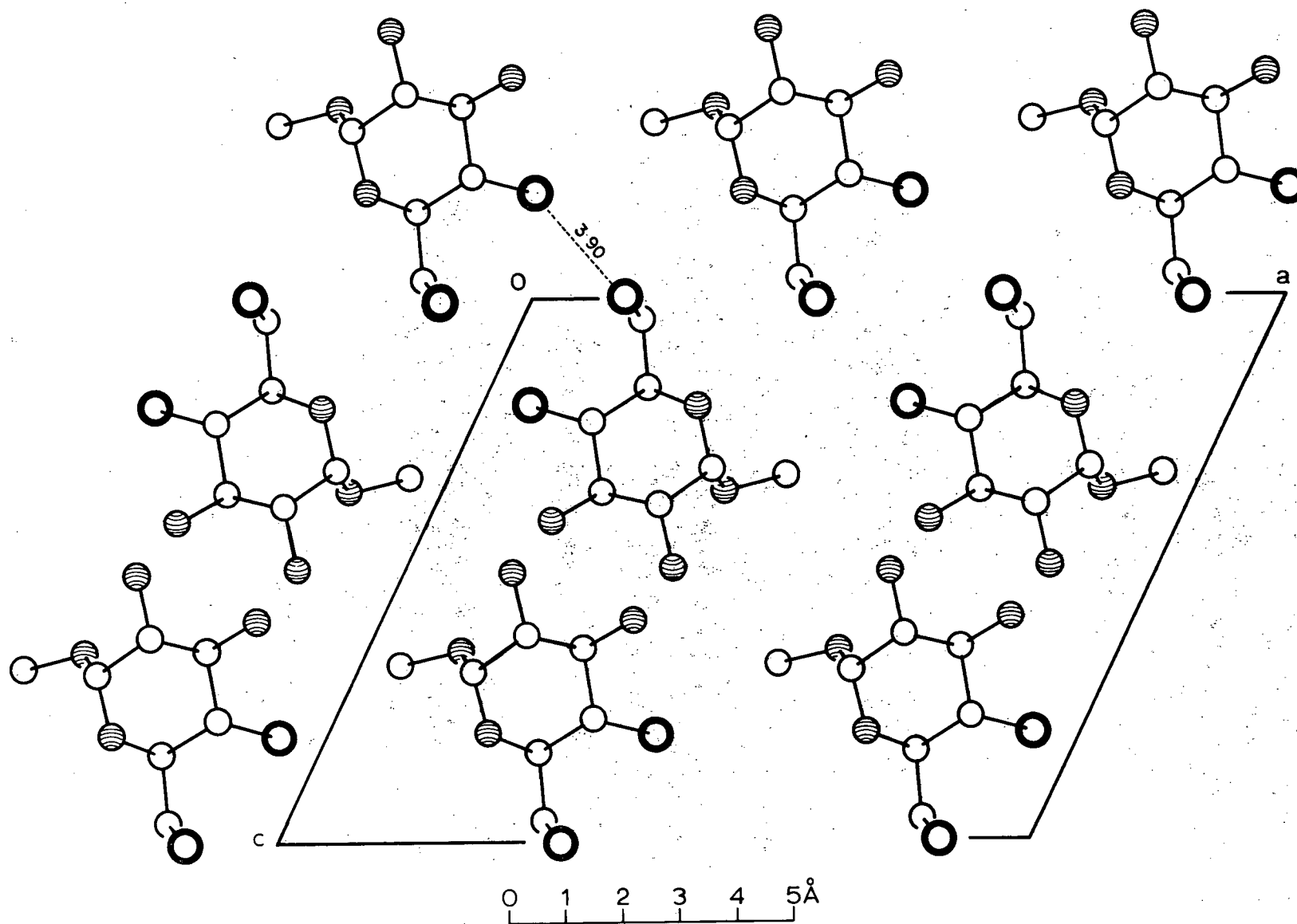


Figure 7. Packing diagram; view along *b*.

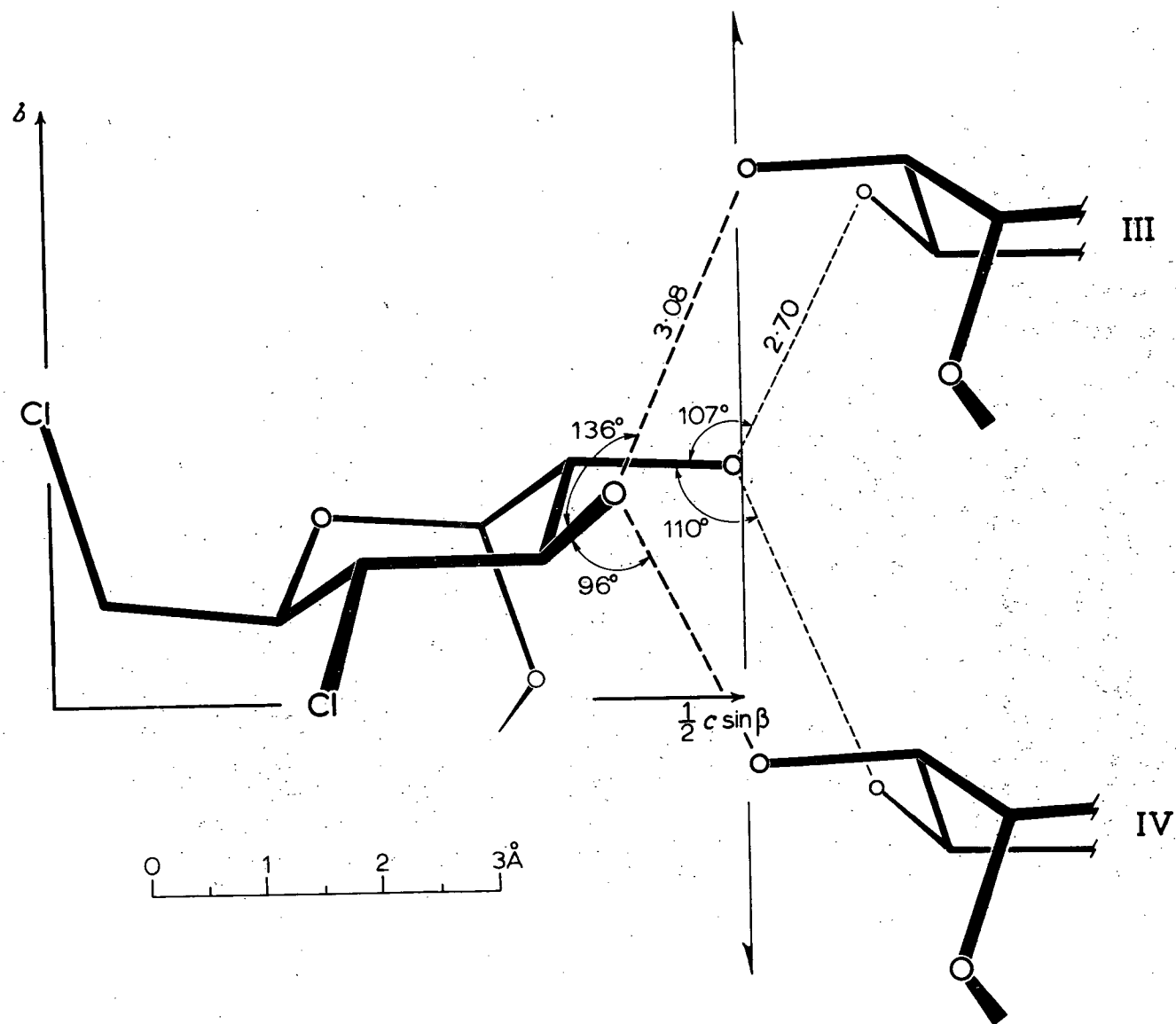


Figure 8. Hydrogen bonding; view along a .

TABLE VI

FINAL POSITIONAL PARAMETERS (fractional), ISOTROPIC THERMAL
PARAMETERS (\AA^2), AND ANISOTROPIC THERMAL PARAMETERS

($\exp - (b_{11}h^2 + b_{12}hk + b_{13}kl + b_{22}k^2 + b_{23}kl + b_{33}l^2)$),
 together with estimated standard deviations in parenthesis,
 referring to the last decimal positions of respective values.

Atom	x	y	z	B
Cl(4)	0.0641(5)	0	0.1968(6)	5.05(17)
Cl(6)	0.1209(6)	0.494(3)	-0.0064(7)	6.59(23)
O(1)	0.3742(10)	0.032(6)	0.3496(14)	4.3(4)
O(2)	0.3543(13)	0.387(6)	0.4963(16)	5.0(5)
O(3)	0.1633(12)	0.344(5)	0.4098(14)	4.7(5)
O(5)	0.2866(12)	0.313(5)	0.1989(14)	4.4(5)
C(1)	0.3441(16)	0.293(7)	0.3131(19)	3.8(6)
C(2)	0.2954(17)	0.401(7)	0.3790(19)	3.9(6)
C(3)	0.2145(15)	0.235(6)	0.3563(18)	3.3(6)
C(4)	0.1548(15)	0.233(7)	0.2269(20)	3.7(6)
C(5)	0.2093(18)	0.141(8)	0.1648(22)	3.9(6)
C(6)	0.1583(22)	0.172(9)	0.0381(26)	5.4(8)
C(7)	0.4457(19)	-0.052(10)	0.3236(25)	6.1(10)

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cl(4)	0.0052(3)	-0.006(3)	0.0053(5)	0.057(4)	-0.002(3)	0.0087(5)
Cl(6)	0.0090(4)	0.003(4)	0.0073(7)	0.061(4)	0.003(4)	0.0092(6)
O(1)	0.0044(7)	-0.001(6)	0.0056(12)	0.054(11)	-0.007(7)	0.0073(11)
O(2)	0.0052(9)	-0.002(6)	0.0038(17)	0.059(12)	-0.008(8)	0.0080(14)
O(3)	0.0053(7)	0.004(6)	0.0066(13)	0.052(12)	0.001(7)	0.0077(12)
O(5)	0.0053(7)	-0.003(6)	0.0062(12)	0.057(11)	0.005(7)	0.0060(10)
C(1)	0.0047(10)	-0.001(8)	0.0047(17)	0.050(15)	0.008(9)	0.0049(14)
C(2)	0.0048(10)	-0.003(7)	0.0052(17)	0.039(13)	-0.005(8)	0.0053(15)
C(3)	0.0040(9)	0.008(6)	0.0050(15)	0.037(12)	0.004(8)	0.0050(14)
C(4)	0.0035(9)	0.002(7)	0.0038(18)	0.045(15)	0.003(9)	0.0059(16)
C(5)	0.0043(11)	0.005(8)	0.0032(21)	0.050(15)	-0.002(10)	0.0060(18)
C(6)	0.0068(14)	-0.004(10)	0.0065(25)	0.060(20)	-0.007(12)	0.0079(20)
C(7)	0.0061(12)	0.010(9)	0.0101(22)	0.072(23)	-0.008(13)	0.0123(22)

Hydrogen positional parameters (B taken as 3.0 Å² for all hydrogen atoms).

Hydrogen atom	Attached to	x	y	z
H(1)	C(1)	0.392	0.417	0.325
H(2)	C(2)	0.275	0.600	0.358
H(3)	C(3)	0.225	0.042	0.375
H(4)	C(4)	0.125	0.433	0.208
H(5)	C(5)	0.233	-0.017	0.167
H(6)	C(6)	0.100	0.000	0.033
H(7)	C(6)	0.200	0.117	0.000
H(8)	C(3)	0.158	0.150	0.467

TABLE VII

Bond Lengths and Valency Angles

Bond Lengths			Valency Angles			
i	j	D(1j)	i	j	k	Angle (ijk)
C1(6)	C(6)	1.75 A	C1(4)	C(4)	C(5)	107.9°
C1(4)	C(4)	1.81	C1(4)	C(4)	C(3)	108.3
O(1)	C(7)	1.43	C1(6)	C(6)	C(5)	114.2
O(1)	C(1)	1.42	C(6)	C(5)	C(4)	112.5
O(2)	C(2)	1.43	C(6)	C(5)	O(5)	106.0
O(3)	C(3)	1.42	O(3)	C(3)	C(4)	108.3
O(5)	C(1)	1.39	O(3)	C(3)	C(2)	110.7
O(5)	C(5)	1.44	O(2)	C(2)	C(3)	108.6
C(1)	C(2)	1.52	O(2)	O(2)	C(1)	108.6
C(2)	C(3)	1.50	C(7)	C(1)	C(1)	113.7
C(3)	C(4)	1.55	O(1)	C(1)	O(5)	114.0
C(4)	C(5)	1.53	O(1)	C(1)	C(2)	109.7
C(5)	C(6)	1.52	O(5)	C(1)	C(2)	108.1
			C(1)	C(2)	C(3)	109.4
			C(2)	C(3)	C(4)	108.0
			C(3)	C(4)	C(5)	110.3
			C(4)	C(5)	O(5)	107.3
			C(5)	O(5)	C(1)	113.0

 $\sigma = 0.04$ A $\sigma = 1.7 - 2.0^\circ$

Bond Lengths and Angles Involving Hydrogens

i	j	D(i,j)	k	Angle (i,j,k)
H(1)	C(1)	1.0 A	{ O(1) O(5) C(2)	113° 105 106
H(2)	C(2)	1.1	{ C(1) C(3) O(2)	112 109 109
H(3)	C(3)	1.0	{ C(2) C(4) O(3)	117 103 109
H(4)	C(4)	1.1	{ C(3) C(5) Cl(4)	105 118 107
H(5)	C(5)	0.9	{ C(4) O(5) C(6)	128 103 99
H(6)	C(6)	1.3	{ C(5) Cl(6)	92 118
H(7)	C(6)	1.1	{ C(5) Cl(6)	109 108
H(8)	O(3)	1.3	C(3)	102

Mean

1.1 A

109°

TABLE VIII

Shorter Intermolecular Distances

x^I	y^I	i	$D(x^I - y^I)$
O(2)	O(3)	III	2.70 Å
O(2)	O(3)	IV	3.08
O(3)	O(2)	III	3.08
O(3)	O(2)	IV	2.70
O(2)	C(3)	III	3.17
O(3)	C(7)	V	3.31
C(2)	O(3)	III	3.40
O(3)	C(3)	III	3.48
Cl(6)	C(6)	II	3.49
C(2)	O(1)	II	3.53

Symmetry Code

I	x	y	z
II	x	$y + 1$	z
III	$-x + \frac{1}{2}$	$y + \frac{1}{2}$	$-z + 1$
IV	$-x + \frac{1}{2}$	$y - \frac{1}{2}$	$-z + 1$
V	$x - \frac{1}{2}$	$y + \frac{1}{2}$	z

TABLE IXDetermination of the Absolute Configuration (CuK α radiation)

h k l	$ F_o(hkl) $	$ F_o(\bar{h}\bar{k}\bar{l}) $	$ F_o(hkl) ^2$	$I_o(hkl)$
			$ F_o(\bar{h}\bar{k}\bar{l}) ^2$	$I_o(\bar{h}\bar{k}\bar{l})$
1 1 0	6.9	6.3	1.20	1.11
1 1 1	45.3	43.4	1.09	1.09
1 1 2	17.7	15.9	1.24	1.30
1 1 4	15.2	13.7	1.23	1.18
1 1 5	6.0	5.4	1.24	1.09
1 1 11	2.1	1.5	1.96	1.44
3 1 0	10.4	11.7	0.79	0.67
3 1 5	27.6	28.8	0.92	0.93
3 1 1	62.4	64.2	0.95	0.91
3 1 10	12.3	11.2	1.21	1.24
5 1 2	6.8	7.4	0.84	0.83
5 1 2	27.1	24.7	1.20	1.18
5 1 12	10.2	8.9	1.31	1.16
7 1 5	44.6	46.5	0.92	0.97
7 1 6	17.5	16.4	1.14	1.15
7 1 10	12.1	13.4	0.82	0.91
9 1 0	16.5	15.5	1.13	1.14
9 1 5	10.9	9.4	1.35	1.26
9 1 6	13.3	14.4	0.85	0.88
11 1 8	9.9	10.7	0.86	1.02
0 2 0	30.1	32.9	0.84	0.85
0 2 1	31.3	28.9	1.17	1.13
0 2 10	10.7	12.0	0.80	0.84
4 2 2	21.1	22.8	0.82	0.87
6 2 5	11.5	10.4	1.22	1.22
8 2 3	13.5	12.5	1.17	1.09
10 2 9	4.4	5.1	0.74	0.85
12 2 7	12.4	11.4	1.18	1.23
12 2 12	7.7	7.1	1.18	1.04
11 3 1	6.2	6.9	0.81	0.73
4 4 3	11.4	10.4	1.20	1.08
4 4 4	12.6	13.5	0.87	0.86

The XZ Projection of the Glucoside by Direct Methods

The set of four programs (described later) for solving centrosymmetric projections by direct methods were written after the glucoside structure had been solved by the conventional methods described earlier. However, the direct methods programs were tried on this structure both to test the initial versions of the programs and to suggest alterations and additions to be made to them. The initial results will not be presented but the following is a description of a run made on the glucoside XZ projection with the programs in their final form:

The PREDIR program was run with all the three-dimensional data with $\sin\theta/\lambda$ less than 0.5 (596 reflexions) placed into 10 ranges of $\sin\theta/\lambda$. A primitive cell was assumed by fitting the data to a structure consisting of 2 molecules in the unit cell. The weights used for the first two ranges were 0.0 and 1.00 respectively. The scale constant found was 2.45, the average temperature factor found was 5.00, and the probability coefficient $\sigma_3/\sigma_2^{3/2}$ was 0.26. The statistics for the 596 reflexions after scaling were $\langle |E| \rangle = 0.84$, $\langle |E|^2 \rangle = 0.99$. $|E(h', 0, 1)|$ where $h' = h/2$ were then put out on tape for those 66 reflexions where $|E| \geq 1.0$.

The 35 reflexions with $|E| \geq 1.4$ were introduced into the Sayre program and 68 Sayre relationships were found.

When the relationships which included reflexions #21 and 22 ((4,7) and (4,8) respectively) were deleted as these reflexions each occurred in only 2 Sayre relationships of "relatively" low probability, the number of relationships was reduced to 64. Each reflexion which occurred in this smaller group occurred in at least 2 relationships and where a reflexion occurred in only 2, those relationships were of "relatively" high probability. The probability that no more than 8 relationships fail in 64 was calculated to be approximately 0.998.

At this stage the signs of these 33 reflexions for the correctly solved structure were calculated to assure that the origin fixing reflexions would be assigned phases to yield the identical solution to that already solved by the conventional methods. As a result reflexion #1 (0 0 5) was assigned as +, and #32 (7 0 -2) as - for the SIGNS program run next. Out of 31931 solutions registering no more than 4 failures in the first group, 1818 solutions satisfy the additional condition that no more than 8 relationships fail in all. Of the latter number the 24 solutions which also satisfy the condition that for no reflexion \bar{h} is the sum over \bar{k} of $|E_{\bar{h}}| |E_{\bar{k}}| |E_{\bar{h}-\bar{k}}|$ (the sum taken only over relations that fail) greater than 10.0. This corresponds to the statement that in no possible solution is any sign indicated to be the opposite of that predicted to a probability of greater than 0.995. A linear

dependence arose such that for any combination of failures reflexion #34 could be arbitrarily assigned a + or - sign. Apart from the two perfectly consistent solutions where no failure of Sayre relationship occur, the correct solution has the lowest value of the above test. However, there are 3 sets of solutions (i.e. 6 solutions) with the same minimum value. Nevertheless, the correct solution would be readily apparent on drawing up all the above 8 possible solutions since such a large number of signs (33) are determined. The E - map for the correct solution with 17 + signs and 16 - signs extracted from tape by the ESIGND program and drawn up by the CONTUR program is shown in Figure 9 with the model of the correct solution superimposed (Note $a' = a/2$).

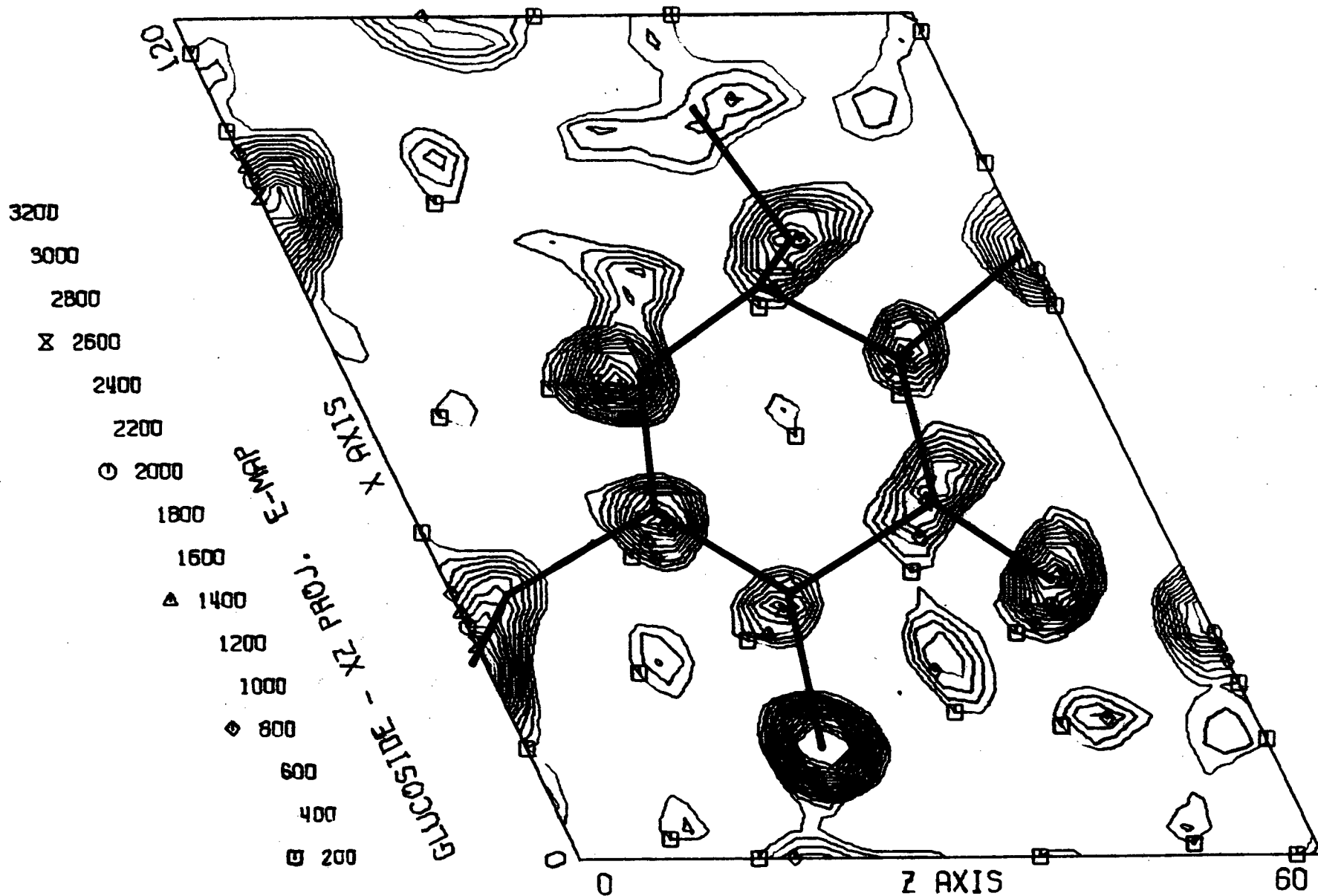


Figure 9. E-map of xz-projection (contours on arbitrary scale) with final refined solution superimposed.

3. THE STRUCTURE OF METHYL 4,6-DICHLORO-4,6-DIDEOXY- α -D-GALACTOPYRANOSIDE

Introduction

Methyl 4,6-dichloro-4,6-dideoxy- α -D-galactopyranoside is prepared by reaction of methyl α -D-glucopyranoside with sulphyryl chloride followed by desulphation.^{13,17} The steps in the reaction are similar to those involved in the preparation of the glucoside whose structure analysis precedes this one.

Although chemical evidence¹³ had established the absolute configuration of the dichloro-dideoxy hexose product, the actual crystal structure and the nature of the hydrogen bonding in the solid were unknown. This compound also showed promise for application of direct methods to its structure determination.

Experimental

Crystals (from chloroform) of this galactoside are colourless needles elongated in the c-direction. A suitable crystal was cut to about 0.10 mm. from a well formed needle of diameter 0.05 mm. and used in all subsequent work. Unit cell and space group data were determined from rotation and Weissenberg photographs and on the G.E. spectrogoniometer. (Approximate values of the cell dimensions were obtained from film. Using these,¹⁸ arbitrarily selected medium intensity reflexions were found on the counter, and their 2θ values accurately measured. More accurate values

of a , b , and c were then found by applying three cycles of refinement by least-squares to these parameters using the 2θ data in a program (CELDIM) written by Simon Whitlow to do this).

Crystal Data (λ , $\text{MoK}\alpha = 0.7107 \text{ \AA}$)

Methyl 4,6-dichloro-4,6-dideoxy- α -D-galactopyranoside

$\text{C}_7\text{H}_{12}\text{O}_4\text{Cl}_2$, $M = 231.1$

m.p. 158°C , $[\alpha]_D = +184$

Orthorhombic: $a = 23.12$ ($\sigma = 0.05$),

$b = 8.18$ ($\sigma = 0.02$)

$c = 5.091$ ($\sigma = 0.004$) \AA

$U = 962.8 \text{ \AA}^3$

$D_m = 1.59 \text{ gm cm}^{-3}$ (suspended in CCl_4 , $\rho_{20^\circ} = 1.595$)

$Z = 4$, $D_x = 1.595 \text{ gm cm}^{-3}$

Absorption coefficient for X-rays,

$$\mu(\text{CuK}\alpha) = 60 \text{ cm}^{-1} \quad \mu(\text{MoK}\alpha) = 6.6 \text{ cm}^{-1}$$

$F(000) = 480$

Absent spectra: $h \ 0 \ 0$ when $h = 2n + 1$

$0 \ k \ 0$ when $k = 2n + 1$

and $0 \ 0 \ l$ when $l = 2n + 1$

Space group is $P2_12_12_1$ (D_2^4)

The intensities of the reflexions were measured on a General Electric XRD 6 automated (Datex card controlled) spectrogoniometer, with a scintillation counter, $\text{MoK}\alpha$ radiation (Zr filter and pulse-height analyser), and a 2θ scan. The crystal (of length 0.10 mm. and diameter

0.05 mm.) was mounted with c parallel to the ϕ axis of the goniostat. Of 807 reflexions with $2\theta(\text{MoK}\alpha) \leq 45.58^\circ$ (minimum interplanar spacing 0.92 Å), 201 whose net intensities (corrected for background which was recorded for each reflexion before and after the scan of $\sim 2^\circ$) were less than 30 counts (maximum counts of 29440 for (800)), were classified as "unobserved" and were included in the analysis (but not in calculation of R-values) with $|F_o| = 0.6F$ (threshold). Lorentz and polarization factors were applied but no absorption corrections were made.

Structure Analysis

a. Direct Methods on the xy-projection.

The shortness of the c-axis indicated that the mean plane of the molecule lay perpendicular to the c-axis. It was hoped that if direct methods were carried out on the xy projection, and several solutions were possible for the structure, the correct one would be apparent on simple inspection of all these solutions (a program had previously been written which could rapidly draw contoured Fourier maps on U.B.C. Calcomp 565 12" drum plotter).

Using the PREDIR program (later described), the full three dimensional data was divided into nine ranges of $\sin \theta/\lambda$ for each of which the average intensity was calculated ($\langle I \rangle_\theta$). The average temperature factor, B, and the overall scale, K, were determined by least-squares using

the $\langle I \rangle_\theta$ versus $\sin \theta / \lambda$ data (the first range was excluded as it included too few reflexions) in the equation

$$\Sigma f^2 = K \exp [B (\sin \theta / \lambda)^2] \langle I \rangle_\theta$$

$$\text{where } \Sigma f^2 = 8f_{Cl}^2 + 16f_0^2 + 28f_C^2 + 48f_H^2$$

B was found to be 6.824 and K to be 22.9. These constants, however, are normally quoted for scaling of \sqrt{I} and not I ($B_{\sqrt{I}} = B/2 = 3.42$ and $K_{\sqrt{I}} = \sqrt{K} = 4.79$). As the reasonableness of the temperature factor indicated that the scaling could now be accepted, $|E(hkl)|$'s where

$$E^2(hkl) = \frac{I(hkl) \exp (B(\sin \theta / \lambda)^2)}{\Sigma f^2},$$

were calculated. $E(hk0)$ data where $|E| \geq 1.0$, were output on tape for subsequent work by direct methods.

The average value of $|E|$ for the three dimensional data was 0.852, a clear indication of an acentric distribution ($\langle |E| \rangle$ is 0.886 for acentric and 0.798 for centric distributions), and further indication for acceptance of the above scaling.

All possible Sayre relationships among the 27 reflexions (hko data only; plane group pgg) with $|E| \geq 1.30$ were found by the SAYRE program (if their probability of holding was greater than 0.60) which was run next. Fifty-four relationships () were found in which each of the 26 reflexions occurring in relationships occur in at least two relationships (reflexion #22, (11 6 0) with $E = 1.68$ occurs in no relationships).

Solutions were then generated by the SIGNS program. Reflexion #12 (9 3 0) and #21 (9 2 0) were given signs of + to define the origin as they were strong reflexions and occurred in the greatest number of Sayre relationships. The probability that, in the correct solution, no more than ten Sayre relationships (out of 54) fail was calculated in the previous program to be approximately 0.88. As the maximum number of failures in the first group that could be handled was at the time of this work limited to four, all solutions satisfying the condition that no more than four relationships fail in the first group and no more than ten fail in all, were examined. Out of the 880 solutions satisfying these conditions, only 16 solutions also satisfy the condition tested for by ITEST, that is, that for no reflexion \vec{h} in a possible solution is the sign indicated be the opposite of that in the solution to a probability greater than 0.985 (i.e. $\sum_{\vec{h}} |E_{\vec{h}}| |E_{\vec{k}}| |E_{\vec{h}-\vec{k}}| \geq 11.5$, the summation being over relations that fail). All 16 of these were plotted, but only the first (the "most probable," i.e. with the lowest value of the opposite indication of sign) had a distribution of peaks to which a model could be fitted. That solution, which proved to be correct in every sign, had only two failures of Sayre relationships,

#21 $E(10\ 1\ 0) * E(9\ 2\ 0) * E(19\ 3\ 0) \approx +$
with probability 0.785; and

#36 $E(9\ 2\ 0) * E(19\ 3\ 0) * E(10\ 5\ 0) \approx -$
with probability 0.782.

For that solution, no relations in the first group failed, and two signs (#17 and #21) were indicated to be the opposite of that in the solution to a probability of 0.93 ($\Sigma EEE = 7.0$). The E-map (a Fourier whose coefficients are the $E(hk0)$'s of known phase) for this solution is given in Figure 10 with the structure initially postulated, superimposed.

Five cycles of refinement by the method of least-squares of only the isotropic temperature factors and scale were carried out (50% of the calculated shifts applied after each cycle). All behaved well except O(1), C(2) and C(4) whose temperature factors went to 10.5, 10.0 and 16.6 \AA^2 , respectively. A Fourier summation based on the calculated phases of the remaining ten atoms was carried out and the missing atoms were relocated (Figure 11). Note that C(7) is noticeably shifted towards O(1) from the position in which it was included in the Fourier summation. Five cycles of least-squares refinement of the positional parameters (x and y) and isotropic temperature factors ($B = 3.0 \text{ \AA}^2$ initially) of all 13 non-hydrogen atoms, together with the scale, K, were carried out, applying after each cycle, 50% of the indicated shifts. The successive values of R were: 0.283 (initially), 0.174, 0.130, 0.113, 0.110 and 0.109. The final Fourier map for the xy-projection appears in Figure 12 with the refined structure superimposed.

GALACTOSIDE.. E - MAP.. X Y PROJECTION

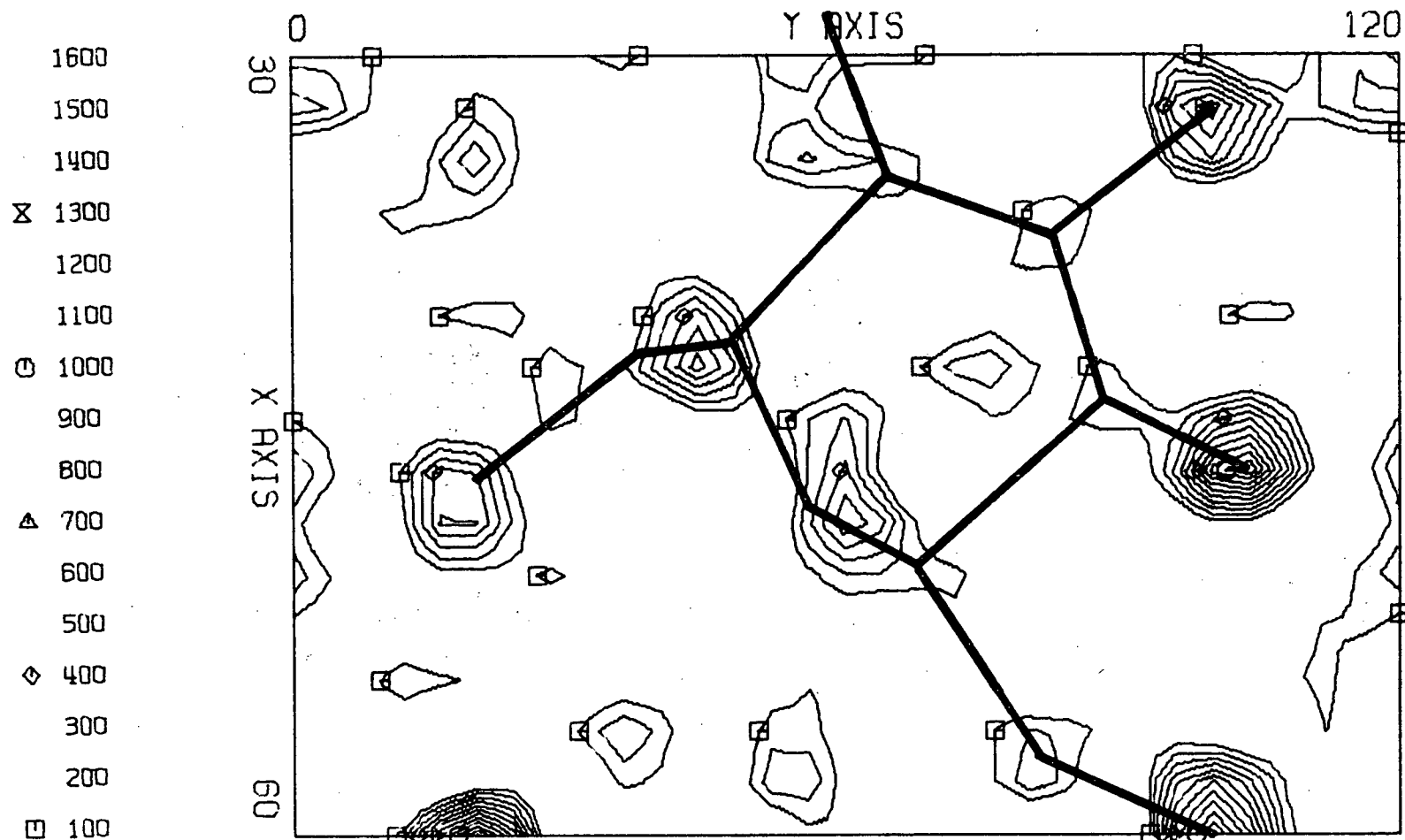


Figure 10. E-map of xy-projection (contours on arbitrary scale) with the initially postulated structure superimposed.

GALACTOSIDE.. F - MAP.. X-Y PROJECTION.. 0-1, C-2, C-4 MISSING

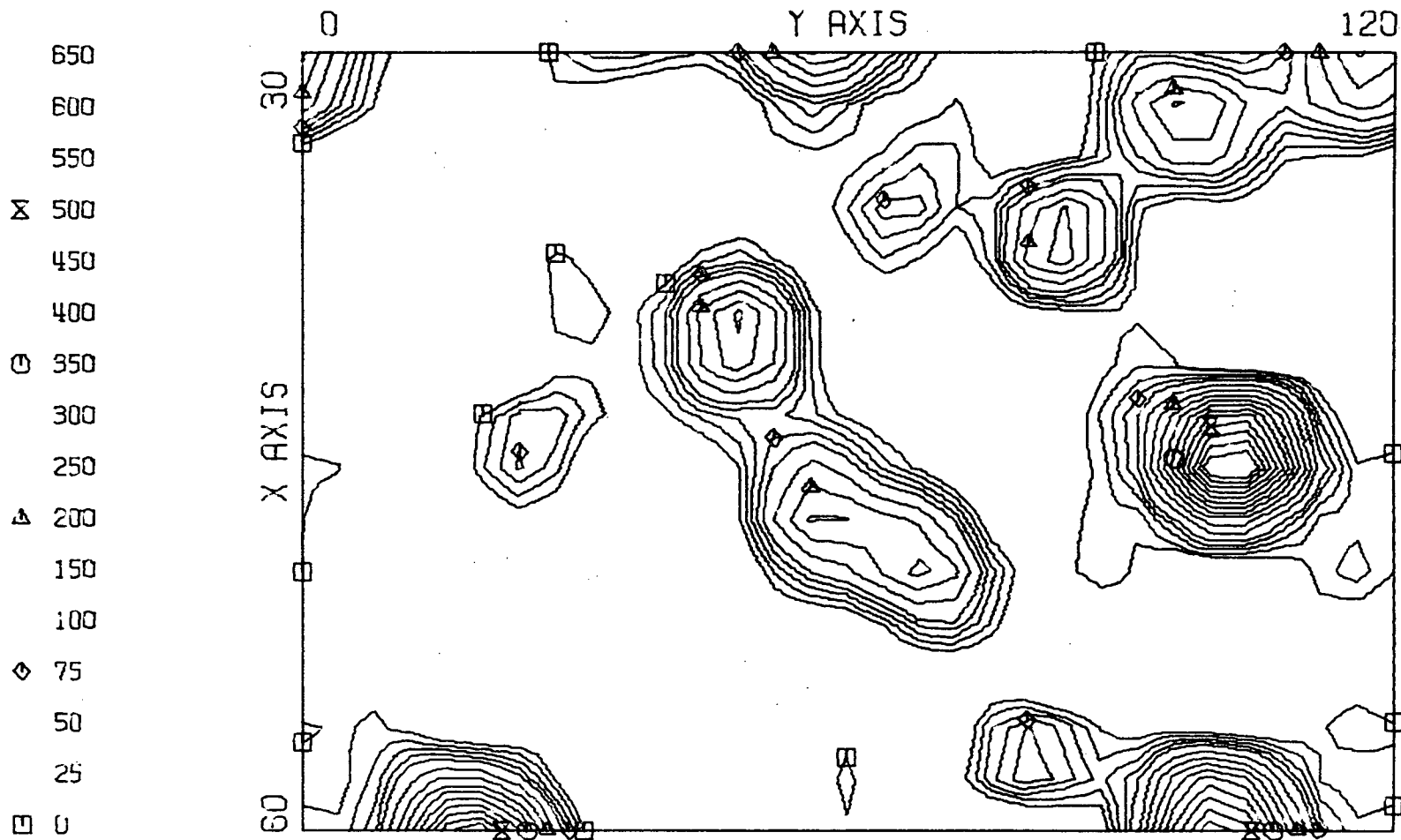


Figure 11. Electron density map of xy-projection (contours on arbitrary scale based on phases calculated using all non-hydrogen atoms except O(1), C(2) and C(4)).

GALACTOSIDE.. F - MAP.. X Y PROJECTION.. AFTER REFINEMENT

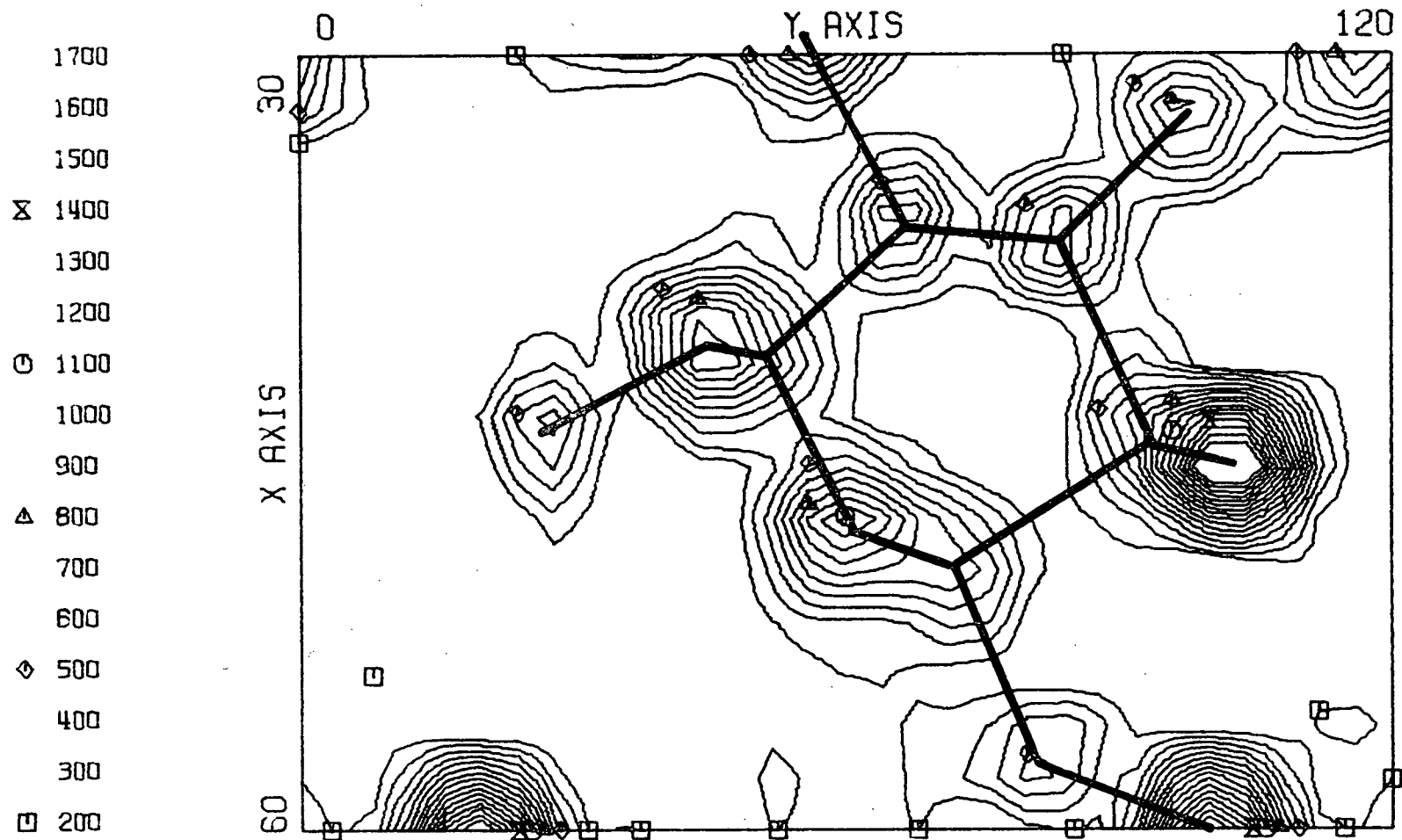


Figure 12. Final electron density map of xy-projection (contours on absolute scale: $e/A^2 \times 100$) with the refined structure superimposed.

As the z-axis is such a short axis some doubt initially existed as to whether the space group was $P2_12_12_1$ or $P2_12_12$, the absence of only 0 0 1 and 0 0 3 not being conclusive proof of the former. After the solution of the projection, the former space group is confirmed to be correct since in the latter space group $Cl(6)...Cl(6)$ across a centre in projection would be across a two-fold axis in three dimensions and would put $Cl(6)...Cl(6)$ non-bonding distance at 2.8 Å.

Attempts were made to solve the structure three dimensionally by superimposing a model on the projection and, to fix the z-coordinate of the molecule, using the postulate that O(3) of one molecule is hydrogen bonded to O(2) of the neighbouring molecule (hydrogen bond distance ~ 2.7 Å). As these attempts proved unsuccessful, it was decided to try direct methods on the xz projection as in that direction there is no overlap of one molecule on another, as the x-coordinates of all the atoms are known, as the phases of the h 0 0 data are known, and as the molecule occupies a roughly predictable position because of the hydrogen bonding of O(3) to O(2).

b. Direct Methods on the xz-projection

PREDIR was again run with the same input parameters as before, but this time normal structure factors (E 's) of the type (h 0 1) where $|E| > 1.0$ were output on tape.

All possible Sayre relationships (59) among the 26

reflexions with $|E| \geq 1.0$ were found by SAYRE but the number of relationships was reduced to 55 by exclusion of those relationships involving reflexions #15 (10 0 3) and #16 (8 0 5) as their signs cannot be determined to a sufficient probability. As a result, no reflexion of either even-odd or odd-even parity occurred in a Sayre relationship. Reflexion #14 (2 0 1) with $|E| = 1.93$ was arbitrarily given a + sign even though it occurred in no relationship. The other origin determining reflexion chosen was #21 (11 0 3) because of its magnitude ($|E| = 1.55$) and because of its frequent occurrence in relationships. The phase of the structure invariant reflexions #1 (8 0 0), #2 (10 0 0), #3 (16 0 0) and #4 (24 0 0) were already known from the solution of the xy-projection.

The SIGNS program was run with the above origin determining reflexions assigned as + and the other four reflexions assigned their proper signs. Out of 514 solutions which satisfied the condition that no more than four Sayre relationships fail in the first group and no more than 15 fail in all (80% probability of finding the correct solution in this set), only eight solutions satisfied the auxiliary condition that for no reflexion is its sign indicated to be opposite to a probability of greater than 0.983 ($\sum EEE > 11.0$).

The two most probable solutions, i.e. the two with the lowest values of ITEST, differed only in the sign

of one minor reflexion, #24 (21 0 3, $|E| = 1.23$). As the E-maps of both solutions would be almost indistinguishable, only one was drawn up, that shown in Figure 13 with the postulated structure superimposed. Subsequent refinement of this postulated structure established that the second most probable solution which contained 14 + signs and 10 - signs was correct in every sign.

Four cycles of least-squares refinement of only the z-coordinates of the 13 non-hydrogen atoms was carried out giving successive R-values of 0.252 (initially), 0.204, 0.180, 0.170, and 0.168. A Fourier based on all 13 atoms with the parameters of the last cycle was summed and, as the shift indicated (but not applied) to the temperature factor of C(7) was abnormally high ($+6.2 \text{ \AA}^2$), this atom was relocated from the resulting contour map (not shown). Five more cycles of least-squares refinement were then carried out, again shifting only the z-coordinate of each atom (50% of calculated shifts applied after each cycle). The successive R-values were 0.167 (initially), 0.145, 0.138, 0.137, 0.136, and 0.137. The final xz projection Fourier map with the refined structure superimposed is shown in Figure 14 following.

c. Full three dimensional refinement.

The xy- and xz- projection data were combined with suitable translations of the coordinates since the projections of the screw axes of $P2_12_12_1$ which become the

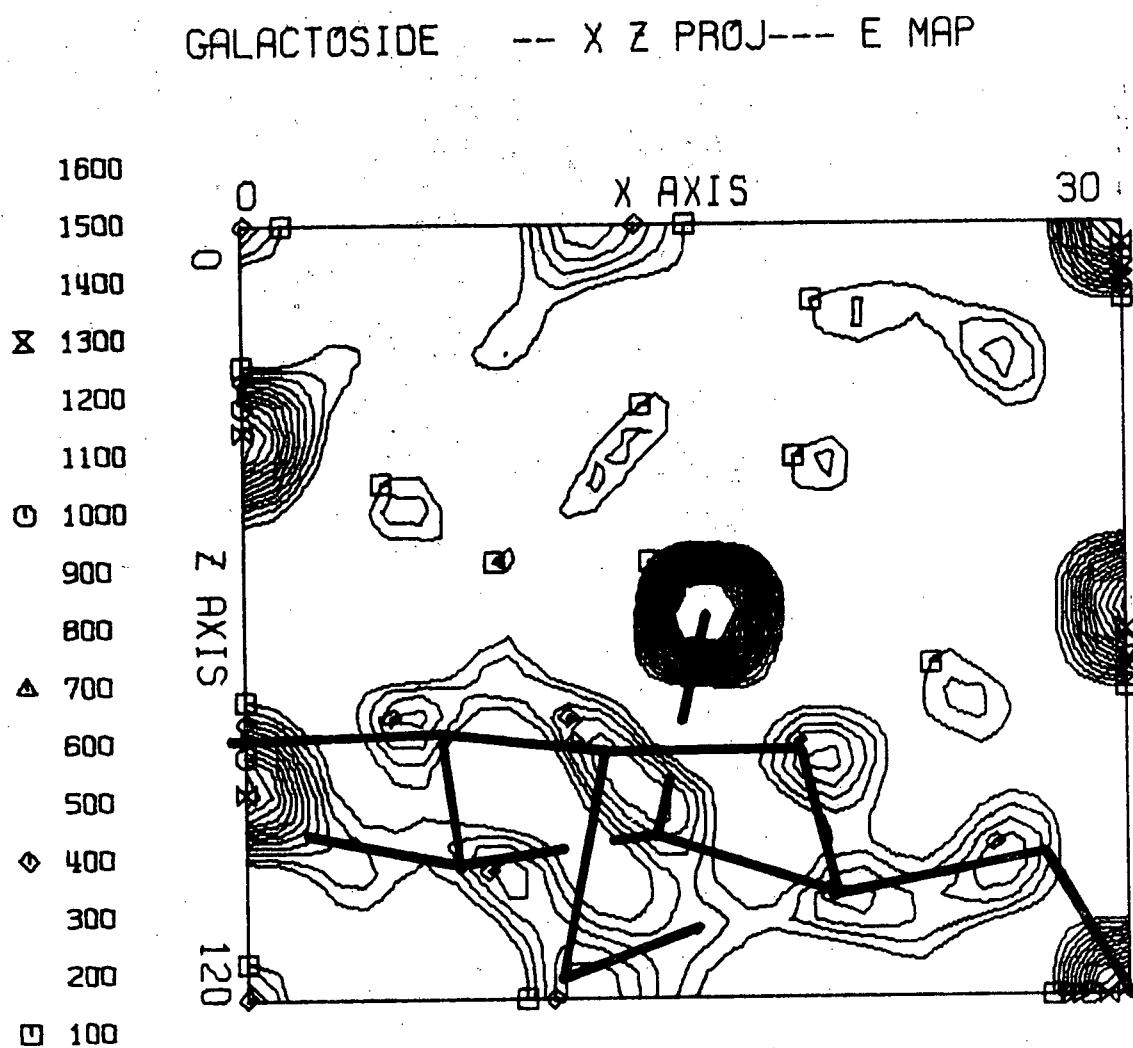


Figure 13. E-map of xz-projection (contours on arbitrary scale) with the initially postulated structure superimposed.

GALACTOSIDE -- X Z PROJ 13 ATOMS, 5 CYCLES

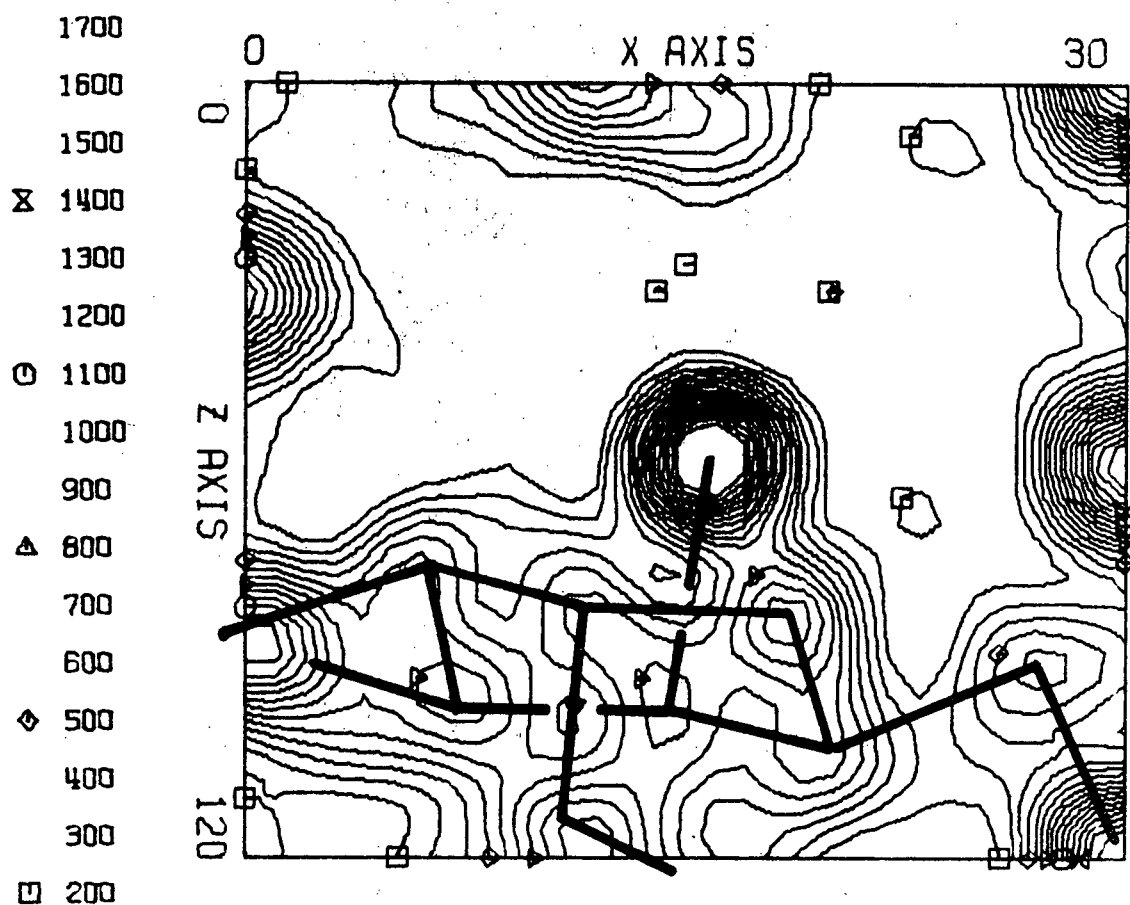


Figure 14. Final electron density map of xz-projection (contours on absolute scale: $e/\text{\AA}^2 \times 100$) with the refined structure superimposed.

centres of inversion in two dimensions, are not at 0,0 as they are in the plane group pgg. Full three dimensional refinement on all parameters (applying 50% of calculated shifts) with $F^* = 25.0$ in the standard weighting scheme noted earlier, was carried out yielding, for 7-cycles of refinement, successive R-values of 0.186 (initially), 0.162, 0.155, 0.151, 0.148, 0.146, 0.144, and 0.143. Refinement was continued incorporating anisotropic temperature factors, and yielding, for four cycles, successive R-values of 0.143 (initially), 0.133, 0.128, 0.126, and 0.125. As this R-value was rather large in comparison to the expected accuracy of the data, a reappraisal was made of the value which should be classified as a minimum observable intensity. It was noted that the background was of the order of 300 counts, (the maximum intensity reflexion (8 0 0) on this scale had a scan of 29440 counts). A value of 100 as the net counts for a minimum observable reflexion was substituted for 30 which was previously used (On the average, 100 would correspond to a reflexion whose standard deviation is $\sqrt{100 + 2 \times 300} = \sqrt{700} \approx 26 \approx 100/4$). On this basis, only reflexions with net counts greater than 4σ are classified as observed. Of the 807 reflexions recorded, only 335 (41.5%) were now classified as observable. Using the parameters which previously gave an R-value of 0.125, a recalculation of R using the new observable reflexions yielded a value

of 0.077. Four cycles of refinement by least-squares, applying 50% of the calculated shifts after each cycle and weighting reflexions by the standard scheme (see before) where $F^* = 25.0$, yielded the R-values: 0.077 (initial), 0.071, 0.070, 0.069 and 0.068. A difference Fourier summed over only observable reflexions indicated the positions of the six hydrogens given in Table XI. The hydrogens on O(2) and O(3), however, were not found. After reflecting the molecule through $z = \frac{1}{2}$ to make the solution contain the correct optical enantiomorph, and after including the previously found hydrogens all with isotropic temperature factors of 3.0 \AA^2 , a structure factor calculation revealed that the R-value had decreased to 0.0596. The measured and final calculated structure factors are listed in Table X. A final difference synthesis showed fluctuation of $-0.3e/\text{\AA}^3$ to $+0.3e/\text{\AA}^3$. The final positional and thermal parameters are in Table XI, bond lengths and valency angles are in Table XII, and the shorter intermolecular distances are in Table XIII.

Discussion

a. Molecular Structure and Dimensions

The foregoing analysis has established the structure of methyl 4,6-dichloro-4,6-dideoxy- α -D-galactopyranoside. That the crystal contains the α -anomer of the galactoside has been established, but that it contains the D-enantio-

morph has not. As the latter can be inferred from the preparation, the anomalous dispersion method was not used on this crystal to ascertain its absolute configuration. All drawings depict the correct enantiomorph referred to a right handed set of axes.

Figure 15 shows the conformation and configuration of the molecule in projection along the z-axis. The conformation adopted is the chair form of the pyranose ring on which substituents are attached in the manner 1a2e3e4a5e (i.e., the expected C1 conformation in Reeves' notation¹⁸). The packing of molecules in the unit cell is shown in Figure 16.

The bond lengths and valency angles in the molecule are given in Table XII. The ranges for the C-C bond lengths is 1.51-1.54 Å ($\sigma = 0.02$ Å), of which the average value is 1.532 Å ($\sigma = 0.01$ Å). The two C-Cl bond lengths have an average value of 1.80 Å ($\sigma = 0.01$). The C-O bond lengths are in the range 1.48-1.41 Å ($\sigma = 0.02$) with the lengths involving the glycosidic oxygen, O(1), at the extremes (Jefferey and Rosenstein¹⁶ have noted that in monosaccharides, C(1)-O(1) tends to be shorter than the normal C-O bond), the other C-O bond lengths covering a narrower range. The average C-O bond length is 1.45 Å ($\sigma = 0.01$). The mean value for C-C is as found in other carbohydrates¹⁶, but the C-O value is at the upper range of those found. Except, perhaps, for those involving O(1), none of the individual bond lengths differ significantly from their means.

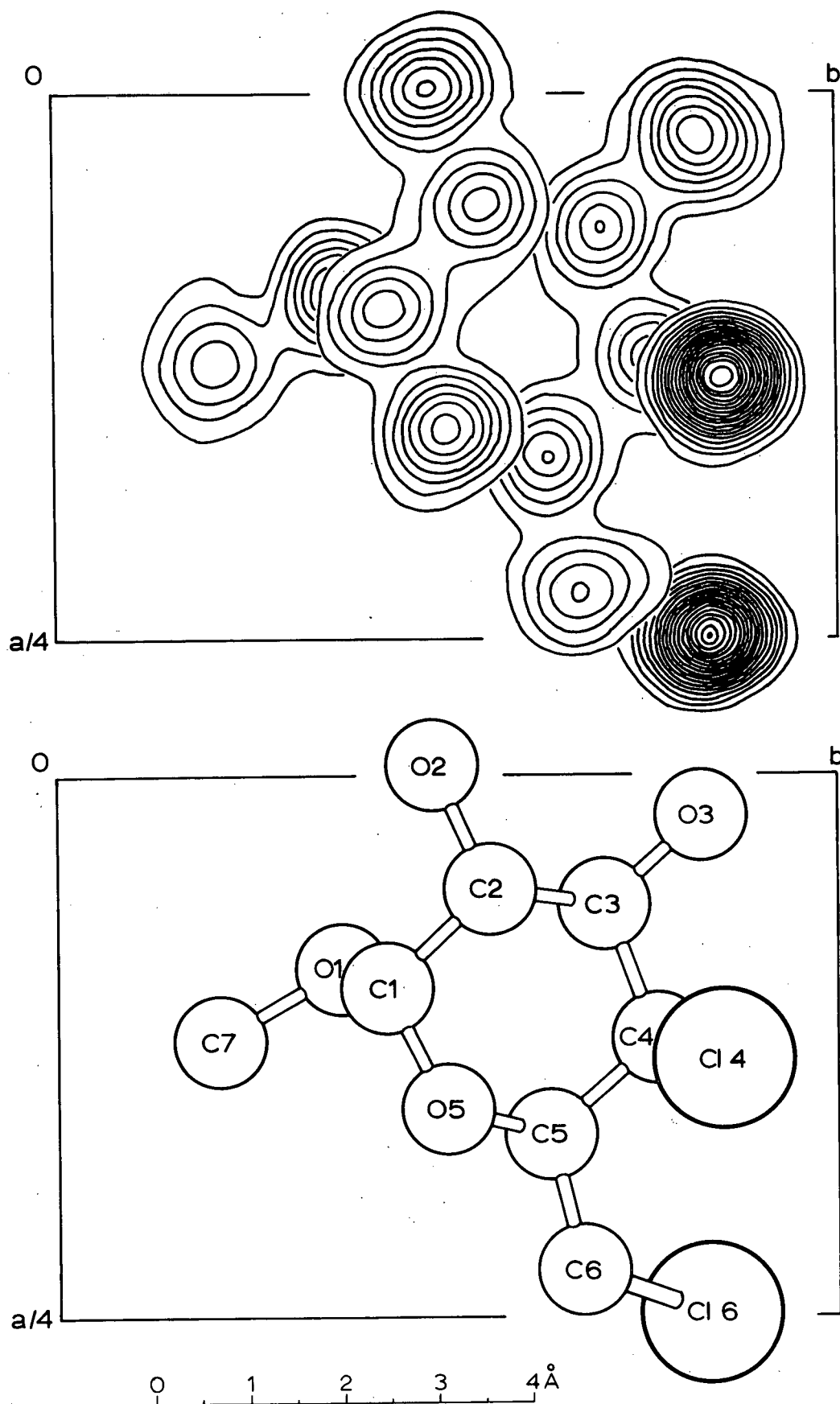


Figure 15. Superimposed sections of the electron density distribution (contours at 1,2,3...e/Å³) and a drawing of the molecule.

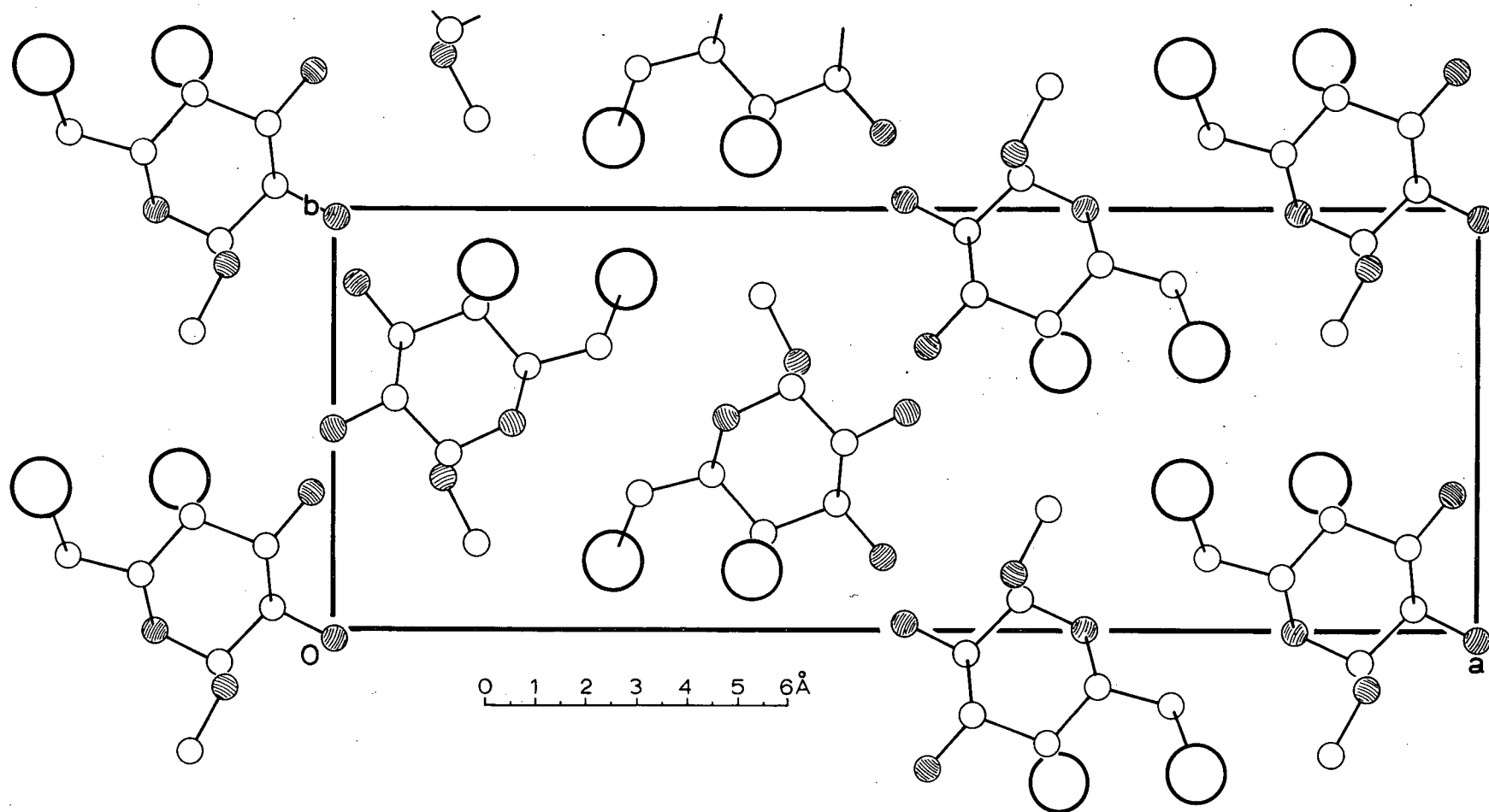
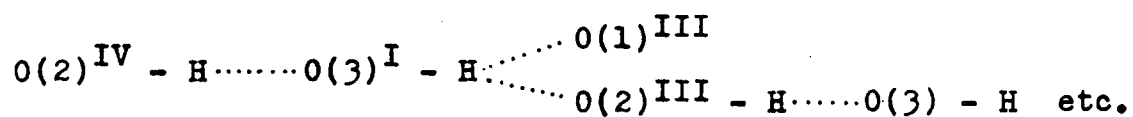


Figure 16. Packing diagram; view along c.

Within the ring the carbon valency angles range between 109.2° and 110.3° ($\sigma = 1.3^\circ$) with a mean value of 109.7° ($\sigma = 0.7^\circ$). The angle at O(5) is 115.0° , larger than the tetrahedral angle as is commonly found in other simple sugars.¹⁶ The external angles are in the range 104° - 116° ($\sigma = 1.3^\circ$). Table XII gives the bond lengths and valency angles for six hydrogens, calculated from their coordinates as they appeared on a difference synthesis. They range in bond length between 0.93 Å and 1.22 Å with a mean value of 1.04 Å. The valency angles in which they occur range between 97° and 134° with a mean value of 109.9° . The standard deviation of the mean values quoted in Table XII is the root-mean-square-deviation from the mean.

b. Hydrogen Bonding in the Structure

Table XIII contains the intermolecular distances which are less than 3.6 Å. The shorter distances represent possible hydrogen bonding and these are included in Fig.17, a view along the y-axis of the near origin region of the unit cell. Only two independent hydrogens per molecule are available for hydrogen bonding: one on O(2), the other on O(3). A possible hydrogen bonding scheme is



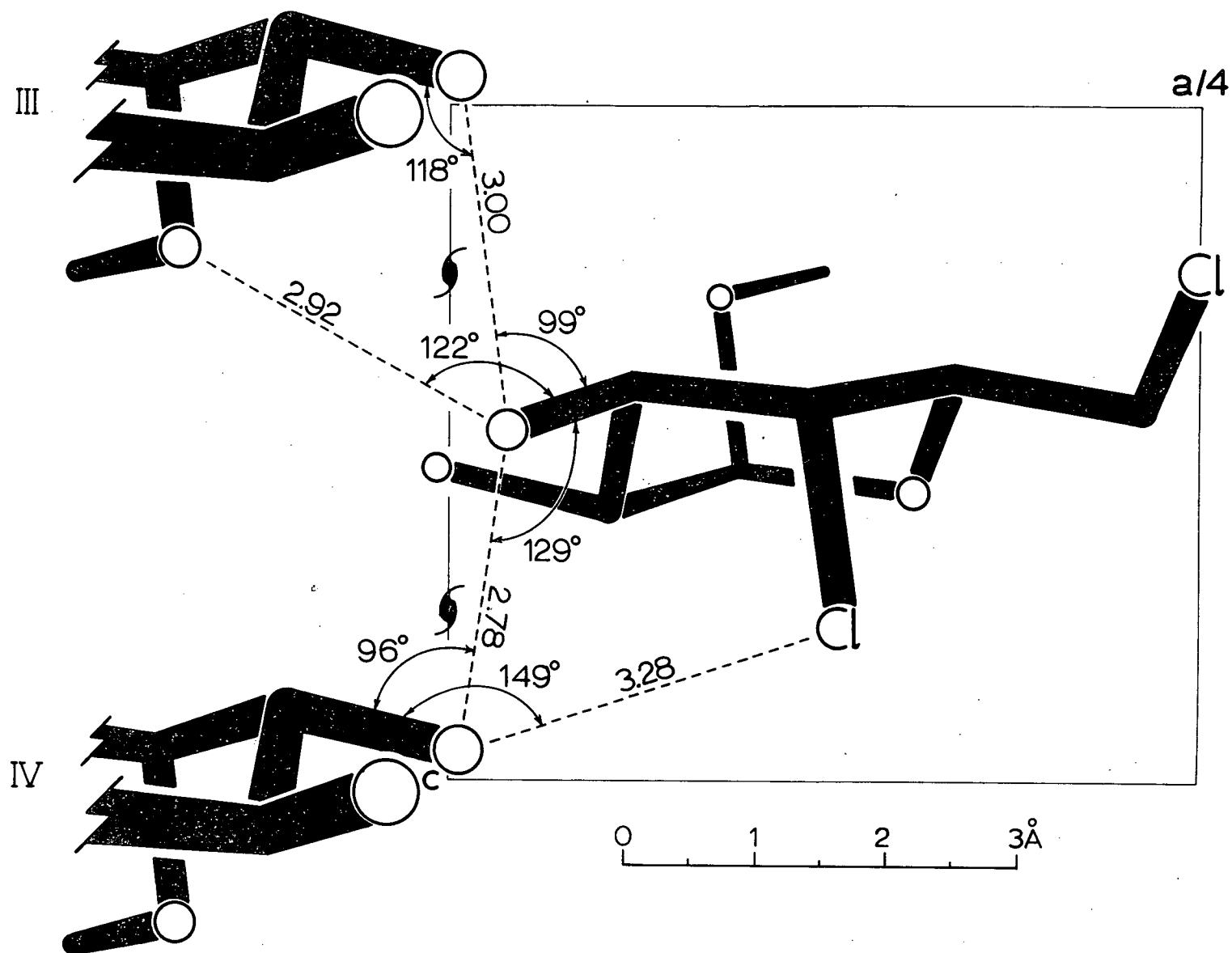


Figure 17. Hydrogen bonding; view along b.

The hydrogen on O(3) of molecule (I) is postulated to be directed between O(1) and O(2) of molecule III to form a bifurcated^{19,20} hydrogen bond. Two reasons make a bifurcated hydrogen bond reasonable:

1. The distances $O(3)^I \dots O(2)^{III}$ and $O(3)^I \dots O(1)^{III}$ are both within the limits of hydrogen bonding found in carbohydrates (2.68-3.04 Å)¹⁶
2. If the hydrogen on $O(3)^I$ is directed between O(1) and O(2) then the angle H-O(3)-C(3) would be closer to the tetrahedral angle than it would be were the hydrogen directed to only one oxygen.

One interesting short approach existing in the structure is that of $O(2)^{IV} \dots Cl(4)^I$ (3.28 Å). It is tempting to postulate hydrogen bonding between the two atoms, possibly as a bifurcated system in which $O(2)^{IV}$ is hydrogen bonded to both $O(3)^I$ and $Cl(4)^I$. However, this oxygen-chlorine distance is longer than that usually found in hydrogen bonding (2.86-3.21 Å; mean 3.07 Å),³ and more probably corresponds to only van der Waals interaction between the two atoms. The other intermolecular distances in Table XIII correspond to van der Waals separations.

TABLE X

Measured and calculated structure amplitudes ($\times 10$).
Unobserved reflexions have $F_o = -0.6 F$ (threshold).

H	K	L	F _o	FC	H	K	L	F _o	FC	H	K	L	F _o	FC	H	K	L	F _o	FC	H	K	L	F _o	FC	H	K	L	F _o	FC	H	K	L	F _o	FC
2	0	0	65	95	3	6	0	-74	106	22	3	1	-90	51	20	1	2	177	164	13	2	3	207	211	5	0	4	-78	67	5	0	4	-78	67
4	0	0	46	419	3	6	0	255	278	22	3	1	-93	48	20	1	2	-58	80	11	2	3	278	207	6	0	4	-78	125	6	0	4	-78	125
6	0	0	172	347	5	6	0	-76	22	0	4	1	-57	13	22	1	2	-96	50	12	2	3	-77	11	7	0	4	-80	52	7	0	4	-80	52
8	0	0	1315	1233	13	6	0	205	212	1	4	1	136	125	23	1	2	-93	37	13	2	3	-78	121	8	0	4	-85	424	8	0	4	-85	424
10	0	0	551	482	11	6	0	213	197	2	4	1	261	250	0	2	2	314	389	14	2	3	-83	23	9	0	4	-82	37	9	0	4	-82	37
12	0	0	281	255	12	6	0	128	145	3	4	1	124	132	1	2	2	325	321	15	2	3	210	162	10	0	4	-83	26	10	0	4	-83	26
14	0	0	136	15	13	6	0	-91	42	4	4	1	383	312	2	2	2	95	90	16	2	3	-84	25	11	0	4	-85	57	11	0	4	-85	57
16	0	0	355	433	14	6	0	-83	61	5	4	1	149	140	3	2	2	486	488	17	2	3	-86	15	12	0	4	-88	17	12	0	4	-88	17
18	0	0	-76	35	15	6	0	-84	43	6	4	1	239	233	4	2	2	141	143	18	2	3	-88	70	13	0	4	-87	15	13	0	4	-87	15
20	0	0	131	124	16	6	0	-86	90	7	4	1	252	266	5	2	2	251	250	19	2	3	-88	105	14	0	4	-89	75	14	0	4	-89	75
22	0	0	-87	14	17	6	0	-88	31	8	4	1	106	121	6	2	2	-59	77	20	2	3	-92	13	15	0	4	-91	59	15	0	4	-91	59
24	0	0	-12	128	18	6	0	-91	104	9	4	1	138	165	7	2	2	-51	54	21	2	3	-94	142	16	0	4	-92	149	16	0	4	-92	149
26	0	0	143	97	1	7	0	-77	40	10	4	1	-67	33	8	2	2	247	250	0	1	3	237	231	17	0	4	-94	11	17	0	4	-94	11
28	0	0	611	618	2	7	0	-77	26	11	4	1	256	272	9	2	2	104	107	1	1	3	199	201	0	1	4	-155	142	0	1	4	-155	142
30	0	0	526	566	3	7	0	-78	15	12	4	1	330	349	10	2	2	126	125	2	1	3	337	322	1	1	4	-192	206	1	1	4	-192	206
32	0	0	137	125	4	7	0	-78	92	13	4	1	271	172	11	2	2	267	189	3	2	3	-102	473	2	1	4	-178	171	2	1	4	-178	171
34	0	0	40	21	5	7	0	-79	132	14	4	1	202	211	12	2	2	174	166	4	1	3	-104	365	3	1	4	-178	171	3	1	4	-178	171
36	0	0	187	163	6	7	0	-79	119	15	4	1	233	238	13	2	2	174	135	5	1	3	-106	365	4	1	4	-178	171	4	1	4	-178	171
38	0	0	392	375	7	7	0	-80	65	16	4	1	-80	11	14	2	2	-74	121	6	1	3	-109	729	5	1	4	-178	171	5	1	4	-178	171
40	0	0	498	473	8	7	0	-81	19	17	4	1	-82	82	15	2	2	-76	104	7	1	3	-109	32	6	1	4	-178	171	6	1	4	-178	171
42	0	0	559	534	9	7	0	-82	127	18	4	1	-84	115	16	2	2	-111	119	8	2	3	-155	149	7	1	4	-179	171	7	1	4	-179	171
44	0	0	501	460	10	7	0	-83	41	19	4	1	-87	131	17	2	2	-73	51	9	1	3	-171	71	8	1	4	-206	213	8	1	4	-206	213
46	0	0	334	321	11	7	0	-84	43	20	4	1	-89	102	18	2	2	-82	60	10	1	3	-173	74	9	1	4	-206	213	9	1	4	-206	213
48	0	0	316	324	12	7	0	-86	38	21	4	1	-91	31	19	2	2	-136	146	11	1	3	-171	225	10	1	4	-173	176	10	1	4	-173	176
50	0	0	-64	11	13	7	0	-85	85	22	4	1	-93	34	20	2	2	-168	140	12	2	3	-174	75	11	1	4	-173	176	11	1	4	-173	176
52	0	0	164	182	14	7	0	-88	15	0	5	1	-64	114	21	2	2	-99	58	13	1	3	-175	247	12	1	4	-173	176	12	1	4	-173	176
54	0	0	171	170	15	7	0	-90	101	1	5	1	-65	10	22	2	2	-92	14	14	1	3	-179	70	13	1	4	-173	176	13	1	4	-173	176
56	0	0	-70	74	16	7	0	-93	34	2	5	1	-170	134	0	1	2	-302	314	15	1	3	-181	68	14	1	4	-178	171	14	1	4	-178	171
58	0	0	474	470	17	7	0	-94	101	3	5	1	-170	403	1	3	2	-293	293	16	1	3	-183	72	15	1	4	-178	171	15	1	4	-178	171
60	0	0	270	270	18	7	0	-95	40	4	5	1	-158	166	2	1	2	-293	293	17	1	3	-183	72	16	1	4	-178	171	16	1	4	-178	171
62	0	0	-78	21	19	7	0	-95	9	5	5	1	-156	373	3	1	2	-241	245	18	1	3	-183	61	17	1	4	-178	171	17	1	4	-178	171
64	0	0	-81	27	20	7	0	-95	197	6	5	1	-203	206	4	1	2	-53	34	19	1	3	-182	160	0	2	4	-157	164	0	2	4	-157	164
66	0	0	-81	27	21	7	0	-95	197	7	5	1	-203	206	5	1	2	-53	34	20	1	3	-182	160	1	2	4	-157	164	1	2	4	-157	164
68	0	0	-81	27	22	7	0	-95	197	8	5	1	-203	206	6	1	2	-53	34	21	1	3	-182	160	2	2	4	-157	164	2	2	4	-157	164
70	0	0	-81	27	23	7	0	-95	197	9	5	1	-203	206	7	1	2	-53	34	22	1	3	-182	160	3	2	4	-157	164	3	2	4	-157	164
72	0	0	-81	27	24	7	0	-95	197	10	5	1	-203	206	8	1	2	-53	34	23	1	3	-182	160	4	2	4	-157	164	4	2	4	-157	164
74	0	0	-81	27	25	7	0	-95	197	11	5	1	-203	206	9	1	2	-53	34	24	1	3	-182	160	5	2	4	-157	164	5	2	4	-157	164
76	0	0	-81	27	26	7	0	-95	197	12	5	1	-203	206	10	1	2	-53	34	25	1	3	-182	160	6	2	4	-157	164	6	2	4	-157	164
78	0	0	-81	27	27	7	0	-95	197	13	5	1	-203	206	11	1	2	-53	34	26	1	3	-182	160	7	2	4	-157	164	7	2	4	-157	164
80	0	0	-81	27	28	7	0	-95	197	14	5	1	-203	206	12	1	2	-53	34	27	1	3	-182	160	8	2	4	-157	164	8	2	4	-157	164
82	0	0	-81	27	29	7	0	-95	197	15	5	1	-203	206	13	1	2	-53	34	28	1	3	-182	160	9	2	4	-157	164	9	2	4	-157	164
84	0	0	-81	27	30	7	0	-95	197	16	5	1	-203	206	14	1	2	-53	34	29	1	3	-182	160	10	2	4	-157	164	10	2	4	-157	164
86	0	0	-81	27	31	7	0	-95	197	17	5	1	-203	206	15	1	2	-53	34	30	1	3	-182	160	11	2	4	-157	164	11	2	4	-157	164
88	0	0	-81	27	32	7	0	-95	197	18	5	1	-203	206	16	1	2	-53	34	31	1	3	-182	160	12	2	4	-157	164	12	2	4	-157	164
90	0	0	-81	27	33	7	0	-95	197	19	5	1	-203	206	17	1	2	-53	34	32	1	3	-182	160	13	2	4	-157	164	13	2	4	-157	164
92	0	0	-81	27	34	7	0	-95	197	20	5	1	-203	206	18	1	2	-53	34	33	1	3	-182	160	14	2	4	-157	164	14	2	4	-157	164
94	0	0	-81	27	35	7	0	-95	197	21	5	1	-203	206	19	1	2	-53	34	34	1	3	-182	160	15	2	4	-157	164	15	2	4	-157	164
96	0	0	-81	27	36	7	0	-95	197	22	5	1	-203	206	20	1	2	-53	34	35	1	3	-182	160	16	2	4	-157	164	16	2	4	-157	164
98	0	0	-81	27	37	7	0	-95	197	23	5	1	-203	206	21	1	2	-53	34	36	1	3	-182	160	17	2	4	-157	164	17	2	4	-157	164
100	0	0	-81	27	38	7	0	-95	197	24	5	1	-203	206	22	1																		

TABLE XI

FINAL POSITIONAL PARAMETERS (fractional), ISOTROPIC THERMAL
PARAMETERS (\AA^2), AND ANISOTROPIC THERMAL PARAMETERS

($\exp - \{b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2\}$),
 together with estimated standard deviations in parenthesis,
 referring to the last decimal positions of the parameters.

Atom	x	y	z	B			
Cl(4)	0.13114(15)	0.8545(5)	0.7650(8)	3.35(7)			
Cl(6)	0.24867(17)	0.8354(6)	0.2494(11)	4.67(10)			
O(1)	0.0912(4)	0.3636(12)	0.283(2)	3.7(2)			
O(2)	-0.0039(4)	0.4807(13)	0.538(2)	3.9(3)			
O(3)	0.0190(4)	0.8233(11)	0.487(2)	3.7(3)			
O(5)	0.1535(4)	0.4975(11)	0.576(2)	2.9(2)			
C(1)	0.0977(6)	0.4213(16)	0.541(3)	3.4(4)			
C(2)	0.0521(5)	0.5526(17)	0.601(3)	2.7(3)			
C(3)	0.0598(5)	0.6982(16)	0.417(3)	2.4(3)			
C(4)	0.1217(6)	0.7667(16)	0.442(3)	3.0(3)			
C(5)	0.1653(5)	0.6295(16)	0.400(3)	2.7(3)			
C(6)	0.2276(6)	0.6713(17)	0.455(3)	3.5(4)			
C(7)	0.1218(7)	0.2077(18)	0.246(4)	5.3(5)			

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cl(4)	0.00170(6)	-0.0006(4)	-0.0008(9)	0.0156(5)	0.009(3)	0.027(1)
Cl(6)	0.00217(8)	-0.0014(5)	-0.0036(11)	0.0203(6)	0.002(3)	0.056(2)
O(1)	0.0024(2)	0.0007(10)	0.004(2)	0.0105(14)	-0.003(7)	0.043(5)
O(2)	0.0016(2)	-0.0057(11)	0.000(2)	0.0209(19)	0.006(7)	0.049(5)
O(3)	0.0024(2)	0.0027(11)	0.002(2)	0.0132(17)	0.014(6)	0.046(5)
O(5)	0.0012(2)	0.0006(10)	0.005(2)	0.0134(16)	0.003(6)	0.035(4)
C(1)	0.0019(3)	-0.0027(14)	0.009(3)	0.0089(21)	0.007(7)	0.019(6)
C(2)	0.0006(2)	-0.0026(14)	0.003(2)	0.0128(24)	-0.021(8)	0.035(7)
C(3)	0.0009(3)	-0.0024(13)	0.004(3)	0.0095(24)	-0.011(7)	0.042(7)
C(4)	0.0022(3)	0.0027(15)	0.013(3)	0.0082(21)	0.007(7)	0.022(6)
C(5)	0.0010(3)	0.0002(12)	0.001(2)	0.0060(20)	-0.030(7)	0.038(6)
C(6)	0.0016(3)	-0.0024(15)	-0.004(3)	0.0124(24)	-0.013(9)	0.046(8)
C(7)	0.0031(4)	0.0017(18)	0.013(5)	0.0136(26)	0.004(12)	0.071(10)

POSITIONAL PARAMETERS OF HYDROGENS (Not refined; B taken
as 3.0 \AA^2 for all hydrogen)

Hydrogen atom	Attached to	x	y	z
H(1)	C(1)	0.1037	0.321	0.700
H(2)	C(2)	0.0691	0.618	0.800
H(3)	C(3)	0.0648	0.630	0.267
H(4)	C(4)	0.1317	0.842	0.300
H(5)	C(7)	0.0994	0.145	0.133
H(6)	C(7)	0.1512	0.182	0.367

TABLE XIIBond Lengths and Valency Angles

<u>i</u>	<u>j</u>	<u>D(ij)</u>	<u>i</u>	<u>j</u>	<u>k</u>	<u>Angle (ijk)</u>
C1(6)	C(6)	1.784	C1(4)	C(4)	C(5)	110.1
C1(4)	C(4)	1.817	C1(4)	C(4)	C(3)	109.6
O(1)	C(7)	1.48	C1(6)	C(6)	C(5)	108.9
O(1)	C(1)	1.41	C(6)	C(5)	C(4)	115.7
O(2)	C(2)	1.46	C(6)	C(5)	O(5)	103.8
O(3)	C(3)	1.44	O(3)	C(3)	C(4)	108.9
O(5)	C(1)	1.45	O(3)	C(3)	C(2)	109.2
O(5)	C(5)	1.44	O(2)	C(2)	C(3)	106.6
C(1)	C(2)	1.54	O(2)	C(2)	C(1)	106.2
C(2)	C(3)	1.54	C(7)	O(1)	C(1)	111.2
C(3)	C(4)	1.54	O(1)	C(1)	O(5)	110.9
C(4)	C(5)	1.53	O(1)	C(1)	C(2)	110.5
C(5)	C(6)	1.51	O(5)	C(1)	C(2)	106.4
			C(1)	C(2)	C(3)	110.3
			C(2)	C(3)	C(4)	110.0
			C(3)	C(4)	C(5)	109.2
			C(4)	C(5)	O(5)	110.3
			C(5)	C(5)	C(1)	115.0

 $\sigma = 0.02 \text{ \AA}$ $\sigma = 1.1^\circ - 1.3^\circ$

Bond Lengths and Angles Involving Hydrogens

i	j	D(i,j)	k	Angle (ijk)
H(1)	C(1)	1.17	{ O(1) O(5) C(2)	115° 97 116
H(2)	C(2)	1.22	{ C(1) C(3) O(2)	105 97 131
H(3)	C(3)	0.96	{ C(2) C(4) O(3)	93 100 134
H(4)	C(4)	0.99	{ C(3) C(5) C1(4)	112 102 113
H(5)	C(7)	0.93	O(1)	107
H(6)	C(7)	0.94	O(1)	117
	σ	0.12		12°
	Mean	1.04		109.9

TABLE XIIIShorter Intermolecular Distances (≤ 3.6 A)

x^I	y^I	i	$D(x^I - y^I)$
Cl(4)	O(2)	IV	3.28
Cl(4)	C(4)	II	3.55
O(3)	O(1)	III	2.92
O(3)	O(2)	IV	2.78
O(3)	O(2)	III	3.00
O(3)	C(2)	IV	3.28
O(3)	C(7)	III	3.60
O(3)	O(2)	III	3.54

Symmetry Code

I	x	y	z
II	x	y	z + 1
III	-x	$y + \frac{1}{2}$	$-z + \frac{1}{2}$
IV	-x	$y + \frac{1}{2}$	$-z + 3/2$

PART II

DESCRIPTION OF PROGRAMS

DIRECT METHODS PROGRAMS

Introduction

A Sayres relationship in a centrosymmetric space group relates the signs of three large reflexions as

$$S(\mathbf{F}_{\mathbf{h}}) \cdot S(\mathbf{F}_{\mathbf{k}}) \cdot S(\mathbf{F}_{\mathbf{h}-\mathbf{k}}) \approx +1$$

where S means "the sign of." The probability of the relation holding is a function of the magnitudes of the reflexions involved.

Following is a description of a set of four programs which attempt to solve two dimensional projections using Sayre relationships in the Vand and Pepinsky approach to the Cochran and Douglas procedure.⁸ The set of programs begins with unscaled three-dimensional (or two dimensional) $|F_o|$'s as output by DATAPREP (our data processing program) and produces in the end a tape suitable for input to FOURIE (our Fourier summation program) containing up to six possible solutions at one time. For working with direct methods, either unitary scattering factors, U's (Woolfson⁸ p.4), or normalized structure factors, E's (Karle & Karle⁷ p.855) can be used. As the trend is toward increasing use of the latter, these are used in all subsequent work. A simple definition of $|E|$ is that it is the ratio of the actual observed (properly scaled) magnitude of F to that expected for its value of $\sin \theta/\lambda$ which is simply $|\sum_n f^2|^{1/2}$ where the summation is over atoms in the unit cell. In terms of E's the expression used to calculate the probability of the above

Sayre relationship holding is

$$P = \frac{1}{2} + \frac{1}{2} \tanh \left\{ \sigma_3 / \sigma_2^{3/2} \left| \vec{E}_{\vec{h}} \cdot \vec{E}_{\vec{k}} \cdot \vec{E}_{\vec{h}-\vec{k}} \right| \right\}$$

where $\sigma_3 / \sigma_2^{3/2}$ is a constant dependent upon the constituents of the unit cell.

No allowance is made in this set of programs for specification of any but the tape unit normally specifiable for all programs, i.e., 00, 01, 02, 03, and 04. With the exception of PREDIR and ESIGND (see later), input and output can be on different files of the same tape. The tape output from these programs has been made to be completely compatible with our regular programs (DPAUTO & LSSQR & PATTER) so that output from any of these programs, except of course ESIGND (c.f. LSSQR) can be intermixed with regular structure factor data, and so that all four direct methods programs, DPAUTO, LSSQR & PATTER are able to read to appropriate files on intermixed tapes.

(1) PREDIR

This program accepts a three-dimensional (preferably but not necessarily) structure factor tape prepared by DATAPREP and scales the $|F_0|$'s based on a knowledge of the composition of the unit cell. The data tape is first scanned to find the limits of $\sin \theta / \lambda$. The tape is then reread and the unscaled intensities placed into a specified number of equal ranges of $\sin \theta / \lambda$. Two tables similar to Tables 1.1 and 1.2 of Woolfson⁸ (p.8) are constructed, and for each range, $\Sigma f^2 / \langle I \rangle$ is computed.

Assuming an average temperature factor (B) can be used for all the data, one can write for each range of $\sin \theta / \lambda$ ($= S$):

$$\sum_N f^2 / \langle I \rangle = K \exp (+ BS^2) \quad (1)$$

This can be rewritten as:

$$\log (\sum_N f^2 / \langle I \rangle) = \log K + BS^2 \quad (2)$$

Least-squares is used to find the 'best' value of K and B in equation (2).

This program then computes and outputs E 's both printed and on tape, the latter exactly identical to the ordinary structure factor tape produced by DATAPREP except that $|F|$ becomes $|E|$ and F^2 becomes E^2 . (For interpretation of EPSILON in the printed output, see the footnote in Karle & Karle⁷, p.855).

As a final check on the method of scaling the data, average values of both $|E|^2$ and $|E|$ are output, the latter indicating the presence or absence of a centric distribution of atoms in the structure.

Two useful options are included to ensure that scaling (and subsequently, calculation of $\langle |E| \rangle$ and $\langle |E|^2 \rangle$) is carried out for only the best part of the data. These are:

- (1) Weights can be specified for the first two ranges of S .
- (2) The limiting value of S can be specified to be smaller than actually contained on tape.

The necessity of the first option is that the first two ranges may not contain enough reflexions to make $\langle I \rangle$

statistically significant there. The necessity of the second is that at high values of S, many reflexions become too weak to be measured and are classified as "unobserved." However, E's are calculated and output for all the data on the input tape.

The data cards for input to the PREDIR program are as follows:

<u>POSITION</u>	<u>DESCRIPTION</u>	<u>FORMAT</u>
<u>Card 1</u>		
1-2	INPUT tape unit no.	I2
3-4	INFILE - file no. (= 1 if left blank)	I2
5-6	OUTPUT tape unit no. (if any) (OUTPUT \neq INPUT)	I2
7-8	OUTFIL - Output file no. (=1 if left blank)	I2
9-10	NINTVL - no. of intervals of S (=10 if left blank)	I2
11-12	I PROJ - if output is projection (along 1=x, 2=y, 3=z)	I2
13-14	I HALF - if an index is to be halved on tape output specify here	I2
16-20	STLMAX - maximum value of S for scaling if other than limit of data on tape	I2.
21-25	MINEPR - minimum value of E for printer output	F5.2
26-30	MINETP - minimum value of E for tape output (usually 1.0)	F5.2
31-35	WEIGHT (1) - weight for first range for scaling	F5.2
36-40	WEIGHT (2) - weight for second range for scaling	F5.2

Card 2 (Multiplicity factors for extending data to whole of reciprocal lattice)

1-5	MULTAX - (as in FOURIE) multiplicity of axial reflexions	F5.3
6-10	MULTPL (1) - of 0 k l data	F5.3
11-15	MULTPL (2) - of h 0 l data	F5.3
16-20	MULTPL (3) - of h k 0 data	F5.3

Card 3 (Specification of systematic absences in data; a blank card must be included if, as in PI, no systematic absences occur)

1-2	NEXT - no. of sets of extinctions following	I2	
3-5	BLANK	3X	
6	IEX (1,1)	Specification of 1st set of extinctions e.g. h k 0 h=2n → 1102 0 0 1 l=4n → 0014 h 0 0 h=2n → 1002	I1
7	IEX (1,2)		I1
8	IEX (1,3)		I1
9	EXMULT (1)		I1
10	BLANK		I1
11-15	repeat of 6-10 for 2nd set of extinctions		
16-20	repeat of 6-10 for 3rd set of extinctions		

etc.

Card 4 (Composition of primitive unit cell)

1-2	NCURV - no. of atom types	I2
3-4	NATOMS (1) - no. of atoms of type 1 present	I2
5-6	NATOMS (2) - no. of atoms of type 2 present	I2
7-8	.	.
	.	.
etc.	.	.

(The specification of atoms must be in the same order as f's are contained on tape produced by DATAPREP)

Cards 5 - (4 + NCURV)

Scattering factor cards in order on card 4 and on input tape. (The contents of these cards are described in writings for the DATAPREP program).

(2) SAYRE

This program accepts the projection data output of PREDIR, and reads into the four parity groups those reflexions whose $|E|$ is not less than a specified value (MINE). For internal workings in the program, the first non-zero index is H, the second K. Each reflexion is given an identity (retained in SIGNS and ESIGND) which is its position on the tape when only those reflexions not less than MINE are counted. The program then systematically finds all Sayre relationships knowing the plane group to which the data belongs (only the following four are handled, p2, pmm, pmg (pgm), or pgg). The probability with which each relation holds is computed and allowance is made for relations of the type $\text{sign}(HK) \approx \pm 1$ (Σ_1 type) as their probability is not given by the same expression as that of a general Sayre relation.

Each reflexion is then listed in parity groups together with the number of relationships in which it occurs non-trivially (i.e. with its sign not squared). The Sayre relations are printed out in two ways, the second being an optional addition to the first:

1. a listing in which each relationship occurs uniquely and in the order in which it is generated, and
2. a listing by reflexion, in descending value of $|E|$, of all relationships in which that reflexion occurs.

The Sayre relations can also be output on tape in a simple binary form which the next program in the series (SIGNS) can use as input for determining the possible signs of reflexions.

This program terminates by beginning again; therefore, several different options may be specified and output can be on separate files of the same tape, delaying the decision of how best to handle the data until the output is seen for each cycle.

The limits of the various dimensional arrays are given in comment cards at the beginning of the source deck for this program. As the output of this program is the input of the next, these dimensions also apply there.

Three options are built into the program to eliminate unwanted relationships (besides the obvious reduction made by specifying a different value of the minimum $|E|$ (MINE) to be read from the input tape). In the order in which they will be applied to the data, these are:

1. Specification of a minimum probability acceptable for a relation. This is done by specifying a minimum value of the triple product of E 's

- ($|E_1| * |E_2| * |E_3|$) going into a relation (ACCREE). The main purpose of this is to eliminate most Σ_1 - type relationships which, because of their modified probability expression, tend to have low probabilities.
2. Specification of reflexions which are not to be considered for relationships (ISCRAT (I), I = 1, NSCRAT). This is done on a rerun of the program and used in a case where MINE is very small, e.g. 1.0, and some reflexions of the low value of $|E|$ have an insufficient number of relationships determining their sign.
 3. Specification that a cyclic process is to be carried out on the relations remaining after 1. and 2. have been applied, during each cycle of which a reflexion is found occurring in only one Sayre relation and that relation is eliminated. The end result of this process is that each reflexion, for which a sign is to be found by the SIGNS program, occurs in at least two different relationships.

The need for 3. is obvious when one looks at the method of generation of solutions by the next program. Two almost identical solutions of a structure in which all signs are identical except the sign of the reflexion which occurs in only one relation will, on elimination of that

relation, be replaced by only one solution in which that sign is indeterminate. (Note that the only difference between the two solutions is that the relationship referred to will hold for one sign of the reflexion and fail for the other). Option 3. should, therefore, be used except when a relationship of the above type has a probability ($\sim .98$) large enough to assume that it does not fail. For this case, that relation should be retained but other less probable relations of the type should be eliminated selectively by the use of option 2.

The data cards for input to the SAYRE program are as follows:

Card 1

1-2	INPUT tape	I2
3-4	INFILE	I2
5-6	OUTPUT tape if any. (OUTPUT = or \neq INPUT)	I2
7-8	OUTFIL	I2
9-10	IPROJ - the type of projection on tape (1=x, 2=y, 3=z)	I2
11-12	ISPACE 1 for p2; 2 for pmm; 3 for pmg, 4 for pgg, 5 for pgm	I2
13-14	IPRINT -1 suppress printout of relation- ships by reflexion	I2
15-16	IONE -1 if elimination of reflexions occurring in only one relationship is desired (option #3)	I2
17-18	NSCRAT -no. of reflexions to be scatched (option #2)	I2
19-20	BLANK	2X

21-30	PROBCF - probability coefficient as output by PREDIR	F10.0
31-40	MINE - minimum value of E for acceptable reflexion input into the program from tape	F10.0
41-50	ACCEEE - minimum acceptable value of triple product for accepting a relationship	F10.0
51-52	ISCRAT (1) - the no. of a reflexion to be eliminated	I2
53-54	ISCRAT (2) - the no. of another reflexion to be eliminated	I2
.	.	.
.	.	.
.	ISCRAT (NSCRAT) NSCRAT \leq 10	I2

Cards 2, 3 etc.: repeat of Card 1 for specifying
different parameters in recycling
of program.

3. SIGNS

This program produces solutions from the output of the SAYRE program by the Vand & Pepinsky method (Woolfson⁸ pp.101-6) which can be viewed as a time saving version of the Cochran & Douglas method (Woolfson⁸ pp.94-100; Rollett⁹ pp. 167-171). No attempt will be made to describe these as they are very adequately described in the references quoted. The original version of this program was based on the Cochran & Douglas method but as the test later described was visualized, the program was rewritten to carry out the failure tests by the Vand & Pepinsky method.

A brief description of the latter program follows:

Individual Sayre relationships are stored in binary form, up to four words, in a way similar to that pictured in Rollett⁹ (p.170) except that provision is made for up to 105 relationships among up to 35 reflexions. These relationships are stored in the variable IXS, dimensioned as IXS (4, 105). The 4 signifies that up to 4 words can be used to store a single relationship. The first word is used exclusively for indicating which x's (in the notation of Woolfson) occur in that relationship. The first bit of the second word is the sign associated with the relation, and each subsequent bit extending to 3 words is used consecutively to indicate S's (again Woolfson's notation),

e.g. $-x_1x_9x_{15} = S_{37}$ would be represented as:

IXS (1,37) = 01000000010000010...0...00

IXS (2,37) = 10000... ...0...00

IXS (3,37) = 00100... ...0...00

IXS (4,37) = (if less than 70 relationships occur, this word would not be used)

The manipulations of "additions of remainders modulo 2" (i.e. addition of bits modulo 2) are accomplished in this program by the use of the built-in functions AND, OR, and COMPL available for the 7040/7044 system as described in the programming manual²¹ (p.38). The actual addition modulo 2 is complicated by the fact that the above are "real" functions.

The addition of I to J modulo 2, in the sense that each bit of I is added modulo 2 to each bit of J, to produce K, would be accomplished by the following statements:

```
EQUIVALENCE (XI,I), (XJ,J), (XK,K)
X = AND (I,J)
X = COMPL (X)
Y = OR (I,J)
XK = AND (X,Y)
```

The complication introduced by EQUIVALENCE is necessary since the variables to be manipulated by AND, OR, and COMPL, when used in other parts of the program, must be used in integer mode but without the conversion accomplished by a statement such as

```
XK = K
```

The identity of a given reflexion here is the same as in SAYRE, i.e. it is its position on the tape containing E's when only those reflexions with $|E| >$ a preset value (MINE in SAYRE) are counted.

It sometimes happens that in trying to systematically solve the set of equations for each of the x 's (by the procedure described in Rollett), a linear dependency of x 's which cannot be resolved, is found for the first group. In this eventuality, instead of only one solution existing for one set of failures of relations in the first group, there now exists 2^N solutions for that set, where N equals (the number of reflections) minus (the number of equations in the first group). This program can handle $N \leq 4$, and will output up to 16 solutions for any one group of failures.

The program now follows Woolfson⁸ (p.101-5) closely. The relations that fail in the second group when none fail in the first are stored in $IVP1(I)$, $I = 1, 3$ [cf. IXS (37,I), $I = 2, 4$]. The relations that fail when e.g. the N th relation in the first group fails is given by $IVP(I, N)$, $I = 1, 3$ [again cf. IXS (37,I), $I = 2, 4$]. Note that $IVP(I, N)$ shows also that the N th relation in the first group fails.

No allowance, though, is made to reject a particular solution on the basis of a partial "summation" as indicated in Rollett⁹ (p.105).

Each solution which is within the limits of a certain test described below (TTEST) and which obeys a preset limit on the number of failures in the first group (≤ 5) and a preset limit on those in all, is printed out together with the value of that test, the number of plus signs in

the solution, the numbers of the particular Sayre relations which fail, and the value of

$$\sum_{\bar{h}} \left(\sum_{\bar{k}} |E_{\bar{h}}| |E_{\bar{k}}| |E_{\bar{h}-\bar{k}}| \right)^2 \quad (3)$$

where \bar{h} is a reflexion contained in a Sayre relation that fails, and

$|E_{\bar{h}}| |E_{\bar{k}}| |E_{\bar{h}-\bar{k}}|$ is the value of the triple product of E 's for a Sayre relationship containing \bar{h} .

There is also an optional output on tape of the signs for the various reflexions in solutions. This output is compatible with the next program which, by merely specifying the number of the solution(s) desired, produces a simulated structure factor tape (of E 's) for input to the Fourier program.

The chief test incorporated into SIGNS is called ITEST and will now be described.

ITEST will reject any solution for which, for any h , the following expression exceeds a preset value:

$$\sum_{\bar{h}} |E_{\bar{h}}| |E_{\bar{k}}| |E_{\bar{h}-\bar{k}}|$$

where \bar{h} is a reflexion contained in a Sayre relationship that fails

and $|E_{\bar{h}}| |E_{\bar{k}}| |E_{\bar{h}-\bar{k}}|$ is the value of the triple product of E 's for that relationship.

For a solution which is within the bounds imposed above, the maximum value attained for any \bar{h} will be printed out under the heading of SMAX.

This test, for any \bar{h} , indicates the probability with which its sign is indicated to be the opposite of that which is predicted. It is in the nature of the solutions

produced by the Vand & Pepinsky method (or Cochran & Douglas method for that matter), that somewhere in the list satisfying the limiting conditions on failures in the first group and failures in all, there exists the correct solution to the structure with each sign correct. If the predicted probabilities of the relations holding for that solution are correct, then it is very unlikely that a relation of say 0.99 probability fails and hence all solutions where such a relation fails can be rejected as improbable. Another way of looking at this failure is that one reflexion in the Sayre relationship is indicated to be the opposite sign to that given in the 'solution' to a probability of 99%.

The preceding indicates a simple way of incorporating a test into the program which uses the actual probabilities of Sayre relationships. However, this test can be extended further to include those cases where no individual relation has a probability of say 99% or better. This extension, which is the actual test in ITEST, follows from the expressions for the probability of Sayre relations holding.

The probability of one relation indicating the sign of reflexion h to be positive is given by

$$P+(\vec{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} |E_{\vec{h}}| E_{\vec{k}} E_{\vec{h}-\vec{k}} \quad (4)$$

But because this function is antisymmetric about $P = \frac{1}{2}$, the equation can be rewritten to express the probability that the sign of $E_{\vec{h}}$, whatever it is, is given by the

particular Sayre relation in question, as follows,

$$P(\vec{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} |\vec{E}_{\vec{h}}| |\vec{E}_{\vec{k}}| |\vec{E}_{\vec{h}-\vec{k}}|. \quad (5)$$

When more Sayre relationships are used to indicate the sign of \vec{h} (4) becomes,

$$P(\vec{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} \sum |\vec{E}_{\vec{h}}| |\vec{E}_{\vec{k}}| |\vec{E}_{\vec{h}-\vec{k}}| \quad (6)$$

(see Rollett⁹ or Karle & Karle⁷)

and if all the relations indicate the same sign for \vec{h} (5) becomes in the general case

$$P(\vec{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} \sum |\vec{E}_{\vec{h}}| |\vec{E}_{\vec{k}}| |\vec{E}_{\vec{h}-\vec{k}}|. \quad (7)$$

Now, by the nature of the method of forming solutions, the actual relations which fail for any solution are known. If (6) contained only Sayre relations that failed, then (7) becomes the probability that the sign of $\vec{E}_{\vec{h}}$ is predicted to be the opposite of that which appears in the solution.

The foregoing now indicates the test in its most general form. Because of the form of equation (7), it is easier to work with a value of the summation of triple products, rather than an actual value of the probability, and hence, the criterion becomes a maximum on the value of triple products of E 's (EMAX in the program).

Note that a better expression for the probability that the sign of $\vec{E}_{\vec{h}}$ is opposite to that predicted is

$$P(\vec{h}) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} \left(\sum_{\text{failures}} |\vec{E}_{\vec{h}}| |\vec{E}_{\vec{k}}| |\vec{E}_{\vec{h}-\vec{k}}| \right. \\ \left. - \sum_{\text{successes}} |\vec{E}_{\vec{h}}| |\vec{E}_{\vec{k}}| |\vec{E}_{\vec{h}-\vec{k}}| \right)$$

but the simpler form where only the first term in brackets

is used, should be sufficient if its limiting value is set high enough, (e.g. a value of the triple product corresponding to a probability of ~ 0.99).

Also note, that the test is only a method of rejecting a large number of improbable solutions and does not necessarily indicate which of the remaining solutions is the correct one. However, it is nevertheless suggested that the remaining solutions be tried in the order of increasing value of SMAX. The test's chief usefulness is that it permits one to extend the Sayre relationships to low values of E (as low as say, 1.0), and provides a good criterion for the rejection of the vast majority of possible solutions which are produced when, as in this case, individual Sayre relations have a probability of holding only a little removed from 50%.

The data cards for the SIGNS program are as follows:

Card 1

1-2	INPUT tape unit	I2
3-4	INFILE	I2
5-6	OUTPUT tape unit no. (if any) (preferable = INPUT)	I2
7-8	OUTFIL	I2
9-10	NFAIL1 limiting value of no. of failures in first group (≤ 5)	I2
11-12	NFAIL2 limiting value of no. of failures in all (≤ 20)	I2
13-20	EMAX - upper limit of ΣEEE in ITEST	F8.0

Card 2

1-2	NCON - number of reflexions whose sign is to be specified (≤ 10)	I2
3-5	ICON (1) - \pm the no. of the 1st reflexion to be given sign	I3
6-9	ICON (2) - \pm the no. of the 2nd reflexion to be given sign	I3
9-11	the sign to be	I3
12-14	used for a reflexion	.
.	will be the sign	.
.	attached here	.
.	ICON (NCON)	I3

4. ESIGND program

This program accepts a tape of $|E|(hkl)$'s and a tape (which may be the same as the last) containing solutions from SIGN program. It produces another tape suitable for the FOURIE program, containing E-values with their proper signs (if any) for up to six solutions at once specified only by the number of the solution as it appears in the SIGNS program. The six solutions on the output tape are put in consecutive words after the floating point h, k, l 's.

Each solution is, therefore, capable of being called in the Fourier program by specifying different numbers, 1-6, as coefficients for Fourier summation (F_o, F_c, A_c, B_o, B_c now no longer have their original meaning but are just E_o 's for different (up to 6) solutions of the SIGNS program).

A typical run would have E's in file 14 of P69 on unit 03 and have signs in file 16 of the same tape; the output of five different solutions would be the scratch unit 02. The input for the Fourier program run immediately after on IBSYS, would be 02 with output on the disk unit 11 for the first pass (coefficient = 1); the next four passes would be output on the same unit 11, with the Fourier cards duplicated for each pass except that the coefficients specified would be 2, 3, 4, and 5 for respective passes. Unit 11 then provides the input for the CONTUR program where one specifies that that unit contains five passes to be drawn (IPROJ = +1 for labelling), and the contoured map would be output as usual on Unit 04 for which a small L - tape should suffice.

Note that the contouring interval to be used for the CONTUR program is roughly predictable. For the case of ~25 reflexions of average $E \sim 1.5$, specify $C/V = 1.0$, and $mF(000)$ as 0.0. Then, as the trigonometric functions in the summation can never exceed a value of 1.0, the Fourier summation can never exceed 40 (a value with FOURIE outputs as 4000). A highest value of 1000 should suffice to contour any E-map that results. The data card for the ESIGND program contains the following information:

1-2	INE - input tape unit for E's	I2
3-4	IFE - file # on INE	I2
5-6	INS - input tape unit for signs (solutions)	I2

7-8	IFS - file # on INS	I2
9-10	OUTPUT - tape unit no.	I2
11-12	NPOSS - no. of solutions to be output (≤6)	I2
13-20	MINE - same as in <u>SAYRE</u> (but not as in <u>PREDIR</u>)	F8.0
21-25	IPOSS (1) - the no. of the first solution	I5
26-30	IPOSS (2) - the no. of the second solution	I5
31-35	.	.
	.	.
.	.	.
.	.	.
.	IPOSS (NPOSS)	I5

The following two points should be noted:

1. the numbers in IPOSS must be in increasing order.
2. IFE is usually the same as IFS.

ROT PROGRAM

This program was written exclusively for the methyl 2-chloro-2-deoxy- α -D-galactopyranoside structure to find the correct solution in the xy projection knowing the position of only the chlorine and the relative positions (in radial coordinates) of up to six carbon atoms and up to six oxygen atoms. This program calculates the R-value for h k 0 projection data (≤ 300) with $|F_o|(h\ k\ 0) \geq$ a specified value, as the molecule is rotated by small increments about the fixed chlorine position. The various (R, θ) are output on tape unit 11 in preparation for plotting a R versus θ curve by a U.B.C. library program. (In this program it is assumed that $|F_o|(h\ k\ l)$ data [≤ 2000 reflexions including end of group symbols] is in file #3 of a tape mounted on logical tape unit 03).

The data cards for the ROT program are as follows:

<u>POSITION</u>	<u>DESCRIPTION</u>	<u>FORMAT</u>
<u>Card 1</u>		
1-10	A - length of a-axis (A)	F10.0
11-20	B - length of b-axis (A)	F10.0
21-30	THETA - initial value of θ (radians)	F10.0
31-40	THEINC - increment in θ	F10.0
41-50	THEMAX - maximum value of θ	F10.0
<u>Card 2</u>		
1-10	FOMN - minimum $ F_o(h\ k\ 0) $ to be used	F10.0
11-20	TCL - temperature factor (B) of Cl	F10.0

21-30	TO - temperature factor (B) of O	F10.0
31-40	TC - temperature factor (B) of C	F10.0
41-45	NO - no. of O- atoms in molecule in asymmetric unit (≤ 6)	I5
45-50	NC - no. of C- atoms in molecule (≤ 6)	I5
51-55	IFOBS - 0 \Rightarrow no printout of input F _o (h k 0)'s	I5
56-60	IFCAL - 0 \Rightarrow no printout of F _o /F _c for structure with minimum R	I5

Card 3

1-10	CLX - x/a coordinate of Cl	F10.0
11-20	CLY - y/b coordinate of Cl	F10.0

Card 4

1-10	RADO(1) - r for O#1	F10.0
11-20	ANGO(1) - θ for O#1	F10.0

Card 4+NO

1-10	RADO(NO) - r for O#NO	F10.0
11-20	ANGO(NO) - θ for O#NO	F10.0

Card 5+NO

1-10	RADC(1) - r for C#1	F10.0
11-20	ANGC(1) - θ for C#1	F10.0

Card 5+NO+NC

1-10	RADC(NC) - r for C#NC	F10.0
11-20	ANGC(NC) - θ for C#NC	F10.0

CONTUR PROGRAM

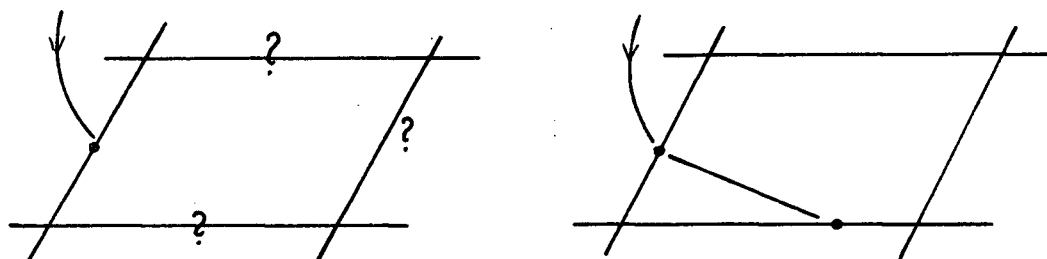
This program accepts a tape (IN12) prepared by the FOURIE program containing a specified number of passes (NPASSS) and produces contoured maps for specified contours (C(I), I = 1, NCONTU) on U.B.C.'s Calcomp 565 12 inch drum plotter. Each map (pass) will normally be contoured in turn, all sections of one pass being done before the next pass is begun. An option, however, exists which will allow two passes to be joined in each section with the result that corresponding sections for two passes are read consecutively and drawn up as one larger section. Another option (NEWZ) allows specification of a different axis of sections to that contained on the input tape, by-passing the need for repreparing the structure factor tape.

The size of the maps are specified in cm./A (SCALER). If not specified, the maps will be drawn ten inches wide, the limit of U.B.C.'s Calcomp plotter. If a scale is specified which requires more than the ten inch width of the plotter, ten inches of the map for all sections will be drawn first, thereafter, units (PARTS) of up to ten inches will be drawn as many times as is needed to complete the map.

Each PART (a "part" of a section not greater than ten inches) is first read in from IN12 and the number of points is increased four-fold (RHOO(61,61)) by linear

interpolation, introducing one point between every two adjacent points of the original Fourier grid. On this finer grid contouring is commenced by searching for possible contours which begin on the outside of the map (and thus finish on the outside). After contours of this type are drawn, interior contours (which finish at the same place they begin) are then searched for along the vertical direction only, and drawn if they have not been drawn already. Regions between grid points are represented in ICON (61,121) and when, for instance, an Nth contour is drawn between two grid points, note is made of it in ICON by adding 2^{N-1} to the appropriate word of core (turning the Nth bit on).

In searching for the start of a contour between 2 grid points, all NCONTU contours are treated simultaneously (but only if they occur between points such that the second has a higher value than the first), before going on to the next interval. In continuing the drawing of a contour line, a note is made of the direction in which the contour has approached a grid quadrilateral to facilitate finding a new exit point for the contour.



direction $\rightarrow (1,0)$

new direction $\downarrow (0,-1)$

Only three possible such exit points exist for the contour depicted above and it becomes a simple matter of checking which can be used. When a contour comes back on itself (or in the case of exterior contours, when a contour again reaches the outside), it is complete and search for new contours can recommence where the now completed one started. Contour lines consist of straight lines between edges of the quadrilateral grid, their position on the edges being determined by linear interpolation.

Labelling of the contour maps consists of identification of each section by its height in 1/120'ths and of each third contour (beginning with C(1)) with special symbols noted at the beginning of the plot. When all contouring to be done on a specified input tape is complete, the message, END OF ALL PASSES, is drawn out on the plotter paper.

As only logical units 03 and 04 can be used for loading and unloading tapes, and as a plotter tape must always be mounted on 04 for the CONTUR program (at U.B.C. plotting is off-line; plotting instructions are first output on tape unit 04 before actual plotting is done), it is impossible to run FOURIE and CONTUR consecutively plotting out a Fourier map and at the same time saving the tape output of the FOURIE program. This leaves two alternatives:

1. Saving the Fourier map - The FOURIE program is run one day inputting the structure factor tape on 04, and outputting the Fourier map on 03. The next day this prepared Fourier map is remounted on 03 to be used by the CONTUR program for preparing a plot tape on 04.
2. Not saving the Fourier map - The FOURIE and CONTUR programs are run consecutively and concurrently with the structure factor tape on 03 and output of the Fourier map on scratch disc utility 11 (or 12). The latter unit provides input to the CONTUR program which prepares a plot tape on unit 04.

NOTE: A program (PROJ) whose input will not be described here, was also written which together with a special version of the CONTUR program (PROJCN), produces projected views of the three dimensional electron density maps (Figures 3, 6 and 15). This was done to save the large amounts of paper and computer time required for contouring on a large scale, full three-dimensional maps which would otherwise have to be produced for this by the regular CONTUR program.

The data cards for the CONT UR program are as follows:

<u>POSITION</u>	<u>DESCRIPTION</u>	<u>FORMAT</u>
<u>Card 1</u>		
1-2	IN12 - input unit no. (02, 03, 11 or 12 only)	I2
3-4	NPASSS - no. of passes on IN12	I2
5-6	NPAIRS - no. of pairs of passes to be joined in each section beginning at pass #1	I2
7-8	NEWZ - new axis of sections, if any (1 for x, 2 for y, 3 for z)	I2
<u>Card 2</u>		
1-80	ANYTHING for identification	13A6, A2
<u>Card 3</u>		
1	IDENTITY OF AAXIS	} 1 for x, 2 for y, 3 for z
2	IDENTITY OF BAXIS	
3-4	NCONTU - no. of contours ≤ 16	I2
5-6	IPASS - +1 if program to begin again after plotting IN12	I2
7-8	ILAB - -1 suppresses all non-essential labeling	I2
9-10	IPR - +1 if Fouriers are a series of projections	I2
11-20	AAXIS - length of axis (A) along plotter paper	F10.0
21-30	BAXIS - length of axis (A) across 10 inch width	F10.0
31-40	THETA - angle (deg.) between AAXIS + BAXIS (90.0 if BLANK)	F10.0
41-50	SCALE - cm./A (plot fills width of paper if BLANK)	F10.0
51-60	CLKMAX - time allowed for this program (normally BLANK)	F10.0

Card 4

1-10	C(1) - first contour	F10.0
:	:	:
:	:	:
:	:	:
71-80	C(8) - eighth contour (read only if NCONTU ≥ 8)	F10.0

Card 5 (included only if NCONTU ≥ 8)

1-10	C(9) - ninth contour	F10.0
:	:	:
:	:	:
:	:	:
71-80	C(16) - sixteenth contour	F10.0

The following points should be noted for the CONTUR program:

1. Repeat cards 1 through 4 (or 5) if last set of 4 (or 5) cards had IPASS = +1.
2. AAXIS + BAXIS are w.r.t. UNIT CELL, not ASYMMETRIC UNIT.
3. Contours must be in increasing order.
4. Plotter tape is always mounted on 04.
5. If two passes are to be joined, they must be in natural order; they must be of equal dimensions along all three directions; and, the end of one pass must be the same as the start of the other pass along one axis in the plane of sections.

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APPENDIX

(Source deck listings of programs in Part II)

PREDIR PROGRAM

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\$IBFTC PREDIR REF,DECK

08/02/68

C THIS PROGRAM IS IDENTICAL TO THAT DATED 07/09/68

INTEGER EXMULT

INTEGER OUTPUT, OUTFIL

REAL MAXSS, MINSS, MAXSL, MINSL, MINEPR, MINETP, MULTAX, MULTPL

DIMENSION FX(3), NREFL(50), SUMF2(50), SUMNF(50), AVRGF2(50)

DIMENSION STOLS2(50), SSOLS2(50), SIGMA2(50), RATIO(50), NATOMS(50)

DIMENSION MULTPL(3), IEX(10,3), EXMULT(10)

DIMENSION FCURV(8), FO(8), P(8), F(8,14)

DATAPREP

DIMENSION WEIGHT(2), OUTTYP(4)

WEIG+T

DATA OUTTYP / 24H H K L O K L H O L H K O /

WEIG+T

READ 1, INPUT, INFILE, OUTPUT, OUTFIL, NINTVL, IPROJ, IHALF, STLMAX,

1 MINEPR, MINETP, WEIGHT(1), WEIGHT(2)

WEIG+T

1 FORMAT (7I2, 1X, 5F5.2)

READ 44, MULTAX, (MULTPL(I), I=1,3)

44 FORMAT (4F5.3)

READ 45, NEXT, (((IEX(I,J), J=1,3), EXMULT(I)), I= 1, NEXT)

45 FORMAT (12, 3X, 10(4I1, 1X))

READ 24, NCURV, (NATOMS(I), I=1, NCURV)

24 FORMAT (9I2)

DO 200 I=1, NCURV

DATAPREP

200 READ 201, P(I), FO(I), (F(I,J), J=1,14)

DATAPREP

201 FORMAT (16F5.3)

DATAPREP

PRINT 48

48 FORMAT (11H DATA CARDS)

PRINT 151, INPUT, INFILE, OUTPUT, OUTFIL, NINTVL, IPROJ, STLMAX,

1 MINEPR, MINETP, WEIGHT(1), WEIGHT(2)

151 FORMAT (5X, 6I2, 3X, 5F5.2)

PRINT 152, MULTAX, (MULTPL(I), I=1,3)

152 FORMAT (5X, 4F5.3)

PRINT 153, NEXT, (((IEX(I,J), J=1,3), EXMULT(I)), I= 1, NEXT)

153 FORMAT (5X, 12, 3X, 10(4I1, 1X))

PRINT 154, NCURV, (NATOMS(I), I=1, NCURV)

154 FORMAT (5X, 9I2)

PRINT 155, NCURV, (FO(I), I = 1, NCURV)

155 FORMAT (5X, 4HPLUS, I3, 61H CARDS OF SCATTERING FACTORS OF RESPECT

1IVE INITIAL MAGNITUDES, 8(1X, F6.2))

INTVL = 0

ITEST1 = 0

ITEST2 = 0

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```

      ITEST3 = 0
      ASSIGN 4 TO IENDF
      CALL EOF (INPUT, IENDF)
2     REWIND INPUT
      NFILE = INFILE
4     IF (NFILE .LE. 1) GO TO 3
      NFILE = NFILE - 1
8     READ (INPUT) II
      GO TO 8
3     IF (ITEST1 .NE. 0) GO TO 6
      ITEST1 = 1
      MINSS = 10.0
      MAXSS = 0.0
5     READ (INPUT) II, IGPEN, SSOLS, FH, FK, FL, FREL, FSQR, (FCURV(I), I=1,8)
      IF (IGPEN .NE. 0) GO TO 5
      IF (II .NE. 0) GO TO 2
      IF (SSOLS .GT. MAXSS) MAXSS= SSOLS
      IF (SSOLS .LT. MINSS) MINSS= SSOLS
      GO TO 5
6     IF (ITEST2 .NE. 0) GO TO 28
      MAXSL = SQRT(MAXSS)
      MINSL = SQRT(MINSS)
      PRINT 7, MAXSL, MINSL
7     FORMAT ( 36H SINE THETA OVER LAMBDA, MAXIMUM = , F7.4, 12H, MINI
1MUM = , F7.4 )
      IF (STLMAX .LE. 0.0) GO TO 68
      MAXSL = STLMAX
      PRINT 69, STLMAX
69     FORMAT (/66H AS INSTRUCTED, ALL DATA WITH SINE THETA OVER LAMBDA G
1REATER THAN , F7.4, 37H WILL BE REJECTED FROM WILSON SCALING
2 / 5X, 116HAND FROM CALCULATIONS OF AVERAGE E@S AND E2@S, BUT WILL
3 BE INCLUDED IN CALCULATIONS AND OUTPUTTING OF INDIVIDUAL E@S /)
68     DIVSL = 10.0
      IF (NINTVL .GT. 4) DIVSL = NINTVL
      IF (NINTVL .LT. 5) NINTVL= 10
      XINTVL = (MAXSL - MINSL) / DIVSL
      ITEST2 = 1
      DO 23 I = 1, NINTVL
      SUMF2(I) = 0.0
      SUMNF(I) = 0.0

```

```

23 NREFL(I) = 0
9 READ (INPUT) II, IGPEN, SSOLS,
1 (FX(I), I=1,3), FREL, FSQR, (FCURV(I), I=1,8)
IF (IGPEN .NE. 0) GO TO 9
IF (II .NE. 0) GO TO 11
STOLS = SQRT(SSOLS)
IF (STOLS .GT. MAXSL) GO TO 9
I = (STOLS - MINSL) / XINTVL + 1.0
IF (STOLS .EQ. MAXSL) I = NINTVL
IF (STOLS .EQ. MINSL) I = 1
NREFL(I) = NREFL(I) + 1
NZEROS = 0
DO 14 J = 1, 3
IF (FX(J).GT. 0.25 .OR. FX(J).LT. (-0.25)) GO TO 14
NZEROS = NZEROS + 1
JZERO = J
14 CONTINUE
IF (NZEROS .NE. 0) GO TO 10
ADDF2 = FSQR
ADDNF = 1
GO TO 17
10 IF (NZEROS .NE. 2) GO TO 12
ADDF2 = FSQR * MULTAX
ADDNF = MULTAX
GO TO 13
12 ADDF2 = FSQR * MULTPL(JZERO)
ADDNF = MULTPL(JZERO)
13 IF (NEXT .EQ. 0) GO TO 17
DO 15 J= 1, NEXT
DO 16 K= 1, 3
IF (IEX(J,K) .EQ. 0 .AND. FX(K).NE.0.0) GO TO 15
16 CONTINUE
ADDNF = ADDNF * FLOAT(EXMULT(J))
GO TO 17
11 CONTINUE
15 CONTINUE
17 SUMF2(I) = SUMF2(I) + ADDF2
SUMNF(I) = SUMNF(I) + ADDNF
GO TO 9
11 PRINT 18
18 FORMAT(///8H RANGE 8H STOLS ,12H REFLEXIONS , 10H SUMREFL ,

```

	1	13H SUMFOBS**2 ,17H AVERAGEFOBS**2)	
		SL = MINSL +XINTVL /2.0	
		DO 20 I = 1,NINTVL	
		AVRGF2(I) = SUMF2(I) / SUMNF(I)	
		PRINT 21, I, SL, NREFL(I), SUMNF(I), SUMF2(I), AVRGF2(I)	
21		FORMAT (3X, I3, 2X, F7.4, 4X, I5, 4X, F8.2, 2X, F10.1, 5X, F10.3)	
20		SL = SL + XINTVL	
		NINTVL = NINTVL - 1	
	DO 400 I=1,8		DATAPREP
400	FCURV(I)=0.		DATAPREP
	PRINT 50		
50	FORMAT(///8H RANGE 8H STOLS ,12H REFLEXIONS , 10H SUMREFL ,		
	1 13H SUMFOBS**2 ,17H AVERAGEFOBS**2		
	2 8H SIGMA2 , 17H SIGMA2/AVRGF2)		
	DO 22 J = 1, NINTVL		
	X = J		
	NREFL(J) = NREFL(J) + NREFL(J+1)		
	SUMNF(J) = SUMNF(J) + SUMNF(J+1)		
	SUMF2(J) = SUMF2(J) + SUMF2(J+1)		
	AVRGF2(J)= SUMF2(J) / SUMNF(J)		
	STOLS2(J)= MINSL + X * XINTVL		
	SSOLS2(J)= STOLS2(J) ** 2		
	STOLS = STOLS2(J)		
	SSOLS = SSOLS2(J)		
	IF (STOLS - 0.1) 203,204,204		DATAPREP
203	DO 202 I=1,NCURV		DATAPREP
202	FCURV(I) = FO(I)/EXP (P(I)*SSOLS)		DATAPREP
	GO TO 105		DATAPREP
204	IF (STOLS - 1.0) 205,206,206		DATAPREP
205	K0 = 1		DATAPREP
207	K1 = K0 + 1		DATAPREP
	E1 = K1		DATAPREP
	F1 = 0.1*E1		DATAPREP
	IF (STOLS - F1) 40,41,41		DATAPREP
41	K0 = K0 + 1		DATAPREP
	GO TO 207		DATAPREP
40	E0 = K0		DATAPREP
	F0 = 0.1*E0		DATAPREP
	K2 = K0 + 2		DATAPREP
	K3 = K0 + 3		DATAPREP

	RANGE=(STOLS-F0)/.1	DATAPREP
	RANG2=RANGE*(RANGE-1.)*0.5	DATAPREP
	RANG3=RANG2*(RANGE-2.)*0.33333	DATAPREP
	DO 402 I=1,NCURV	DATAPREP
402	FCURV(I) = F(I,K0) + (F(I,K1)-F(I,K0))*RANGE +	DATAPREP
	1 (F(I,K2)-2.*F(I,K1)+F(I,K0))*RANG2 +	DATAPREP
	2 (F(I,K3)-3.*F(I,K2)+3.*F(I,K1)-F(I,K0))*RANG3	DATAPREP
	GO TO 105	DATAPREP
206	KLOW = 10	DATAPREP
209	KHIGH= KLOW + 1	DATAPREP
	EHIGH= KHIGH	DATAPREP
	FHIGH= 0.1 * EHIGH	DATAPREP
	IF (STOLS - FHIGH) 42,43,43	DATAPREP
43	KLOW = KLOW + 1	DATAPREP
	GO TO 209	DATAPREP
42	DO 502 I=1,NCURV	DATAPREP
502	FCURV(I) = F(I,KHIGH) + (F(I,KLOW)-F(I,KHIGH))*(FHIGH-STOLS)*10.	DATAPREP
105	SIGMA2(J) = 0.0	
	DO 25 I = 1, NCURV	
25	SIGMA2(J) = SIGMA2(J) + FLOAT(NATOMS(I)) * (FCURV(I) ** 2)	
	RATIO (J) = SIGMA2(J) / AVRGF2(J)	
22	PRINT 51, J, STOLS2(J), NREFL(J), SUMNF(J), SUMF2(J), AVRGF2(J),	
	1 SIGMA2(J), RATIO(J)	
51	FORMAT (3X, I3, 2X, F7.4, 4X, I5, 4X, F8.2, 2X, F10.1, 5X, F10.3,	
	1 4X, F7.1, 5X, F7.2)	
	PRINT 65, WEIGHT(1), WEIGHT(2)	WEIGH
65	FORMAT (/ 45H WEIGHTS OF FIRST TWO RANGES IN REFINEMENT = ,	WEIGHT
	1 F5.2, 5H AND , F5.2, 13H RESPECTIVELY)	WEIG+T
	X1 = ALOG(RATIO(1))	WEIG+T
	X2 = ALOG(RATIO(2))	WEIG+T
	Y1 = SSOLS2(1)	WEIG+T
	Y2 = SSOLS2(2)	WEIG+T
	A11 = NINTVL - 2	WEIG+T
	A11 = A11 +WEIGHT(1) + WEIGHT(2)	WEIG+T
	A12 = WEIGHT(1) * Y1 + WEIGHT(2) * Y2	WEIG+T
	A22 = WEIGHT(1) *Y1 * Y1 + WEIGHT(2) * Y2 *Y2	WEIG+T
	B1 = WEIGHT (1) * X1 + WEIGHT(2) * X2	WEIGHT
	B2 = WEIGHT(1) * Y1 * X1 + WEIGHT(2) * Y2 *X2	WEIG+T
	DO 26 I = 3,NINTVL	WEIG+T
	X = ALOG(RATIO(I))	

```

Y= SSOLS2(I)
A12 = A12 + Y
A22 = A22 + Y ** 2
B1 = B1 + X
26 B2 = B2 + Y * X
DETERM = A11 * A22 - A12 * A12
XLOGK = (B1 * A22 - B2 * A12) / DETERM
B = (B2 * A11 - B1 * A12) / DETERM
XK = EXP(XLOGK)
52 PRINT 52, A11, A12, A22, B1, B2, DETERM, XLOGK, B
FORMAT(/5H A11=, F8.4, 5H A12=, F8.4, 5H A22=, F8.4, 4H B1=, F9.4,
1 4H B2=, F8.4, 5H DET=, F8.4, 7H XLOGK=, F8.4, 3H B=, F8.4)
PRINT 63
63 FORMAT ( // 26H CONSTANTS FOR INTENSITIES )
PRINT 27, XK, B
27 FORMAT ( 5X, 18H SCALE CONSTANT = , F10.4, 5X, 23H TEMPERATURE FACT
10R = F10.4)
PRINT 64
64 FORMAT ( // 32H CONSTANTS FOR STRUCTURE FACTORS )
X = SQRT (XK)
Y = B / 2.0
PRINT 27, X, Y
SIG2 = 0.0
SIG3 = 0.0
DO 61 I = 1, NCURV
SIG2 = SIG2 + FLOAT(NATOMS(I)) * (FO(I) ** 2)
61 SIG3 = SIG3 + FLOAT(NATOMS(I)) * (FO(I) ** 3)
PROBCF = SIG3 / (SIG2 ** 1.5)
PRINT 62, PROBCF
62 FORMAT(/51H PROBABILITY COEFFICIENT, SIGMA3 / SIGMA2 ** 3/2 =
1 , F8.5)
GO TO 2
12 PRINT 35
11 35 FORMAT (4H1 H, 4X, 1HK, 4X, 1HL, 8X, 2HF0, 5X, 5HF0**2, 4X, 7H/F0**2/,
10 3X, 2HE2, 5X, 1HE, 3X, 7HEPSILON / )
9
8 SUME = 0.0
7 SUME2 = 0.0
6 XNO = 0.0
5 NO = 0
4 SSLMAX = MAXSL ** 2
3

```

PROBCF
 PROBCF
 PROBCF
 PROBCF
 PROBCF
 PROBCF
 PROBCF

WEIG+T

	IF (OUTPUT .EQ. 0) GO TO 34	
	REWIND OUTPUT	
	ASSIGN 46 TO IENDF	
	CALL EOF (OUTPUT, IENDF)	
	NFILE = OUTFIL	
46	IF (NFILE .LE. 1) GO TO 34	
	NFILE = NFILE - 1	
47	READ (OUTPUT) II	
	GO TO 47	
34	READ (INPUT) II, IGPEN, SSOLS, FH, FK, FL, FREL, FSQR, (FCURV(I), I=1,8)	
	IF (II .NE. 0 .OR. IGPEN .NE. 0) GO TO 37	
	ABSF2 = FSQR * EXP((B) * SSOLS) * XK	
	IEPSLN = 1	
	IF (NEXT .EQ. 0) GO TO 31	
	IF (FH .NE. 0.0 .AND. FK .NE. 0.0 .AND. FL .NE. 0.0) GO TO 31	
	DO 29 J =1, NEXT	
	IF (IEX(J, 1) .EQ. 0 .AND. FH .NE. 0.0) GO TO 29	
	IF (IEX(J, 2) .EQ. 0 .AND. FK .NE. 0.0) GO TO 29	
	IF (IEX(J, 3) .EQ. 0 .AND. FL .NE. 0.0) GO TO 29	
	IEPSLN = EXMULT(J)	
	GO TO 31	
29	CONTINUE	
31	E2 = ABSF2	
	SIGMAS = 0.0	
	DO 32 I = 1, NCURV	
32	SIGMAS = SIGMAS + FLOAT(NATOMS(I))* (FCURV(I) ** 2)	
	E2 = E2 / SIGMAS	
	IF (IEPSLN .EQ. 1) GO TO 33	
	EPSLN = IEPSLN	
	E2 = E2 / EPSLN	
33	E = SQRT(E2)	
	IF (SSOLS .GT. SSLMAX) GO TO 70	
	I = 10	WEIG+T
	IF (FH .EQ. 0.0) I = I -9	WEIG+T
	IF (FK .EQ. 0.0) I = I -8	WEIG+T
	IF (FL .EQ. 0.0) I = I -7	WEIGHT
	X = 1.0	WEIG+T
	IF (I .GT. 3) GO TO 67	WEIG+T
	IF (I .LT. 0) X = MULTAX	WEIGHT
	IF (I .GT. 0) X = MULTPL(I)	WEIGHT

67	NO = NO + 1	WEIG+T
	XNO = XNO + X	WEIG+T
	SUME = SUME + ABS(E) * X	WEIG+T
	SUME2 = SUME2 + E2 * X	WEIGHT
70	CONTINUE	
	IF (E .GE. MINEPR) PRINT 36, FH, FK, FL, FREL, FSQR, ABSF2, E2, E,	
1	IEPSLN	
36	FORMAT (3(1X, F4.0), 3X, F7.1, F8.1, F12.1, 2F6.2, 4X, I2)	
	IF (OUTPUT .LE. 0) GO TO 34	
	IF (IPROJ .EQ. 0) GO TO 56	PROJ
	IF (IPROJ - 2) 57, 58, 59	PROJ
57	FPROJ = FH	PROJ
	GO TO 60	PROJ
58	FPROJ = FK	PROJ
	GO TO 60	PROJ
59	FPROJ = FL	PROJ
60	IF (FPROJ .NE. 0.0) GO TO 34	PROJ
	IF (IHALF .EQ. 0) GO TO 56	
	GO TO (71, 72, 73), IHALF	
71	FH = FH / 2.0	
	GO TO 56	
72	FK = FK / 2.0	
	GO TO 56	
73	FL = FL / 2.0	
56	IF (E .GE. MINETP) WRITE(OUTPUT) II, IGPEN, SSOLS, FH, FK, FL, E, PROJ	
1	E2, (FCURV(I), I=1,8)	
	GO TO 34	
37	IF (OUTPUT .GT. 0) WRITE(OUTPUT) II, IGPEN, SSOLS, FH, FK, FL, E,	
1	E2, (FCURV(I), I=1,8)	
	IF (II .NE. 0) GO TO 38	
	GO TO 34	
38	END FILE OUTPUT	
	IF (OUTPUT .GT. 0) PRINT 66, OUTTYP(IPROJ + 1), MINETP, OUTPUT	WEIGHT
66	FORMAT (A6, 30H DATA WITH @E@ NOT LESS THAN , F5.2, 24H HAS BEEN	WEIGHT
	1OUTPUT ON TAPE, I3)	WEIGHT
	REWIND INPUT	
	REWIND OUTPUT	
	PRINT 39	
39	FORMAT (/25H END DATA TO BE PROCESSED)	
	X2 = SUME / XNO	WEIG+T

X1 = SUME2 / XNO

PRINT 53,NO, SUME, SUME2, X2, X1

53 FORMAT (// 11H NO. REFL =, I7, 3X, 8H SUM E =, F9.1, 3X

1 , 9H SUM E2 =, F9.1, 3X, 12H AVERAGE E =, F6.3, 3X,

2 13H AVERAGE E2 =, F6.3)

PRINT 54

54 FORMAT (/ 102H (NOTE... IDEALLY, @AVERAGE E@ HAS THE VALUE 0.798 F

10R CENTRIC AND 0.886 FOR NON-CENTRIC DISTRIBUTIONS)

PRINT 55

55 FORMAT (10X, 49H WHILE @AVERAGE E2@ HAS THE VALUE 1.000 FOR BOTH

1))

STOP

END

\$ENTRY

SAYRE PROGRAM

12
11
10
9
8
7
6
5
4
3

R. L. CRAIN LIMITED

\$IBFTC SAYRE DECK

C THIS PROGRAM IDENTICAL TO 07/15/68 EXCEPT FOR FORMATS OF TAPE

C AND THAT EMPTY PARITY GROUPS ARE ALLOWED FOR

C ISPACE IS..... 1 FOR P2, 2 FOR PMM, 3 FOR PMG, 4 FOR PGG, AND 5 FOR PGM

C NO MORE THAN 35 REFLEXIONS IN ALL

C NO MORE THAN 20 REFLEXIONS PER PARITY GROUP

C NO MORE THAN 105 SAYRE RELATIONS TO BE GENERATED

C NO MORE THAN 10 REFLEXIONS TO BE SCRATCHED BY @ISCRAT@

INTEGER OUTPUT, OUTFIL

INTEGER PLUS

PRINTOUT

REAL MINE

DATA PLUS, MINUS / 1H+, 1H- /

PRINTOUT

DIMENSION F(3), FCURV(8), ICOUNT(4), IH(4,20), IK(4, 20), E(4,20)

DIMENSION IOCCUR(4, 20), IDENT(4, 20)

DIMENSION I2N(35), IXS(4,105), PROBIB(105)

DIMENSION IREFL(35), EREFL(35), ID(3,105), ISIGID(105), EEEID(105) PRINTOU

DIMENSION IR1(20), IR2(20), EE(20), IS(20), PRO(20)

PRINTOUT

DIMENSION NOCCUR(35), ISCRAT(10)

*

INTEGER OPLUS, OMINUS

*

DATA OPLUS, OMINUS / 0000000000000, 0400000000000 /

*

DIMENSION NA(35)

FRR

DATA NA/3H 1,3H 2,3H 3,3H 4,3H 5,3H 6,3H 7,3H 8,3H 9,3H 1FOR

10, 3H 11,3H 12,3H 13,3H 14,3H 15,3H 16,3H 17,3H 18,3H 19,3H 1FOR

20, 3H 21,3H 22,3H 23,3H 24,3H 25,3H 26,3H 27,3H 28,3H 29,3H 2FOR

30, 3H 31,3H 32,3H 33,3H 34,3H 35 / FOR

EQUIVALENCE (XL, IL)

DUMMY = 0.0

52 READ 9, INPUT, INFILE, OUTPUT, OUTFIL, IPROJ, ISPACE, IPRINT

1, IONE, NSCRAT

*

2, PROBCF, MINE, ACCEEE, (ISCRAT(I), I = 1, NSCRAT)

9 FORMAT (9I2, 2X, 3F10.0, 10I2)

C @ACCEEE@ IS ACCEPTABLE VALUE OF TRIPLE PRODUCT

CALL POSN (INPUT, INFILE)

DO 20 I = 1, 4

IH(I,1) = 0

IK(I,1) = 0

E (I,1) = 0.0

20 ICOUNT(I) = 0

DO 23 I = 1, 4

DO 23 J = 1, 20

```

23      IOCCUR(I, J) = 0
        DO 55 I = 1, 35
55      NOCCUR(I) = 0
        I2N(35) = 1
        DO 29 I = 1, 34
          J = 35 - I
          I2N(J) = I2N(J+1) * 2
29      CONTINUE
        IPH = 1
        IPK = 3
        IF (IPROJ .EQ. 1) IPH = 2
        IF (IPROJ .EQ. 3) IPK = 2
        IDEN = 0
        PRINT 46, MINE
46      FORMAT (53H THE REFLEXIONS CONTAINED ON THE INPUT TAPE WITH @E@ ,
1       13H GREATER THAN , F5.2, 9H ARE ... )
        PRINT 47
47      FORMAT (76H IDENT, 5X, 1HH, 3X, 1+K, 4X, 1HE )
7       READ (INPUT) II, IGPEN, SSOLS, (F(I), I = 1,3), E1, E2, (FCURV(I),
1       I = 1,8)
        IF (IGPEN .NE. 0) GO TO 7
        IF (II .NE. 0) GO TO 8
        IF (E1 .LT. MINE) GO TO 7
        IDEN = IDEN + 1
        IREFL(IDEN) = IDEN
        EREFL(IDEN) = E1
        IHO = F(IPH)
        IKO = F(IPK)
        PRINT 21, IDEN, IHO, IKO, E1
        I = 1
        IF (IHO .NE. IHO / 2 * 2) I = 3
        IF (IKO .NE. IKO / 2 * 2) I = I + 1
        ICOUNT(I) = ICOUNT(I) + 1
        IQ = ICOUNT(I)
        IH(I, IQ) = IHO
        IK(I, IQ) = IKO
        E(I, IQ) = E1
        IDENT(I, IQ) = IDEN
        GO TO 7
8       PRINT 10

```

PRINTOUT

PRINTOUT

PRINTOUT

PRINTOUT

PRINTOUT

```

10  FORMAT (6H1  H1 ,2X, 2HK1, 4X, 2HH2, 2X, 2HK2, 4X, 2HH3, 2X, 2HK3
1    , 3X, 8HE1*E2*E3, 4X, 5HSAYRE, 7X, 11HPROBABILITY /)  *

```

```

AVPROB = 1.0

```

```

NSAYRE = 0

```

```

DO 6 I = 1, 4

```

```

IQ1 = ICOUNT(I)

```

```

IF (IQ1 .EQ. 0) GO TO 6

```

```

DO 6 J = 1, IQ1

```

```

I1 = I

```

```

DO 6 K = I1, 4

```

```

IQ2 = ICOUNT(K)

```

```

IF (IQ2 .EQ. 0) GO TO 6

```

```

J1 = J

```

```

IF (K .NE. I1) J1 = 1

```

```

DO 6 L = J1, IQ2

```

```

IALPHA = 1

```

```

KK = IK(I, J) + IK(K, L)

```

```

DO 2 IA = 1, 2

```

```

II = IH(I, J) + IALPHA * IH(K, L)

```

```

IF (IA .NE. 2) GO TO 54

```

```

IF (IH(I, J) .EQ. 0 .OR. IK(I, J) .EQ. 0) GO TO 2

```

```

54 IIS = 1

```

```

IF (II .LT. 0 .AND. KK .NE. 0) IIS = -1

```

```

IF (ISPACE .GT. 1) II = IABS(II)

```

```

IF (I .NE. K) IFIND = 9 - I - K

```

```

IF (I .EQ. 1) IFIND = K

```

```

IF (I .EQ. K) IFIND = 1

```

```

IC = ICOUNT(IFIND)

```

```

IF (IC .EQ. 0) GO TO 3

```

```

DO 1 M = 1, IC

```

```

IF (II .NE. IH(IFIND, M)) GO TO 1

```

```

IF (KK .NE. IK(IFIND, M)) GO TO 1

```

```

EEE = E(I, J) * E(K, L) * E(IFIND, M)

```

```

IF (EEE .LT. ACCEEE) GO TO 3

```

```

IF (K .NE. I .OR. L .NE. J) GO TO 82

```

```

EEE = (EEE - E(IFIND, M)) / 2.0

```

```

IF (EEE .LT. ACCEEE) GO TO 3

```

```

IOCCUR(IFIND, M) = IOCCUR(IFIND, M) + 1

```

```

GO TO 84

```

```

82 IF (I .NE. IFIND .OR. J .NE. M) GO TO 83

```

	EEE = (EEE - E(K, L)) / 2.0	
	IF (EEE .LT. ACCEEE) GO TO 3	
	IOCCUR(K , L) = IOCCUR(K , L) + 1	
	GO TO 84	
83	IOCCUR(I , J) = IOCCUR(I , J) + 1	
	IOCCUR(K , L) = IOCCUR(K , L) + 1	
	IOCCUR(IFIND, M) = IOCCUR(IFIND, M) + 1	
84	PROB = 0.5 + 0.5 * TANH(PROBCF * EEE)	
	AVPROB = AVPROB * PROB	
	NSAYRE = NSAYRE + 1	
	IQ = IDENT(I, J)	*
	NOCCUR(IQ) = NOCCUR(IQ) + 1	*
	IR = IDENT(K, L)	*
	NOCCUR(IR) = NOCCUR(IR) + 1	*
	IF (IQ .EQ. IR) NOCCUR(IQ) = NOCCUR(IQ) - 2	*
	IR = IDENT (IFIND, M)	
	NOCCUR(IR) = NOCCUR(IR) + 1	
	IF (IQ .EQ. IR) NOCCUR(IQ) = NOCCUR(IQ) - 2	
	PROBIB(NSAYRE) = PROB	
	ID1 = IDENT(I, J)	
	ID2 = IDENT(K, L)	
	ID3 = IDENT(IFIND, M)	
	IXS(1, NSAYRE) = I2N(ID1) + I2N(ID2) + I2N(ID3)	
	IF (ID1 .EQ. ID2) IXS(1, NSAYRE) = I2N(ID3)	
	IF (ID1 .EQ. ID3) IXS(1, NSAYRE) = I2N(ID2)	07/04/68
	IF (ID2 .EQ. ID3) IXS(1, NSAYRE) = I2N(ID1)	07/04/68
	IF (ID2.GE. ID1) GO TO 36	PRINTOUT
	IQ = ID1	PRINTOUT
	ID1 = ID2	PRINTOUT
	ID2 = IQ	PRINTOUT
36	IF (ID3 .LE. ID1) GO TO 37	PRINTOUT
	IF (ID3 .LT. ID2) GO TO 38	PRINTOUT
	GO TO 39	PRINTOUT
37	IQ = ID2	PRINTOUT
	ID2 = ID3	PRINTOUT
	ID3 = IQ	PRINTOUT
	IQ = ID1	PRINTOUT
	ID1 = ID2	PRINTOUT
	ID2 = IQ	PRINTOUT
	GO TO 39	PRINTOUT

38	IQ = ID2 ID2 = ID3	PRINTOUT PRINTOUT
39	ID3 = IQ CONTINUE ID(1, NSAYRE) = ID1 ID(2, NSAYRE) = ID2 ID(3, NSAYRE) = ID3 ISIGID(NSAYRE) = PLUS EEEID (NSAYRE) = EEE IXS(3, NSAYRE) = 0 IXS(4, NSAYRE) = 0 MULT = 1 GO TO (30, 30, 31, 32, 81), ISPACE	PRINTOUT PRINTOUT PRINTOUT PRINTOUT PRINTOUT PRINTOUT PRINTOUT
81	IF (K.NE. 1.AND. K .NE. 3 .AND. IALPHA .EQ. (-1))	
1	MULT = MULT * (-1) IF (IFIND .NE. 1 .AND. IFIND .NE. 3) MULT = MULT * IIS GO TO 33	
31	IF (K .GT. 2 .AND. IALPHA .EQ. (-1)) MULT = MULT * (-1) IF (IFIND .GT. 2) MULT = MULT * IIS GO TO 33	
32	IF (K.NE. 1.AND. K .NE. 4 .AND. IALPHA .EQ. (-1))	
1	MULT = MULT * (-1) IF (IFIND .NE. 1 .AND. IFIND .NE. 4) MULT = MULT * IIS	
33	ID1 = ID1 * MULT IF (ID1 .LT. 0) ISIGID(NSAYRE) = MINUS IXS(2, NSAYRE) = OPLUS	PRINTOUT *
30	IF (MULT .LT. 0) IXS(2, NSAYRE) = OMINUS PRINT 5, IH(I,J), IK(I,J), IH(K,L), IK(K,L), II, KK, EEE 1 ,ID1, ID2, ID3, PROB	* *
5	FORMAT(2X, 3(2I4,2X), F6.1,3X, 2(I3, 2H *), I3, 3X, F7.4) GO TO 3	*
1	CONTINUE	
3	IF (ISPACE .EQ. 1) GO TO 6 IALPHA = -1	
2	CONTINUE	
6	CONTINUE	
85	PRINT 85 FORMAT (127H (NOTE THAT @EEE@ FOR SIGMA1 IYPE RELATIONSHIPS HAS BE 1EN MODIFIED SO THAT @PROBABILITY@ CAN BE COMPUTED BY ONLY ONE EXPR 2ESSION))	

```

      XSAYRE = NSAYRE
      AVPROB = AVPROB ** (1.0 / XSAYRE)
      PRINT 28, NSAYRE
28    FORMAT(/ / 30H NO. OF SAYRE RELATIONSHIPS = , I4)
      PRINT 27, AVPROB
27    FORMAT ( / / 25H @AVERAGE@ PROBABILITY = , F7.4)
      PRINT 22
22    FORMAT (6HIDENT, 5X, 1HH, 3X, 1HK, 4X, 1HE, 3X, 9HOCCURANCE / )
      DO 24 I = 1, 4
      J1 = ICOUNT(I)
      DO 25 J = 1, J1
25    PRINT 21, IDENT(I, J), IH(I, J), IK(I, J), E(I, J), IOCCUR(I, J)
21    FORMAT (I5, 4X, I3, I4, F7.2, 4X, I2)
24    PRINT 26
26    FORMAT (2H )
      CALL PROBN (NSAYRE, AVPROB)
      IF (NSCRAT .EQ. 0 ) GO TO 56
      IQ = 0
      DO 57 I = 1, NSCRAT
      IR = ISCRAT(I)
57    IQ = IQ + I2N(IR)
      DO 58 I = 1, NSAYRE
      XL = AND(IQ, IXS(1, I))
      IF (IL .EQ. 0) GO TO 58
      IXS(1, I) = 0
      DO 59 J = 1, 3
      IR = ID(J, I)
59    NOCCUR(IR) = NOCCUR(IR) - 1
      ID(1, I) = 1000
58    CONTINUE
      PRINT 60, NSCRAT, (ISCRAT(I), I = 1, NSCRAT)
60    FORMAT(/61H0AFTER ELIMINATING RELATIONSHIPS WHICH INCLUDE THE FOLL
10    OWING , I3, 14H REFLEXION(S) , 10(I3, 1H,))
      PRINT 61
61    FORMAT ( 13H WE HAVE..... / )
      PRINT 62, (NA(I), I = 1, IDEN)
62    FORMAT (5X, 11H REFLEXIONS , 35A3)
      PRINT 63, (NOCCUR(I), I = 1, IDEN)
63    FORMAT (5X, 11H OCCURANCE , 35I3)
56    IF (IONE .NE. (-1)) GO TO 64

```

FOR

```

      PRINT 65
65  FORMAT (/97H THE FOLLOWING CYCLES WERE CARRIED OUT, EACH OF WHICH*
      1 REMOVES ONE REFLEXION OCCURRING ONLY ONCE ,
      2 // 5X, 53H THE FOLLOWING LIST SHOWS OCCURANCES AFTER EACH CYCLE)*
      PRINT 80, (NA(I), I = 1, IDEN)
      FOR
80  FORMAT (7X, 2H N, 5X, 35A3)
      N = 0
80  PRINT 71, N, (NOCCUR(I), I = 1, IDEN)
80  FORMAT (6X, I3, 5X, 35I3)
      DO 66 I = 1, IDEN
      IF (NOCCUR(I) .NE. 1) GO TO 66
      IQ = 12N(I)
      GO TO 67
66  CONTINUE
      GO TO 64
80  N = N + 1
      DO 68 I = 1, NSAYRE
      IF (IXS(1, I) .EQ. 0) GO TO 68
      XL = AND(IQ, IXS(1, I))
      IF (IL .EQ. 0) GO TO 68
      DO 69 J = 1, 3
      IQ = ID(J, I)
80  NOCCUR(IQ) = NOCCUR(IQ) - 1
      ID(1, I) = 1000
      IXS(1, I) = 0
      GO TO 70
80  CONTINUE
80  PRINT 72
80  FORMAT ( 13H ERROR AT 72 )
80  IF (IONE .NE. (-1) .AND. NSCRAT .EQ. 0 .AND. OUIPUT .LE. 0) GO TO
1  73
12  PRINT 74
11  FORMAT ( 25H1FINAL FORM OF DATA USED ///)
10  PRINT 76
9  FORMAT(4X, 2H N, 8X, 5HSAIRE, 7X, 11HPROBABILITY, 7H EEE
8  1 , 7X, 18HSTORAGE FOR OUIPUT /)
7  NS = 0
6  AVPROB = 1.0
5  NSA = (NSAYRE - 1) / 35 + 2
4  DO 75 I = 1, NSAYRE
3

```

	IF (IXS(1, 1) .EQ. 0) GO TO 75	*
	NS = NS + 1	*
	IQ = (NS - 1) / 35 + 2	
	IR = NS - (IQ - 2) * 35	
	XL = OR(IXS(IQ, 1), I2N(IR))	
	IXS(IQ, 1) = IL	
	PRINT 77, NS, ISIGID(1), (ID(J, 1), J = 1, 3), PROBIB(1), EEEID(1)	
	1, (IXS(J, 1), J = 1, NSA)	
77	FORMAT (3X, I3, 4X, A1, I2, 2H *, I3, 2H *, I3, 3X, F7.4, 3X, F5.1,	
	1 10X, 40I3)	
	AVPROB = AVPROB * PROBIB(1)	*
75	CONTINUE	*
	IF (IONE .NE. (-1) .AND. NSCRA1 .EQ. 0) GO TO 73	*
	XS = NS	*
	AVPROB = AVPROB ** (1.0 / XS)	*
	PRINT 28, NS	*
	PRINT 27, AVPROB	*
	CALL PROBN (NS, AVPROB)	*
73	IF (IPRINT .EQ. (-1)) GO TO 53	*
	DO 35 I = 1, IDEN	PRINTOUT
	JINIT = I	PRINTOUT
	EMAX = 0	PRINTOUT
	DO 34 J = JINIT, IDEN	PRINTOUT
	IF (EREFL(J) .LE. EMAX) GO TO 34	PRINTOUT
	EMAX = EREFL(J)	PRINTOUT
	IREFJ = J	PRINTOUT
34	CONTINUE	PRINTOUT
	IF (I .EQ. IREFJ) GO TO 35	PRINTOUT
	IQ = IREFL(I)	PRINTOUT
	IREFL(I) = IREFL(IREFJ)	PRINTOUT
	IREFL(IREFJ) = IQ	PRINTOUT
	XQ = EREFL(I)	PRINTOUT
	EREFL(I) = EREFL(IREFJ)	PRINTOUT
	EREFL(IREFJ) = XQ	PRINTOUT
35	CONTINUE	PRINTOUT
	PRINT 48	PRINTOUT
48	FORMAT(3H1HK, 3X, 3H(E), 7X, 3(7X, 5H\$AYRE, 5X, 11H(EEE, PROB), 3X) /)	PRINTOUT
	DO 40 I = 1, IDEN	PRINTOUT
	PRINT 49, IREFL(I), EREFL(I)	PRINTOUT
49	FORMAT(/I3, 2H (, F5.2, 2H))	

	INS = 0	PRINTOUT
	DO 41 J = 1, NSAYRE	PRINTOUT
	DO 42 K = 1, 3	PRINTOUT
	IF (IREFL(I).LT. ID(K, J)) GO TO 41	PRINTOUT
	IF (IREFL(I).NE. ID(K, J)) GO TO 42	PRINTOUT
	INS = INS + 1	PRINTOUT
	IR1(INS) = ID(1, J)	PRINTOUT
	IR2(INS) = ID(3, J)	PRINTOUT
	IF (K .EQ. 1) IR1(INS) = ID(2, J)	PRINTOUT
	IF (K .EQ. 3) IR2(INS) = ID(2, J)	PRINTOUT
	EE(INS) = EEEID(J)	
	PRO(INS) = PROBIB(J)	PRINTOUT
	IS(INS) = ISIGID(J)	PRINTOUT
	GO TO 41	PRINTOUT
42	CONTINUE	PRINTOUT
41	CONTINUE	PRINTOUT
	IF (INS .NE. 0) GO TO 44	PRINTOUT
	PRINT 50	PRINTOUT
50	FORMAT (11X, 47HNO SAYRE RELATIONSHIPS EXIST FOR THIS REFLEXION	PRINTOUT
	1 //)	PRINTOUT
	GO TO 40	PRINTOUT
44	INIT = 1	PRINTOUT
	LIM = 3	PRINTOUT
51	IF (INS .LT. LIM) LIM = INS	
	PRINT 43, (IS(J), IR1(J), IR2(J), EE(J), PRO(J), J = INIT, LIM)	PRINTOUT
43	FORMAT (16X, 3(5X , A1, I3, 2H *, I3, 2H (, F5.1, 1H,,	PRINTOUT
	1 F6.3, 1H), 2X) /)	PRINTOUT
	INIT = INIT + 3	PRINTOUT
	LIM = LIM + 3	PRINTOUT
	IF (INS - LIM .GT. (-3)) GO TO 51	PRINTOUT
	PRINT 45	PRINTOUT
45	FORMAT (/ 2H)	PRINTOUT
	IF (INS / 3 * 3 .NE. INS) PRINT 45	PRINTOUT
40	CONTINUE	PRINTOUT
53	REWIND INPUT	
	IF (OUTPUT .EQ. 0) GO TO 52	
	CALL POSN (OUIPUT, OUIFIL)	
	WRITE (OUTPUT) IDEN, NS, PROBCF, (DUMMY, I = 4, 16)	
	NR = (NS - 1) / 35 + 2	
	N = NR + 2	

```

DO 78 I = 1, NSAYRE
IF (IXS(1, I) .EQ. 0) GO TO 78
WRITE (OUTPUT) (IXS(J, I), J = 1, NR), EEEID(I), (DUMMY, J = N, 16)
78 CONTINUE
END FILE OUTPUT
REWIND OUTPUT
PRINT 4, NS, OUTPUT, OUTFIL
4 FORMAT(// 4H THE, I3,

```

```

1 63H RELATIONSHIPS AS DESCRIBED EARLIER HAS NOW BEEN OUTPUT
2 ON UNIT , I3, 5H FILE, I3)
GO TO 52
END

```

```

$IBFTC POSN DECK
SUBROUTINE POSN ( INPUT, INFILE)

```

```

ASSIGN 14 TO IENDF
CALL EOF (INPUT, IENDF)
12 REWIND INPUT
NFILE = INFILE
14 IF (NFILE .LE. 1) GO TO 13
NFILE = NFILE - 1
18 READ (INPUT) II
GO TO 18
13 RETURN
END

```

```

$IBFTC PROBN DECK
SUBROUTINE PROBN (NSAYRE, AVPROB)
PRINT 2

```

```

2 FORMAT ( 102H1PROBABILITY THAT CORRECT STRUCTURE INVOLVES NO MORE
1THAN N FAILURES OF INDIVIDUAL SAYRE RELATIONSHIPS )

```

```

DIMENSION P(100), IADD(10)
XSAYRE = NSAYRE
P(1) = AVPROB ** XSAYRE
P1 = P(1)
X = 1.0
DO 3 I = 1, NSAYRE
X = X * FLOAT(NSAYRE - I + 1) / FLOAT(I)
P1 = P1 / AVPROB * (1.0 - AVPROB)
3 P(I + 1) = P(I) + X * P1
DO 4 I = 1, 10
4 IADD(I) = I - 1

```

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U
V
W
X
Y
Z

```
7 PRINT 7, (IADD(J), J = 1, 10)
  FORMAT ( // 9H FAILURES, I4, 9I7)
  NS = NSAYRE + 1
  DO 5 I = 1, NS, 10
  IQ1 = I - 1
  IQ2 = I
  IQ3 = IQ2 + 9
  IF (IQ3 .GT. NS) IQ3 = NS
5 PRINT 6, IQ1, (P(J), J = IQ2, IQ3)
6 FORMAT ( / I5, 2H /, 2X, 10F7.4)
  RETURN
  END
$ENTRY
```

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SIGNS PROGRAM

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\$IBFTC SIGNS REF,DECK

08/02/68

C THIS PROGRAM IDENTICAL TO 07/15/68 EXCEPT FOR FORMATS OF IAPE

C RELATIONSHIPS OF RANK DOWN TO FOUR LESS THAN THE NO. OF

C REFLEXIONS OCCURRING IN THEM CAN BE HANDLED

C THE @SECOND GROUP@ MUST NOT BE COMPLETELY EMPTY

C UP TO FIVE FAILURES IN THE FIRST GROUP

07/15/68

COMMON EEE, EMAX, I2N, IDMISS, IFAIL, IFIN, IMULT,

1 ISIG, ISIGS, IXS, IXT, NFAIL, NMULT,

2 NPOSS, NS, OUTPUT

DATA INEG, IZERO / 04000000000000 , 00000000000000 /

INTEGER OUTPUT, OUTFIL, BLANK, PLUS

DIMENSION NA(35)

FOR

DATA NA/2H 1, 2H 2, 2H 3, 2H 4, 2H 5, 2H 6, 2H 7, 2H 8, 2H 9, 3H 10, FOR

1 2H 1, 2H 2, 2H 3, 2H 4, 2H 5, 2H 6, 2H 7, 2H 8, 2H 9, 3H 20, FOR

2 2H 1, 2H 2, 2H 3, 2H 4, 2H 5, 2H 6, 2H 7, 2H 8, 2H 9, 3H 30, FOR

3 2H 1, 2H 2, 2H 3, 2H 4, 2H 5 / FOR

DATA BLANK, PLUS, MINUS / 2H , 2H +, 2H - /

DIMENSION IXS(4,105), I2N(35), EEE(105), IDMISS(20), IS(3), IQS(3)

DIMENSION IS1(35), ISIG (35)

DIMENSION ICON(10)

DIMENSION IARB(4), ICOMP(16), IMULT(35, 16), ISIGS(35)

ARBITRAR

DIMENSION IXT(105), PEEE(105), AS(3), IVP1(3), AVP1(3),

1 IVP(3, 35), XVP(3, 35)

DIMENSION IFAIL (3), XFAIL (3)

1 ,IFAIL1(3), XFAIL1(3)

2 ,IFAIL2(3), XFAIL2(3)

3 ,IFAIL3(3), XFAIL3(3)

4 ,IFAIL4(3), XFAIL4(3)

EQUIVALENCE (XL, IL),(IS, XS),(IX, XX),(XQ1, IQ1),(XVP1, IVP1)

EQUIVALENCE (IVP, XVP),(IFAIL, XFAIL),(IFAIL1, XFAIL1),(IFAIL2,

1 XFAIL2),(IFAIL3, XFAIL3),(IFAIL4, XFAIL4)

READ 10, INPUT, INFILE, OUTPUT, OUTFIL, NFAIL1, NFAIL2, EMAX

10 FORMAT (6I2, F8.0)

READ 4, NCON, (ICON(I), I = 1, NCON)

4 FORMAT (I2, 10I3)

PRINT 51, NCON, (ICON(I), I = 1, NCON)

51 FORMAT (14H THE FOLLOWING, I3, 52H REFLEXIONS HAVE THEIR SIGNS SPE

1CIFIED IN INPUT ... , 10(I3, 1H,D)

CALL POSN (INPUT, INFILE)

READ (INPUT) N, M, PROBCF

C THE PROBABILITY COEFFICIENT IS READ BUT IS NOT PRESENTLY USED
C PEEE IS THE TRIPLE PRODUCT OF E@S PER REFEXION

K = (M - 1) / 35 + 2

DO 99 I = 1, M

READ (INPUT) (IXS(J,I), J = 1, K), PEEE(I)

NOFILING

EEE(I) = PEEE(I)

99 IXT(I) = IXS(1, I)

PRINT 6, INPUT, INFILE

FOR

6 FORMAT (75H UNIT, I3, 5H FILE, I3,

FOR

1 54H CONTAINS THE FOLLOWING RELATIONSHIPS (OCIAL NOTATION) /) FOR

NS = (M - 1) / 35 + 1

J = NS + 1

DO 62 K = 1, M

FOR

62 PRINT 30, (IXS(I, K), I = 1, J)

IF (N .EQ. 35) GO TO 8

FOR

K = N + 1

FOR

DO 7 I = K, 35

FOR

7 NA(I) = BLANK

FOR

8 CONTINUE

FOR

I2N(35) = 1

DO 56 I = 1, 34

J = 35 - I

56 I2N(J) = I2N(J+1) * 2

IF (NCON .EQ. 0) GO TO 58

DO 60 I = 1, NCON

IAB = IABS(ICON(I))

ISI = +1

IF (ICON(I) .LT. 0) ISI = -1

DO 61 J = 1, M

XL = AND(IXS(1, J), I2N(IAB))

IF (IL .EQ. 0) GO TO 61

IXS(1,J) = IXS(1,J) - I2N(IAB)

IXS(2,J) = IXS(2,J) * ISI

61 CONTINUE

60 CONTINUE

58 CONTINUE

DO 53 I = 1, 20

53 I4MISS(I) = 0

NMISS = 0

DO 2 I = 1, N

PROBMX = 0.0
JINIT = 1 - NMISS

DO 1 J = JINIT, M
IF (PEEE(J) .LE. PROBMX .OR. IXS(1, J) / I2N(1) .EQ. 0) GO TO 1
PROBMX = PEEE(J)

JNOTE = J

1 CONTINUE

IF (PROBMX .NE. 0.0) GO TO 24

C OTHERWISE REFLEXION CONSIDERED IS MISSING FROM THE SAYRE RELATIONSHIP

NMISS = NMISS + 1

IDMISS(NMISS) = 1

GO TO 2

24 XQ = PEEE(JINIT)

PEEE(JINIT) = PEEE(JNOTE)

PEEE(JNOTE) = XQ

J = NS + 1

DO 25 K = 1, J

IQ = IXS(K, JINIT)

IXS(K, JINIT) = IXS(K, JNOTE)

25 IXS(K, JNOTE) = IQ

DO 3 K = 1, M

IF (K .EQ. JINIT) GO TO 3

XL = AND(IXS(1, K), I2N(1))

IF (IL .EQ. 0) GO TO 3

DO 26 KQ = 1, J

XL = AND(IXS(KQ, JINIT), IXS(KQ, K))

XL = COMPL(XL)

X = OR(IXS(KQ, JINIT), IXS(KQ, K))

XL = AND(XL, X)

26 IXS(KQ, K) = IL

3 CONTINUE

2 CONTINUE

PRINT 27, M

27 FORMAT (4H1THE, I4,105H SAYRE RELATIONSHIPS HAVE BEEN MANIPULATED
1 AND RESTORED IN THE FOLLOWING MANNER (GIVEN IN OCIAL NOIATION))

PRINT 28

28 FORMAT (5X, 8HIXS(1,M), 9X, 8HIXS(2,M), 9X, 8HIXS(3,M),

1 9X, 8HIXS(4,M) /)

DO 29 K = 1, M

J = NS + 1

29	PRINT 30, (IXS(I, K), I = 1, J)	
30	FORMAT (4017)	
C	NOW TO FIND WHICH S@S OCCUR IN THE FIRST GROUP	
	IFIN = N - NMISS	
	DO 120 K = 1, NS	
120	IS(K) = IABS(IXS(K + 1, 1))	
	DO 31 I = 2, IFIN	
	DO 31 J = 1, NS	
	IQ1 = IABS(IXS(J + 1, 1))	
	XS(J) = OR(IS(J), IQ1)	
31	CONTINUE	
	PRINT 32, (IS(K), K = 1, NS)	
32	FORMAT (/ 63H OCTAL REPRESENTATION OF S@S OCCURING IN THE FIRST G	
	1ROUP , 3013)	
C	NOW TO IDENTIFIY THESE S@S	
	II = 1	
	DO 121 K = 1, NS	
121	IQS(K) = IS(K)	
	K = 1	
	DO 33 I = 1, M	
	J = (I - 1) / 35 + 1	
	L = I - (J - 1) * 35	
	IF (IQS(J) / I2N(L) .EQ. 0) GO TO 33	
	IS1(K) = I	
	IQS(J) = IQS(J) - I2N(L)	
	K = K + 1	
33	CONTINUE	
	PRINT 70, (IS1(I), I = 1, IFIN)	*
70	FORMAT (20H THIS CORRESPONDS TO, 2X, 35(I2, 1H,))	*
C	NOW TO FIND WHICH REFLEXIONS OCCUR WITH ARBITRARY SIGN	ARBITRAR
	IF (NMISS .EQ. 0) GO TO 75	ARBITRAR
	IX = IXS(1,1)	ARBITRAR
	DO 73 I = 2, IFIN	ARBITRAR
73	XX = OR(IX, IXS(1, I))	
	IQ1 = 0	ARBITRAR
	DO 74 I = 1, NMISS	ARBITRAR
	J = IDMISS(I)	ARBITRAR
74	IQ1 = IQ1 + I2N(J)	ARBITRAR
	XL = AND(IX, IQ1)	
	IF (IL .EQ. 0) GO TO 75	

	IQ1 = IL	
	NARB = 0	ARBITRAR
	DO 77 I = 1, NMISS	ARBITRAR
	J = IDMISS(I)	ARBITRAR
	IF (IQ1 / I2N(J) .EQ. 0) GO TO 77	ARBITRAR
	NARB = NARB + 1	ARBITRAR
	IARB(NARB) = J	ARBITRAR
	IQ1 = IQ1 - I2N(J)	ARBITRAR
77	CONTINUE	ARBITRAR
	PRINT 78, NARB, (IARB(I), I = 1, NARB)	ARBITRAR
78	FORMAT (/86H EACH SET OF COCHRAN + DOUGLAS SOLUTIONS IS BASED ON	ARBITRAR
	IRBITRARY SIGNS OF THE FOLLOWING , I3, 17H REFLEXION(J),	ARBITRAR
	2 4(I3, 1H,))	ARBITRAR
	NMULT = 2 ** NARB	ARBITRAR
	GO TO 76	ARBITRAR
75	NARB = 0	ARBITRAR
	NMULT = 1	ARBITRAR
76	DO 79 I = 1, 35	ARBITRAR
	DO 79 J = 1, NMULT	NARBETRA
79	IMULT(I, J) = 1	ARBITRAR
	IF (NARB .EQ. 0) GO TO 96	IRBITRAR
	ICOMPM(1) = 0	ARBITRAR
	I = IARB(1)	ARBITRAR
	ICOMPM(2) = I2N(I)	ARBITRAR
	IF (NARB .EQ. 1) GO TO 83	ARBITRAR
	J = IARB(2)	ARBITRAR
	J = I2N(J)	ARBITRAR
	DO 84 I = 1, 2	ARBITRAR
84	ICOMPM(I + 2) = ICOMPM(I) + J	ARBITRAR
	IF (NARB .EQ. 2) GO TO 83	ARBITRAR
	J = IARB(3)	ARBITRAR
	J = I2N(J)	ARBITRAR
	DO 85 I = 5, 8	ARBITRAR
85	ICOMPM(I) = ICOMPM(I - 4) + J	ARBITRAR
	IF (NARB .EQ. 3) GO TO 83	ARBITRAR
	J = IARB(4)	ARBITRAR
	J = I2N(J)	ARBITRAR
	DO 86 I = 9, 16	ARBITRAR
86	ICOMPM(I) = ICOMPM(I - 8) + J	ARBITRAR
83	DO 80 J = 1, NMULT	ARBITRAR

	J = IARB(2)	ARBITRAR
	DO 89 I = 1, NMULT, 4	ARBITRAR
89	IMULT(J, I + 2) = -1	
	IMULT(J, I + 3) = -1	
	IF (NARB .EQ. 2) GO TO 88	ARBITRAR
	J = IARB(3)	ARBITRAR
	DO 90 I = 5, 8	
90	IMULT(J, I) = -1	
	IF (NARB .EQ. 3) GO TO 88	ARBITRAR
	DO 91 I = 13, 16	
91	IMULT(J, I) = -1	
	J = IARB(4)	ARBITRAR
	DO 92 I = 9, 16	
92	IMULT(J, I) = -1	
55	CONTINUE	
88	IF (OUTPUT .NE. 0) CALL POSN (OUTPUT, OUTFIL)	ARBITRAR
	NPOSSO = 0	
	DO 102 J = 1, NS	
102	IVP1(J) = IZERO	
	DO 100 I = IFINK, M	
	XL = AND(INEG, IXS(2, I))	
	XL = COMPL(XL)	
	IF (IL .LT. 0) GO TO 100	
	DO 101 J = 1, NS	
101	XVP1(J) = OR (IVP1(J), IXS(J + 1, I))	
100	CONTINUE	
	IVP1(1) = IABS(IVP1(1))	
	DO 107 J = 1, NS	
	XL = COMPL(IXS(J))	
107	XVP1(J) = AND(IVP1(J), IL)	
	DO 108 I = IFINK, M	
108	IXS(2, I) = IABS(IXS(2, I))	
	DO 103 I = 1, IFIN	
	DO 105 K = 1, NS	
105	IVP(K, I) = IZERO	
	K = IS1(I)	
	L = (K - 1) / 35	
	K = K - L * 35	
C	L IS TO BE STORED UNTIL ITS USE JUST BEFORE STATEMENT 103	
	L = L + 1	

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	LL = 12N(K)
	DO 104 J = IFINK, M
	XL = AND (IXS(L + 1, J), LL)
	IF(IL .EQ. 0) GO TO 104
	DO 110 K = 1, NS
110	XVP(K, I) = OR(IVP(K,I), IXS(K + 1, J))
104	CONTINUE
C	NOW SUBTRACT S@S OF FIRST GROUP
	DO 111 K = 1, NS
	XL = COMPL(IS(K))
111	XVP(K, I) = AND(IVP(K,I), IL)
C	THE FOLLOWING STATEMENT MAKES @IVP@ SHOW ALSO FAILURES IN GROUP 1
	IVP(L, I) = IVP(L,I) + LL
103	CONTINUE
	NFAIL = 0
	DO 148 I = 1, NS
	IFAIL(I) = IVP1(I)
	CALL ICOUNT (IFAIL(I), NONES)
148	NFAIL = NFAIL + NONES
	NINALL = 1
	IF (NFAIL .GT. NFAIL2) GO TO 48
	NPOSS0 = NPOSS0 + NMULT
	CALL ITEST
48	CONTINUE
	IF (NFAIL1 .LT. 1) GO TO 49
	DO 47 I1 = 1, IFIN
	NFAIL = 0
	DO 147 I = 1, NS
	X = AND (IVP1(I), IVP(I, I1))
	X = COMPL(X)
	Y = OR(IVP1(I), IVP(I, I1))
	XFAIL (I) = AND(X, Y)
	CALL ICOUNT (IFAIL(I), NONES)
147	NFAIL = NFAIL + NONES
	NINALL = NINALL + 1
	IF (NFAIL .GT. NFAIL2) GO TO 47
	NPOSS0 = NPOSS0 + NMULT
	CALL ITEST
47	CONTINUE
	IF (NFAIL1 .LT. 2) GO TO 49


```

      IFIN1 = IFIN - 1
      DO 45 I1 = 1, IFIN1
      DO 145 I = 1, NS
      X = AND (IVP1(I), IVP(I, I1))
      X = COMPL(X)
      Y = OR(IVP1(I), IVP(I, I1))
145   XFAIL1(I) = AND(X, Y)
      I2INIT = I1 + 1
      DO 45 I2 = I2INIT, IFIN
      NFAIL = 0
      DO 245 I = 1, NS
      X = AND (IFAIL1(I), IVP(I, I2))
      X = COMPL(X)
      Y = OR(IFAIL1(I), IVP(I, I2) )
      XFAIL (I) = AND(X, Y)
      CALL ICOUNT (IFAIL(I), NONES )
245   NFAIL = NFAIL + NONES
      NINALL = NINALL + 1
      IF (NFAIL .GT. NFAIL2) GO TO 45
      NPOSS0 = NPOSS0 + NMULT
      CALL ITEST
45   CONTINUE
      IF (NFAIL1 .LT. 3) GO TO 49
      IFIN1 = IFIN - 2
      IFIN2 = IFIN - 1
      DO 42 I1 = 1, IFIN1
      DO 142 I = 1, NS
      X = AND (IVP1(I), IVP(I, I1))
      X = COMPL(X)
      Y = OR(IVP1(I), IVP(I, I1))
142   XFAIL1(I) = AND(X, Y)
      I2INIT = I1 + 1
      DO 42 I2 = I2INIT, IFIN2
      DO 242 I = 1, NS
      X = AND (IFAIL1(I), IVP(I, I2))
      X = COMPL(X)
      Y = OR(IFAIL1(I), IVP(I, I2) )
242   XFAIL2(I) = AND(X, Y)
      I3INIT = I2 + 1
      DO 42 I3 = I3INIT, IFIN

```

```

NFAIL = 0
DO 342 I = 1, NS
  X = AND (IFAIL2(I), IVP(I, I3))
  X = COMPL(X)
  Y = OR(IFAIL2(I), IVP(I, I3))
  XFAIL (I) = AND(X, Y)
  CALL ICOUNT (IFAIL(I), NONES )
342  NFAIL = NFAIL + NONES
  NINALL = NINALL + 1
  IF (NFAIL .GT. NFAIL2) GO TO 42
  NPOSS0 = NPOSS0 + NMULT
  CALL ITEST
42  CONTINUE
  IF (NFAIL1 .LT. 4) GO TO 49
  IFIN1 = IFIN - 3
  IFIN2 = IFIN - 2
  IFIN3 = IFIN - 1
  DO 34 I1 = 1, IFIN1
  DO 134 I = 1, NS
    X = AND (IVP1(I), IVP(I, I1))
    X = COMPL(X)
    Y = OR(IVP1(I), IVP(I, I1))
134  XFAIL1(I) = AND(X, Y)
    I2INIT = I1 + 1
    DO 34 I2 = I2INIT, IFIN2
    DO 234 I = 1, NS
      X = AND (IFAIL1(I), IVP(I, I2))
      X = COMPL(X)
      Y = OR(IFAIL1(I), IVP(I, I2) )
234  XFAIL2(I) = AND(X, Y)
      I3INIT = I2 + 1
      DO 34 I3 = I3INIT, IFIN3
      DO 334 I = 1, NS
        X = AND (IFAIL2(I), IVP(I, I3))
        X = COMPL(X)
        Y = OR(IFAIL2(I), IVP(I, I3))
334  XFAIL3(I) = AND(X, Y)
      I4INIT = I3 + 1
      DO 34 I4 = I4INIT, IFIN
      NFAIL = 0

```

```

DO 434 I = 1, NS
X = AND (IFAIL3(I), IVP(I, 14))
X = COMPL(X)
Y = OR(IFAIL3(I), IVP(I, 14))
XFAIL (I) = AND(X, Y)
CALL ICOUNT (IFAIL(I), NONES )
434 NFAIL = NFAIL + NONES
NINALL = NINALL + 1
IF (NFAIL .GT. NFAIL2) GO TO 34
NPOSS0 = NPOSS0 + NMULT
CALL ITEST
34 CONTINUE
IF (NFAIL1 .LT. 5) GO TO 49
IFIN1 = IFIN - 4
IFIN2 = IFIN - 3
IFIN3 = IFIN - 2
IFIN4 = IFIN - 1
DO 44 I1 = 1, IFIN1
DO 144 I = 1, NS
X = AND (IVP1(I), IVP(I, I1))
X = COMPL(X)
Y = OR(IVP1(I), IVP(I, I1))
144 XFAIL1(I) = AND(X, Y)
I2INIT = I1 + 1
DO 44 I2 = I2INIT, IFIN2
DO 244 I = 1, NS
X = AND (IFAIL1(I), IVP(I, I2))
X = COMPL(X)
Y = OR(IFAIL1(I), IVP(I, I2) )
244 XFAIL2(I) = AND(X, Y)
I3INIT = I2 + 1
DO 44 I3 = I3INIT, IFIN3
DO 344 I = 1, NS
X = AND (IFAIL2(I), IVP(I, I3))
X = COMPL(X)
Y = OR(IFAIL2(I), IVP(I, I3))
344 XFAIL3(I) = AND(X, Y)
I4INIT = I3 + 1
DO 44 I4 = I4INIT, IFIN4
DO 444 I = 1, NS

```

```

X = AND (IFAIL3(I), IVP(I, I4))
X = COMPL(X)
Y = OR(IFAIL3(I), IVP(I, I4))
444 XFAIL4(I) = AND(X, Y)
I5INIT = I4 + 1
DO 44 I5 = I5INIT, IFIN
NFAIL = 0
DO 544 I = 1, NS
X = AND (IFAIL4(I), IVP(I, I5))
X = COMPL(X)
Y = OR(IFAIL4(I), IVP(I, I5))
XFAIL (I) = AND(X, Y)
CALL ICOUNT (IFAIL(I), NONES )
544 NFAIL = NFAIL + NONES
NINALL = NINALL + 1
IF (NFAIL .GT. NFAIL2) GO TO 44
NPOSS0 = NPOSS0 + NMULT
CALL ITEST
44 CONTINUE
49 PRINT 150, NFAIL1, NINALL
150 FORMAT ( // 33H THE NO. OF COMBINATIONS OF UP TO, I2, 55H FAILURE
1S THAT WERE CONSIDERED FOR THE FIRST GROUP WERE , I8)
PRINT 50, NPOSS0, NFAIL1, NFAIL2, EMAX
50 FORMAT ( /7H OUT OF, I7, 56H SOLUTIONS WHICH SATISFY THE CONDITION
1 THAT NO MORE THAN , I3, 20H SAYRE RELATIONSHIPS
2 / 41H FAIL IN THE FIRST GROUP AND NO MORE THAN , I4,
3 55H FAIL IN ALL, ONLY THE ABOVE PRINTED ONES ALSO SATISFY
4 / 83H THE CONDITION THAT FOR NO REFLEXION IS THE SUM OF EEE@S OVER
5ER FAILURES GREATER THAN , F8.2 )
IF (OUTPUT .NE. 0) END FILE OUTPUT *
IF (OUTPUT .NE. 0) PRINT 5, OUTPUT, OUTFIL
5 FORMAT (/ 40H THOSE PRINTED HAVE BEEN OUTPUT ON UNIT ,
1 I3, 5H FILE, I3)
STOP
END
$IBFTC POSN DECK
SUBROUTINE POSN ( INPUT,INFILE)
ASSIGN 14 TO IENDF
CALL EOF (INPUT, IENDF)
12 REWIND INPUT

```

14 NFILE = INFILE
IF (NFILE .LE. 1) GO TO 13

18 NFILE = NFILE - 1
READ (INPUT) II
GO TO 18

13 RETURN
END

\$IBFTC ITEST DECK

SUBROUTINE ITEST

COMMON EEE, EMAX, I2N, IDMISS, IFAIL, IFIN, IMULT,

1 ISIG, ISIGS, IXS, IXT, NFAIL, NMULT,

2 NPOSS, NS, OUTPUT

DATA INEG, IZERO / 04000000000000 , 00000000000000 /
INTEGER OUTPUT, OUTFIL, BLANK, PLUS

DIMENSION IFAIL(3), XFAIL(3), I2N(35), NF(20), IDX(35), IXS(4, 105)

DIMENSION ISIG(35), ISIGS(35), IMULT(35, 16), IDMISS(20), EEE(105)

DIMENSION IXT(105)

EQUIVALENCE (IFAIL, XFAIL), (IX, XX), (IL, XL)

DATA BLANK, PLUS, MINUS, COMMA / 2H , 2H +, 2H -, 1H, /

DUMMY = 0.0

NF(1) = 0

NF(2) = 0

J = 0

IF(NFAIL .EQ. 0) GO TO 36

IX = IZERO

DO 1 I = 1, NFAIL

2 J = J + 1

K = (J - 1) / 35

L = J - K * 35

XL = AND (I2N(L), IFAIL(K + 1))

IF (IL .EQ. 0) GO TO 2

NF(I) = J

XX = OR (IX, IXT(J))

1 CONTINUE

C NOW TO IDENTIFY THE X@S

C IDX = IDENTITY OF X@S

J = 0

I = 0

3 I = I + 1

4 J = J + 1

IF (J .GT. 35) GO TO 5
XL = AND(I2N(J), IX)

IF (IL .EQ. 0) GO TO 4
IDX(I) = I2N(J)
GO TO 3

5 NX = I - 1
C NX NOW HAS IDENTITY OF NO. OF DISTINCT X@S IN FAILURES
C NOW TO TEST IF ANY X@S SUM TOO HIGH

SUMMAX = 0.0
SSUME2 = 0.0
DO 6 I = 1, NX
SUME = 0.0
L = IDX(I)
DO 7 J = 1, NFAIL

K = NF(J)
XL = AND (IXT(K), L)
IF (IL .NE. 0) SUME = SUME + EEE(K)

7 CONTINUE
IF (SUME .GT. EMAX) GO TO 57
IF (SUME .GT. SUMMAX) SUMMAX = SUME
SSUME2 = SSUME2 + SUME ** 2

6 CONTINUE
36 CONTINUE

J = 0
IFAIL(1) = - IFAIL(1)
DO 37 I = 1, IFIN

52 K = I + J
IF (K .NE. IDMISS(J + 1)) GO TO 51
J = J + 1

GO TO 52
51 NONES = 0
DO 68 L = 1, NS
XL = AND(IXS(L + 1, I), IFAIL(L))
CALL ICOUNT (XL, NONES1)
68 NONES = NONES + NONES1

ISIG (K) = +1
37 IF (NONES / 2 * 2 .NE. NONES) ISIG (K) = -1
DO 93 JK = 1, NMULT
NPLUS = 0
DO 94 JL = 1, 35

ARBITRAR
ARBITRAR
ARBITRAR
ARBITRAR
ARBITRAR

	IQ = ISIG(JL) * IMULT(JL, JK)	ARBITRAR
	ISIGS(JL) = BLANK	ARBITRAR
	IF (IQ .LT. 0) ISIGS(JL) = MINUS	ARBITRAR
	IF (IQ .LE. 0) GO TO 94	ARBITRAR
	ISIGS(JL) = PLUS	ARBITRAR
	NPLUS = NPLUS + 1	ARBITRAR
94	CONTINUE	ARBITRAR
	NPOSS = NPOSS + 1	ARBITRAR
	PRINT 40, NPOSS, (ISIGS(I), I = 1, 35), NPLUS,	ARBITRAR
	1 SUMMAX, SSUME2, NF(1), (COMMA, NF(I), I = 2, NFAIL)	
40	FORMAT (1X, I4, 2X, 3(10A2, 1X), 5A2, 1X, I3, 2X,	
	1 F5.1, 1X, F8.0, 2X, 10(I2, A1) / (102X, 10(I2, A1)))	
	WRITE (OUTPUT) (ISIGS(I), I = 1, 16)	
	WRITE (OUTPUT) (ISIGS(I), I = 17, 32)	
	WRITE (OUTPUT) (ISIGS(I), I = 33, 35), (DUMMY, I = 4, 16)	
93	CONTINUE	ARBITRAR
	IF (NMULT .NE. 1) PRINT 95	ARBITRAR
95	FORMAT (/ 1H)	ARBITRAR
57	RETURN	
	END	

\$IBMAP	ICOUNT	DECK
	ENTRY	ICOUNT
ICOUNT	SAVE	1,2,4
	LAC	ICOUNT,4
	ANA	=077777777777
	CAL*	2,4
	TNZ	*+3
	STZ*	3,4
	TRA	RET
	LGR	36
	AXT	36,1
	AXT	36,2
	ZAC	
10	LOOP	LGL 1
	LBT	
	TIX	*+1,1,1
	TIX	LOOP,2,1
	PXA	,1
	STO*	3,4
4	RET	BRN ICOUNT-5

RETURN ICOUNT
END

SENTRY

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ESIGND PROGRAM

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\$IBFTC ESIGND DECK,REF
REAL MINUS, MINE

INTEGER OUTPUT

DATA PLUS, MINUS, BLANK / 2H +, 2H -, 2H /
DIMENSION SIGNS(6, 35), SE(6), FH(3), IPOSS(6)

READ 1, INE, IFE, INS, IFS, OUTPUT, NPOSS, MINE, (IPOSS(I), I = 1,
1 NPOSS)

1 FORMAT (6I2, F8.0, 6I5)

CALL POSN(INS, IFS)

K = 0

DO 15 I = 1, NPOSS

16 K = K + 1

READ (INS) (SIGNS(I, J), J = 1, 16)

READ (INS) (SIGNS(I, J), J = 17, 32)

READ (INS) (SIGNS(I, J), J = 33, 35)

IF (IPOSS(I) .NE. K) GO TO 16

DO 17 J = 1, 35

IF (SIGNS(I, J) .NE. PLUS) GO TO 18

SIGNS(I, J) = 1.0

GO TO 17

18 IF (SIGNS(I, J) .NE. MINUS) GO TO 19

SIGNS(I, J) = -1.0

GO TO 17

19 SIGNS(I, J) = 0.0

17 CONTINUE

15 CONTINUE

REWIND INS

REWIND OUTPUT

CALL POSN(INE, IFE)

DO 7 L = 1, 6

7 SE(L) = 0.0

PRINT 11, INE, IFE, MINE, INS, IFS, OUTPUT

11 FORMAT (24H THE REFLEXIONS ON UNIT , I2, 6H FILE , I2,

1 23H WITH @E@ NOT LESS THAN , F7.3, 34H WILL BE ASSIGNED SIGNS AS 0

2N UNIT , I3, 5H FILE , I3, 4H ANDT / 10X, 24H WILL BE OUTPUT ON UN

3IT , I2, 12H AS FOLLOWS //)

PRINT 12

12 FORMAT(1X, 5HIGPEN, 3X, 2HFK, 4X, 2HFK, 4X, 2HFL, 8X, 2HE1, 5X,

1 2HE2, 5X, 2HE3, 5X, 2HE4, 5X, 2HE5, 5X, 2HE6 /)

DO 2 I = 1, 36

```

8  READ (INE ) II, IGPEN, SSOLS, (FH(K), K = 1, 3), E
   IF(IGPEN .NE. 0) GO TO 4
   IF(II .NE. 0) GO TO 14
   IF (E .LT. MINE) GO TO 8
   IF (I .EQ.36) GO TO 2
   DO 6 K = 1, NPOSS
6   SE(K) = E * SIGNS(K, I)
   WRITE (OUTPUT) IGPEN, (FH(K), K = 1, 3), (SE(K), K = 1, 6)
   PRINT 13, IGPEN, (FH(K), K = 1, 3), (SE(K), K = 1, 6)
13  FORMAT (2X, I2, 2X, 3(2X, F4.0), 3X, 6(2X, F5.2) )
   GO TO 2
4   WRITE (OUTPUT) IGPEN, (FH(K), K = 1, 3), E, E, E, E, E, E
   PRINT 13, IGPEN, (FH(K), K = 1, 3), E, E, E, E, E, E
   GO TO 8
2   CONTINUE
   PRINT 10, MINE
10  FORMAT (// 71H ERROR... TAPE HAS MORE THAN 35 REFLEXIONS ON IT WIT
14  1H @E@ NOT LESS THAN , F7.3 )
   REWIND INE
   END FILE OUTPUT
   REWIND OUTPUT.
   STOP
   END
$IBFTC POSN DECK
   SUBROUTINE POSN ( INPUT,INFILE)
   ASSIGN 14 TO IENDF
   CALL EOF (INPUT, IENDF)
12  REWIND INPUT
   NFILE = INFILE
14  IF (NFILE .LE. 1) GO TO 13
   NFILE = NFILE - 1
18  READ (INPUT) II
   GO TO 18
13  RETURN
   END
$ENTRY

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ROT PROGRAM

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\$IBFTC ROT

DIMENSION FF(8), FH(300), FK(300), FOBS(300), FCL(300), FC(300)
DIMENSION TFCL(300), TFC(300), RADO(6), RADC(6), ANGO(6), ANG(6)
DIMENSION IEVOD(300), XC(6), YC(6), FCALC(300), FOBSSC(300)
DIMENSION FO(300), TFO(300), XO(6), YO(6)
DIMENSION FOBSMN(300), FMIN(300), XOM(6), YOM(6), XCM(6), YCM(6)
IN = 3

REWIND 11

CALL POSN (IN, 3)

253 NN = 0

READ 7, A, B, THETA, THEINC, THEMAY

7 FORMAT (5F10.0)

READ 170, FOMN, TCL, TO, TC, NO, NC, IFOBS, IFCALC

170 FORMAT (4F10.0, 4I5)

PRINT 180, FOMN

180 FORMAT (1X, 7HFOMN = , F7.1 //)

DO 2 N = 1, 2000

READ (IN) II, IGPEN, SSOLS, XH, XK, XL, XOBS, XOBS2, (FF(I), I=1,8)

IF (II .NE. 0) GO TO 1

IF (IGPEN .NE. 0) GO TO 2

IF (XL .NE. 0.0) GO TO 2

IF (XOBS .LT. FOMN) GO TO 2

NN = NN + 1

FH(NN) = XH

FK(NN) = XK

FOBS(NN) = XOBS

FCL(NN) = FF(1)

FO(NN) = FF(2)

FC(NN) = FF(3)

TFCL(NN) = EXP(-TCL * SSOLS)

TFO(NN) = EXP(-TO * SSOLS)

TFC(NN) = EXP(-TC * SSOLS)

2 CONTINUE

1 PRINT 3

3 FORMAT (45H THE 001 PROJECTION OF SPACE GROUP P 21,21,2 //)

IF (IFOBS .EQ. 0) GO TO 175

PRINT 4

4 FORMAT (8X, 1HH, 4X, 1HK, 6X, 4HFOBS, 4X, 57HS.F.CHLOR S.F.OXYG S.F.CA

1RB T.F.CHLOR T.F.OXYG T.F.CARB)

DO 5 I = 1, NN

```

5      PRINT 6, FH(I), FK(I), FOBS(I), FCL(I), FO(I), FC(I), TFCL(I),
1      TFO(I), TFC(I)
6      FORMAT (5X, 2F5.0, F10.1 , 3F10.2, 3F10.5 )
175     READ 7, CLX, CLY
        DO 8 I = 1, NO
8      READ 7, RADO(I), ANGO(I)
        DO 171 I = 1, NC
171     READ 7, RADC(I), ANGC(I)
        PI = 3.14159
        DO 9 I=1, NN
            SUMHK = FH(I) + FK(I)
            ISUM1 = SUMHK
            ISUM2 = ISUM1 / 2 * 2
            IF (ISUM1 .NE. ISUM2 ) GO TO 10
            IEVOD(I) = 2
            FCL(I) = FCL(I)* TFCL(I)* 4.0 * COS(2.0 * PI * FH(I) *CLX )
1            * COS(2.0 * PI * FK(I) * CLY )
            GO TO 9
10     IEVOD(I) = 1
            FCL(I) = FCL(I)* TFCL(I)*(-4.)* SIN(2.0 *PI * FH(I)* CLX )
1            * SIN(2.0 * PI * FK(I) * CLY )
9      CONTINUE
C      NOTE THAT FCL(I) IS NOW THE CHLORINE@S CONTR. TO STRUCTURE FACTORS
        S = ABS(THEMAX - THETA)
        T = S / ABS(THEINC)
        IDO = T
        IDO = IDO + 1
        DO 11 I = 1 , NN
            FO(I) = FO(I) * 4.0 * TFO(I)
            FC(I) = FC(I) * 4.0 * TFC(I)
            FH(I) = 2.0 * PI * FH(I)
            FK(I) = 2.0 * PI * FK(I)
11     C      NOTE THAT FC(I) NOW CONTAINS THE TEMP. FACTOR AND THE MULTIPLIER 4
        C      NOTE THAT FH AND FK ARE REDEFINED
        SUMFO = 0.0
        THETA=THETA-THEINC
        DO 27 I=1, NN
27     SUMFO = SUMFO + ABS(FOBS(I))
        PRINT 150, SUMFO
150    FORMAT (/9H SUMFO = , F7.0 )

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      PRINT 151, CLX, CLY
151  FORMAT (// 1X, 29HCOORDINATES OF CHLORINE ARE (, 1X, F5.3, 1H,,
      1      1X, F5.3, 1X, 1H) //)
      PRINT 100
100  FORMAT(/119H THETA      SUMFC      R      X 1      Y 1      X 2      Y 2
      1      X 3      Y 3      X 4      Y 4      X 5      Y 5      X 6      Y 6 )
      RM = 2.0
      WRITE (11) IDO
      DO 101 K = 1, IDO
      THETA = THETA + THEINC
      DO 102 L = 1, NO
      ROTANG = ANGO(L) + THETA
      XO(L) = ( COS( ROTANG ) * RADO(L) ) / A + CLX
102  YO(L) = ( SIN( ROTANG ) * RADO(L) ) / B + CLY
      DO 172 L = 1, NC
      ROTANG = ANGC(L) + THETA
      XC(L) = ( COS( ROTANG ) * RADC(L) ) / A + CLX
172  YC(L) = ( SIN( ROTANG ) * RADC(L) ) / B + CLY
      SUMFC=0
      DO 24 I = 1, NN
      FCC = 0.0
      FCO = 0.0
      IF (IEVOD(I).EQ. 1) GO TO 20
      DO 21 J = 1, NO
      21  FCO = FCO + COS(FH(I) * XO(J)) * COS(FK(I) * YO(J))
      DO 121 J = 1, NC
      121 FCC = FCC + COS(FH(I) * XC(J)) * COS(FK(I) * YC(J))
      GO TO 22
      20  DO 23 J = 1, NO
      23  FCO = FCO - SIN(FH(I) * XO(J)) * SIN(FK(I) * YO(J))
      DO 123 J = 1, NC
      123 FCC = FCC - SIN(FH(I) * XC(J)) * SIN(FK(I) * YC(J))
      22  FCALC(I) = FCL(I) + FCO * FO(I) + FCC * FC(I)
      24  SUMFC = SUMFC + ABS(FCALC(I))
      SCALE = SUMFC / SUMFO
      R = 0.0
      DO 26 I = 1, NN
      FOBSSC(I) = SCALE * FOBS(I)
      26  R = R + ABS( ABS( FOBSSC(I) ) - ABS(FCALC(I)))
      R = R / SUMFC

```

```

      IF ( R .GE. RM ) GO TO 126
      DO 127 I = 1, NN
        FOBSMN(I) = FOBSSC(I)
127    FMIN(I) = FCALC(I)
        DO 25 I = 1, NO
          XOM(I) = XO(I)
25    YOM(I) = YO(I)
          DO 125 I = 1, NC
            XCM(I) = XC(I)
125    YCM(I) = YC(I)
          RM = R
          THETAM = THETA
126    PRINT 28, THETA, SUMFC, R, ((XO(I), YO(I)), I = 1, NO )
28    FORMAT(1X,F6.3,1X,F7.0, 2X, F6.3, 12(2X, F6.3) )
          WRITE (11) THETA, R
101    PRINT 128, ((XC(I), YC(I)), I = 1, NC )
128    FORMAT ( 23X, 12(2X, F6.3)/)
          PRINT 162, THETAM, RM
162    FORMAT (////// 1X, 52HCOORDINATES OF VARIOUS ATOMS IN 1/120@S FOR T
1HETA = , F6.3, 9H AND R = , F6.3, / )
          CLX = CLX * 120.0
          CLY = CLY * 120.0
          DO 163 I = 1, NO
            XOM(I) = XOM(I) * 120.0
163    YOM(I) = YOM(I) * 120.0
            DO 164 I = 1, NC
              XCM(I) = XCM(I) * 120.0
164    YCM(I) = YCM(I) * 120.0
            PRINT 165, CLX, CLY
165    FORMAT ( 10X, 8HCHLORINE, 5X, 2(2X, F6.1) / )
            PRINT 166, (( XOM(I), YOM(I) ), I = 1, NO)
166    FORMAT ( 10X, 7HOXYGENS , 6X, 12(2X, F6.1) )
            PRINT 167, (( XCM(I), YCM(I) ), I = 1, NC )
167    FORMAT (/10X, 7HCARBONS , 6X, 12(2X, F6.1) / )
            IF ( IFCALC .EQ. 0 ) STOP
            PRINT 161
161    FORMAT (////// 3X, 1HH, 4X, 1HK, 5X, 9HFOBSMN(I), 3X, 8HFMIN(I) ,//)
            DO 29 I = 1, NN
              FH(I) = FH(I) / ( 1.9999 * PI )
              FK(I) = FK(I) / ( 1.9999 * PI )

```


29 PRINT 160, FH(I), FK(I), FOBSMN(I), FMIN(I)
160 FORMAT (2(1X, F4.0), F10.1, 2X, F10.1)

STOP

END

\$IBFTC POSN

SUBROUTINE POSN (INPUT, INFILE)

ASSIGN 14 TO IENDF

CALL EOF (INPUT, IENDF)

12 REWIND INPUT

NFILE = INFILE

14 IF (NFILE .LE. 1) GO TO 13

NFILE = NFILE - 1

18 READ (INPUT) II

GO TO 18

13 RETURN

END

\$ENTRY

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CONTUR PROGRAM

(THE UTV SUBROUTINE IS A U.B.C. COMPUTING CENTRE PROGRAM TO
RESERVE BUFFERS FOR, AND TO ALLOW THE USE AS VARIABLES OF,
TAPE UNITS 01, 02, 03, 04, 11, 12, 13, AND 14)

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\$IBFTC CONTUR DECK

```

C   THIS PROGRAM WRITTEN AT THE UNIV. OF BRITISH COLUMBIA BY R. HOGE
    START = CLOCK(0.0)
    REWIND 4
    CALL PLOTS
    DIMENSION LAXI(3)
    DIMENSION RHO(31, 31), IDIV(16)
    DIMENSION LABEL(14), LQ(12)
    DIMENSION LIMIT(10), TDELTA(10), HGHIY(10)
    DATA LAXI / 18HX AXISY AXISZ AXIS /
    DIMENSION XYZ(3)
    DATA XYZ(1), XYZ(2), XYZ(3) / 1HX, 1HY, 1HZ /
    REAL LX, LY, LYSECT, LYAXIS(10), LY10, LYLEFT
    INTEGER SIL, SYMBL(16)
    DIMENSION ICYCLX(241), ICYCLY(241)
    DIMENSION RHOO(61, 61), ICON(61, 121)
    DIMENSION C(16)
    COMMON IN12, NPASSS, NEWZ, ICON, ICYCLX, LABEL, LIMIT, HGHIY, IDIV, C
    SYMBL(1) = 0
    SYMBL(4) = 5
    SYMBL(7) = 2
    SYMBL(10) = 1
    SYMBL(13) = 12
100  FORMAT (5I2)
101  FORMAT (13A6, A2)
102  FORMAT (2I1, 4I2, 5F10.0)
108  FORMAT ( 8F10.0 )
117  FORMAT ( 1X, 12HTAPE UNIT = , I2, 3X, 10HNPPASSES = , I2, 3X,
1      9HNPAIRS = , I2, 3X, 7HNEWZ = , I2 )
118  FORMAT (9H TITLE- ,13A6, A2)
119  FORMAT (1X, 5HNA = , I2, 3X, 5HNB = , I2, 3X, 9HNCONTOUR = , I2, 3X,
1      8HIPASS = , I2, 3X, 7HILAB = I2, 3X, 6HIPR = , I2)
120  FORMAT(5X, 8HAAXIS = , F8.3, 3X,
1      8HBAXIS = , F8.3, 3X,
2      8HTHETA = , F8.2, 3X,
3      9HSCALER = , F7.2, 3X,
4      9HCLKMAX = , F6.1)
121  FORMAT (1X, 12HCONTOURS AT 16F7.0)
123  FORMAT (// 1X, 94HALL TIMES SHOWN BELOW ARE MINUTES ELAPSED SINCE

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1 THE BEGINNING OF EXECUTION OF @CONJURE PROGRAM )
122  FORMAT ( 11H1DATA CARDS /)
52  READ 100, IN12, NPASSS,NPAIRS ,NEWZ
    PRINT 122
    PRINT117, IN12, NPASSS,NPAIRS , NEWZ
    IF (NEWZ .NE. 0) CALL AL1Z
    REWIND IN12
    READ 101, (LABEL(I), I = 1, 14)
    PRINT 118,(LABEL(I), I = 1, 14)
    READ 102, NA, NB, NCONTU, IPASS, ILAB, IPR, AAXIS, BAXIS, THETA,
1    SCALER, CLKMAX
    PRINT 119,NA, NB, NCONTU, IPASS, ILAB, IPR
    PRINT 120,AAXIS, BAXIS, THETA, SCALER, CLKMAX
    READ 108, (C(I), I = 1, 8)
    IF (NCONTU .GT. 8) READ 108, (C(I), I = 9, NCONTU)
    PRINT 121, (C(I), I = 1, NCONTU)
    PRINT 123
    DO 270 I = 2, NCONTU
270  IF(C(I) .LT. C(I-1)) GO TO 237
    NP = NPASSS - NPAIRS
    DO 275 IP = 1, NP
    IF (NPASSS .NE. 1 .OR. NPAIRS .NE. 0) GO TO 276
    INPUT1 = 0
    INPUT = IN12
    GO TO 277
276  READ (IN12 ) IZ0, IX0, IY0, IDZ, IDX, IDY, INZ, INX, INY, KK,II,JJ
    REWIND 13
    WRITE(13) IZ0, IX0, IY0, IDZ, IDX, IDY, INZ, INX, INY, KK,II,JJ
    DO 281 K = 1, INZ
281  READ (IN12 ) (( RHOO(I,J), I = 1, INX), J = 1, INY )
    WRITE( 13 ) (( RHOO(I,J), I = 1, INX), J = 1, INY )
    INPUT = 13
    INPUT1 = 0
    IF (NPAIRS .EQ. 0) GO TO 277
    REWIND 14
    INPUT1 = 14
    READ (IN12 ) IZ0, IX0, IY0, IDZ, IDX, IDY, INZ, INX, INY, KK,II,JJ
    WRITE(14) IZ0, IX0, IY0, IDZ, IDX, IDY, INZ, INX, INY, KK,II,JJ
    DO 282 K = 1, INZ
    READ (IN12 ) (( RHOO(I,J), I = 1, INX), J = 1, INY )

```

```

282  WRITE( 14 ) (( RHOO(I,J), I = 1, INX), J = 1, INY )
      REWIND INPUT1
      NPAIRS = NPAIRS - 1
277  REWIND INPUT
      READ (INPUT) IZ0, IX0, IY0, IDZ, IDX, IDY, INZ, INX, INY, KK,II,JJ
      IF ((NA - II + NB - JJ) .NE. 0) GO TO 239 @
      ORIGIN = 0.0
      NPASS = 1 *
      IF (THETA .EQ. 0.0) THETA = 90.00
      IF (INPUT1 .LT. 2) GO TO 1
      NPASS = 2 *
      READ(INPUT1) IZ01, IX01, IY01, IDZ1, IDX1, IDY1, INZ1, INX1, INY1,*
1      KK1, II1, JJ1 *
      IF (IDZ .NE. IDZ1 .OR. IDX .NE. IDX1 .OR. IDY .NE. IDY1) GO TO 238$
      IF (INZ .NE. INZ1 .OR. INX .NE. INX1 .OR. INY .NE. INY1) GO TO 238$
      IF (KK .NE. KK1 .OR. II .NE. II1 .OR. JJ .NE. JJ1) GO TO 238$
      IF (IX0 .NE. IX01 .AND. IY0 .NE. IY01) GO TO 238 $
      IF (IX0 .EQ. IX01 .AND. IY0 .EQ. IY01) GO TO 238 $
      IF (IZ0 .NE. IZ01 ) GO TO 238 $
      NOTE = II $
      IF(IY0 .NE. IY01) NOTE = JJ $
      IF (NOTE .NE. NA) GO TO 51 *
      GO TO 1
51  Q = AAXIS
      AAXIS = BAXIS
      BAXIS = Q
      IQ = NA
      NA = NB
      NB = IQ
1  IF ((NA - NB) .EQ. 1 .OR. (NA - NB) .EQ. (-2)) ORIGIN = 10.0
      IORDER = 0
      IF (NA .EQ. II) GO TO 3
      IORDER = -1
      IQ = IX0
      IX0 = IY0
      IY0 = IQ
      IQ = IDX
      IDX = IDY
      IDY = IQ
      IQ = INX

```

INX = INY
INY = IQ

IQ = II
II = JJ
JJ = IQ

IF (INPUT1 .LT. 2) GO TO 3

IX01 = IY01
IDX1 = IDY1

INX1 = INY1

3 REWIND INPUT

IF (INPUT1 .GE. 2) REWIND INPUT1

IF (INPUT1 .GE. 2 .AND. (IX0 + IDX * (INX - 1)) .NE. IX01) GO TO
1 238

TOTAL = CLOCK(START) / 3600.0

PRINT 103, TOTAL

103 FORMAT(///9X,39HAXES ADJUSTED FOR PROPER PLOTTER FORMAI,
1 14X, 7HTIME = , F10.2)

PI = 3.14159

RADTHA = PI / 180.0 * IHEIA

IF (SCALER .NE. 0.0) GO TO 278

X = (INY - 1) * IDY

SCALER = 25.4 * 120.0 / BAXIS / X / SIN(RADTHA)

278 SCALE = 1.0 / 0.393700 / SCALER

C SCALE = ANGSTOMS / INCH

Q = (INX - 1) * IDX

LX = Q * AAXIS / 120.0 / SCALE

Q = (INY - 1) * IDY

LY = Q * BAXIS / 120.0 / SCALE

Q = IDY

DLY = Q * BAXIS / 120.0 / SCALE

HY = LY * SIN(RADTHA)

DHY = DLY * SIN(RADTHA)

CONST1 = 2 * INY - 2

CONST2 = 2 * INX - 2

CONST2 = LX / CONST2

CONST3 = LY * COS(RADTHA) / CONST1

CONST1 = HY / CONST1

LY10 = 10.0 / SIN(RADTHA)

GRITY = 0.0

IDIV(1) = 2

```

7      DO 7 I = 2, NCONTU
      IDIV(I) = IDIV( I - 1 ) * 2
      IF (LY .GT. LY10) GO TO 232
      NPARTS = 1
      GO TO 10
232    DO 11 J = 2, INY
      GRITY = GRITY + DHY
      IF (GRITY - 10.0 .LE. 0.0) GO TO 11
      LIMIT(1) = J- 1
      GO TO 8
11     CONTINUE
8      IJ = LIMIT(1) - 1
      DO 9 I = 2, 10
      NPARTS = I
      IQ = I * IJ + 1
      IF (INY - IQ .LE. 0) GO TO 10
9      LIMIT(I) = IQ
10     LIMIT(NPARTS) = INY
      Q = (LIMIT(1) - 1) * IDY
      LYSECT = Q * BAXIS / 120.0 / SCALE
      DO 12 I = 1, 10
12     LYAXIS(I) = LYSECT
      Q = NPARTS - 1
      LYAXIS(NPARTS) = LY - Q * LYSECT
      DO 14 I = 1, 10
      TDELTA(I) = LYAXIS(I) * COS(RADT+A)
14     HGHTY(I) = LYAXIS(I) * SIN(RADTHA)
      SHIFT = 0.0
      IF ( THETA .GT. 90.0 )  SHIFT = LY10 * COS(PI - RAD1HA)
      THETA1 = THETA
      IF ( ORIGIN .EQ. 10.0 ) THETA1 = 180.0 - THETA
      RADTH1 = THETA1 * PI / 180.0
      STALAB = 0.0
      IF ( THETA1 .GT. 90.0 ) STALAB = LY10 * COS(PI - RAD1H1)
      JINIT = 1
      NINX = 2*INX - 1
      NINX2 = NINX - 2
      TOTAL = CLOCK(START) / 3600.0
      PRINT 104, TOTAL
104    FORMAT (/ 9X, 28HVARIOUS CONSTANTS CALCULATED,

```

25X, @

```

1      7HTIME = , F10.2 )
      TOT = 0.0
      CALL PLOT (2.0, 0.0, -3)
      IF (NP .EQ. 1) GO TO 279
      IF (IPR.EQ. 1) GO TO 279
      CALL SYMBOL (0.0, 0.0, 0.28, 5HPASS-, THEIA1, 5)
      X =      6.0 / 7.0 * 0.28 * 5.0 * COS(RADTH1)
      Y =      6.0 / 7.0 * 0.28 * 5.0 * SIN(RADTH1)
      XP = IP
      CALL NUMBER ( X, Y, 0.28, XP, THEIA1, -1)
      CALL PLOT ( 1.0, 0.0, -3 )
279    IF (IP .EQ. 1) GO TO 284
      IF (IPR .EQ. 1 .OR. ILAB .EQ. (-1) ) GO TO 280
284    Q = 0.0
      IF (THETA .NE. 90.0) Q = 1.0/ TAN(RADTH1)
      DO 271 J = 1, NCONTU
      Y = J - 1
      Y = Y * 0.3
      X = Y * Q + STALAB
      IF ( J .EQ. 1 .OR. J .EQ. 4 .OR. J .EQ. 7 .OR. J .EQ. 10 .OR.
1      J .EQ. 13 ) CALL SYMBOL(X - 0.2, Y + 0.05, 0.1, SYMBL(J),0.0,-1)@
271    CALL NUMBER (X, Y, 0.1, C(J), 0.0, -1)
      CALL PLOT ( 1.0, 0.0, -3 )
      X = 0.1 + STALAB
      CALL SYMBOL ( X, 0.0, 0.14, LABEL(1), THEIA1, 80 )
280    DO 15 IPARTS = 1, NPARTS
      QPARTS = IPARTS
      LIMJ = LIMIT(IPARTS)
      NINY = 2 * (LIMJ - JINIT) + 1
      NINY2 = NINY - 2
      IINY = LIMJ - JINIT + 1
      NICONY = 2*NINY - 1
      NCYCL = 2 * NINX + 2 * NINY - 4
      DO 204 I = 1, NINX
      ICYCLX( I) = I
204    ICYCLY( I) = 1
      DO 205 I = 2, NINY
      I1 = I + NINX - 1
      ICYCLX( I1) = NINX
205    ICYCLY( I1) = I

```



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      IQ = NINX - 1
      DO 206 I= 2, IQ
        I1 = 2*NINX + NINY -1 -I
        ICYCLX( I1) = I
206     ICYCLY( I1) = NINY
        DO 207 I = 2, NINY
          I1 = 2*NINX + 2*NINY - 2 - I
          ICYCLX( I1) = 1
207     ICYCLY( I1) = I
          ICYCLX(ICYCL + 1) = 1
          ICYCLY(ICYCL + 1) = 1
        READ (INPUT) (LQ(I) , I = 1, 12)
        IF (INPUT1 .GE. 2) READ(INPUT1) (LQ(I), I = 1, 12)
        X = 0.4 + STALAB
        IF (NPARTS .EQ. 1) GO TO 283
        CALL SYMBOL ( X, 0.0, 0.14, 5HPART-, THETA1, 5 )
        X = X + 6.0 / 7.0 * 0.14 * 5.0 * COS(RADTH1)
        Y =      6.0 / 7.0 * 0.14 * 5.0 * SIN(RADTH1)
        CALL NUMBER ( X, Y, 0.14, QPARTS, THETA1, -1 )
283     CALL PLOT ( 0.8, 0.0, -3 )
        TOTAL = CLOCK(START) / 60.0 / 60.0
        PRINT 105, IPARTS, TOTAL
105     FORMAT ( / 9X, 14HLABEL FOR PART , I2, 8H WRITTEN , 29X,
1       7HTIME = , F10.2 )
        DO 24 K = 1, INZ
          IF ( CLKMAX .EQ. 0.0 ) GO TO 25
          TOTAL = CLOCK(START) / 3600.0
          IF ( CLKMAX - TOTAL -1.00 .LT. TOTAL - TOT ) GO TO 21
          TOT = TOTAL
25     QK = ( K-1 ) * IDZ + IZ0
          IF (IPR .EQ. 1) QK = IP
          X = STALAB + 0.2
          CALL NUMBER ( X, 0.0, 0.28, QK, THETA1, -1 )
          IF (IPR .EQ. 1) GO TO 272
C      STATEMENTS LABLED ***** ARE INCLUDED BECAUSE @CALL NUMBER@ CANNOT
C      FORM A ZERO ( 0 )
          IF (QK .EQ. 0.0) CALL SYMBOL ( X, 0.0, 0.28, 1HU, THETA1, 1 )
          IF (K .NE. 1.AND. K .NE. INZ) GO TO 272
          X = X + 6.0 / 7.0 * 0.28 * COS(RADTH1) * 3.0
          Y =      6.0 / 7.0 * 0.28 * SIN(RADTH1) * 3.0

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```

CALL SYMBOL ( X, Y, 0.14, 10H/120 ALONG, THETA1, 10 )
X = X + 6.0 / 7.0 * 0.14 * COS(RADTH1) * 12.0
Y = Y + 6.0 / 7.0 * 0.14 * SIN(RADTH1) * 12.0
CALL SYMBOL ( X, Y, 0.28, XYZ(KK), THETA1, 1 )
272 CALL PLOT ( 0.8, ORIGIN, -3 )
DO 24 M = 1, NPASS
IF (K .NE. 1.AND. K .NE. INZ) GO TO 234
X = SHIFT + LX/2.0-0.34
Y = -0.24
IF (ORIGIN .NE. 0.0) Y = +10.1
CALL SYMBOL (X, Y, 0.14, LAXI(II), 0.0, 6)
X = LX + SHIFT - 0.32
Q = IX0 + (INX - 1) * IDX
IF (M .NE. 1)
1Q = IX01+ (INX1- 1) * IDX1
IF (NPASS .NE. 2 .OR. M .NE. 1)
1CALL NUMBER ( X, Y, 0.14, Q, 0.0, -1)
IF (Q .EQ. 0.0) CALL SYMBOL ( X , Y , 0.14, 1H0, 0.0 , 1 )
IF ( M .NE. 1) GO TO 234
Q = IX0
CALL NUMBER ( SHIFT, Y, 0.14, Q, 0.0, -1 )
IF (Q .EQ. 0.0) CALL SYMBOL (SHIFT, Y , 0.14, 1H0, 0.0 , 1 )
X = SHIFT - 0.1
Y = 0.0
Q = IY0 + (JINIT- 1) * IDY
IF (ORIGIN .NE..0) X= SHIFT - 0.32 * COS(RADTH1) - 0.1
IF ( ORIGIN .NE..0) Y = 9.68
CALL NUMBER (X, Y , 0.14, Q, THETA1, -1 )
IF (Q .EQ. 0.0) CALL SYMBOL ( X , Y , 0.14, 1H0, THETA1, 1 )
X = TDELTA(IPARTS) + SHIFT - 0.32 * COS(RADTH1) - 0.1
Y = HGHTY(IPARTS) - 0.32
IF (ORIGIN .NE. 0.0) Y = 10.0 - HGHTY(IPARTS)
IF (ORIGIN .NE. 0.0) X = TDELTA(IPARTS) + SHIFT - 0.10
Q = IY0 + (LIMJ - 1) * IDY
CALL NUMBER (X, Y, 0.14, Q, THETA1, -1)
IF (Q .EQ. 0.0) CALL SYMBOL ( X , Y , 0.14, 1H0, THETA1, 1 )
X = SHIFT + TDELTA(IPARTS) / 2.- 0.34 * COS(RADTH1) - 0.1
Y = HGHTY(IPARTS) / 2.- 0.34 * SIN(RADTH1)
IF (ORIGIN .NE.0.0) Y= 10.0-HGHTY(IPARTS) /2.-0.34 * SIN(RADTH1)
CALL SYMBOL (X, Y, 0.14, LAXI(JJ), THETA1, 6)

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```

234  CALL PLOT ( SHIFT, ORIGIN, +3 )
      Y = HGHTY(IPARTS)
      IF (ORIGIN .EQ. 10.0) Y = 10.0 - Y
      X = TDELTA(IPARTS) + SHIFT
      IF ( M .NE. 1)
1CALL PLOT ( X, Y, +3 )
      CALL PLOT ( X, Y, +2 )
      X = TDELTA( IPARTS) +LX + SHIFT
      CALL PLOT ( X, Y, +1 )
      X = LX + SHIFT
      IF (NPASS .NE. 1 .AND. M .NE. 2)
1CALL PLOT ( X, ORIGIN, +3 )
      CALL PLOT ( X, ORIGIN, +2 )
      CALL PLOT (SHIFT,ORIGIN, +1 )
      TOTAL = CLOCK(START) / 3600.0
      PRINT 109, K, M, TOTAL
109  FORMAT (/12X, 18HLAYOUT FOR SECTION, 12, 5H PASS, 12,
1          9H COMPLETE , 14X,
2          7HTIME = , F10.2 )
      INPU = INPUT
      IF (M .GT. 1) INPU = INPUT1
      IF ( IORDER .EQ. 0 ) GO TO 20
      READ (INPU ) (( RHOO(J,I), I = 1, INY), J = 1, INX )
      GO TO 23
20  READ (INPU ) (( RHOO(I,J), I = 1, INX), J = 1, INY )
23  DO 233 I = 1, INX
      N = 0
      DO 233 J = JINIT, LIMJ
      N = N+1
233  RHO(I, N) = RHOO(I, J)
      I1 = LIMJ - JINIT +1
      DO 201 I = 1, INX
      DO 201 J = 1, I1
      RHOO(2*I-1,2*J-1) = RHO(I,J)
      IF(I.NE.INX) RHOO(2*I, 2*J-1) = 0.5*(RHO(I,J) + RHO (I+1,J))
      IF(J.NE.I1) RHOO(2*I-1, 2*J) = 0.5*(RHO(I,J) + RHO (I,J+1))
201  IF(I.NE.INX .AND. J.NE.I1) RHOO(2*I,2*J) = 0.25 * (RHO(I,J) +
1          RHO(I+1,J) + RHO(I,J+1) + RHO(I+1,J+1))
      DO 202 I = 1,NINX
      DO 202 J = 1,NICONY

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202  ICON (I,J) = 0
      ITYPE = 1
      LEFTX   = 1
      STL = 1
208  DO 260 I = LEFTX, NCYCL, 2
      I1X = ICYCLX( I)
      I1Y = ICYCLY( I)
      I2X = ICYCLX( I + 2 )
      I2Y = ICYCLY( I + 2 )
      IF (RHOO(I1X, I1Y) .LT. RHOO(I2X, I2Y)) GO TO 264
      STL = 1
      GO TO 260
264  IF (STL .GT. NCONTU) GO TO 260
      DO 261 L = STL, NCONTU
      IF (RHOO(I1X, I1Y) .GE. C(L)) GO TO 261
      STL = L
      IF (RHOO(I2X, I2Y) .LT. C(L)) GO TO 260
      STL = L + 1
      LINCL = L
      GO TO 262
261  CONTINUE
      STL = NCONTU + 1
      GO TO 260
262  IMINX   = ICYCLX( I+1)
      IMINY   = ICYCLY( I+1)
      IMAXX = I2X
      IMAXY = I2Y
      IF(RHOO (IMINX, IMINY) .LT. C(LINCL))GO TO 265
      IMAXX = IMINX
      IMAXY = IMINY
      IMINX = I1X
      IMINY = I1Y
265  I3 = (IMAXX + IMINX ) / 2
      I4 = IMAXY + IMINY - 1
      LEFTX = I
      ICON(I3, I4) = ICON(I3, I4) + IDIV(LINCL) / 2
      I3 = 1
      IF(I4/2 * 2 .EQ. I4) I3 = -1
      IDIRX   = (IMAXY - IMINY ) * I3
      IDIRY   = (IMAXX - IMINX ) * I3
```

	GO TO 213	
260	CONTINUE	@
	ITYPE = 2	@
	LEFTX = 3	
	LEFTY = 1	
	STL = 1	@
218	DO 250 I = LEFTX, NINX2, 2	@
	IF (I .EQ. LEFTX) GO TO 257	@
	STL = 1	@
	LEFTY = 1	@
257	DO 250 J = LEFTY, NINY2, 2	@
	IF (RH00(I, J) .LT. RH00(I, J+2)) GO TO 254	@
	STL = 1	@
	GO TO 250	@
254	IF (STL .GT. NCONTU) GO TO 250	@
	DO 251 L = STL, NCONTU	@
	IF (RH00(I, J) .GE. C(L)) GO TO 251	@
	STL = L	@
	IF (RH00(I, J+2) .LT. C(L)) GO TO 250	@
	STL = L + 1	@
	LINCL = L	@
	GO TO 252	@
251	CONTINUE	@
	STL = NCONTU + 1	@
	GO TO 250	@
252	IMAXX = I	@
	IMAXY = J + 2	@
	IMINX = I	@
	IMINY = J + 1	@
	IF (RH00(IMINX, IMINY) .LT. C(LINCL)) GO TO 255	@
	IMAXY = IMINY	@
	IMINY = J	@
255	I3 = (IMAXX + IMINX) / 2	@
	I4 = IMAXY + IMINY - 1	@
	IF (ICON(I3, I4) / IDIV(LINCL) * 2 .NE. ICON(I3, I4) / (IDIV(LINCL)	@
	1) / 2)) GO TO 256	@
	LEFTX = I	@
	LEFTY = J	@
	ISTARX = I3	@
	ISTARY = I4	@

	IMAXY = IMAXY + IDIRY	
	IMINX = I1	
	IMINY = I2	
	GO TO 200	@
222	CONTINUE	
C	I1 AND I2 ARE FUTURE IMINS, NO CHECK IS NEEDED TO ESTABLISH THIS	
	I3 = (IMINX * 2 + IDIRX) / 2	
	I4 = IMINY * 2 + IDIRY - 1	
	I5 = IMINX + IDIRX	
	I6 = IMINY + IDIRY	
	IDIRX = IMINX - IMAXX	
	IDIRY = IMINY - IMAXY	
	IMAXX = I5	
	IMAXY = I6	
	GO TO 200	@
C	213 FOR STARTING CONTOUR, I.E., POSITIONING PEN (WITH SYMBOL FOR	
C	CONTOUR NUMBERS 1, 4, 7, 10, AND 13)	
C	223 FOR CONTINUING CONTOUR	
213	INQU = 0	@
200	XMAXX = IMAXX	@
	XMAXY = IMAXY	
	XMINX = IMINX	
	XMINY = IMINY	
	Q=(C(LINCL)-RHOO(IMINX, IMINY))/URHOO(IMAXX, IMAXY) - RHOO(IMINX, L	
1	IMINY))	
	POSIT1 = XMINX + (XMAXX - XMINX) * Q	
	POSIT2 = XMINY + (XMAXY - XMINY) * Q	
	X = CONST2 * (POSIT1 - 1.0) + CONST3 * (POSIT2 - 1.0) + SHIFT	@
	Y = CONST1 * (POSIT2 - 1.0)	@
	IF (ORIGIN .GT. 5.0) Y = 10.0 - Y	
	IF (INQU .NE. 0) GO TO 223	@
	INQU = 1	@
	IF (LINCL .EQ. 1 .OR. LINCL .EQ. 4 .OR. LINCL .EQ. 7 .OR. LINCL	@
1	.EQ. 10 .OR. LINCL .EQ. 13) CALL SYMBOL (X, Y, 0.1,	@
2	SYMBL(LINCL), 0.0, -1)	@
	CALL PLOT (X, Y, +3)	@
	CALL PLOT (X, Y, +2)	
	GO TO 220	
223	CALL PLOT (X, Y, +1)	@
	ICON(I3, I4) = ICON(I3, I4) + ID+V(LINCL) / 2	@

```

      GO TO 226
C *****@
22  X = LX + 1.0 @
      IF (NPASS .EQ. 2 .AND. M .EQ. 1) X = LX *
      TOTAL = CLOCK(START) / 3600.0
      PRINT 107, K, M, TOTAL *
107  FORMAT ( 12X, 7HSECTION , 12, 5H PASS, 12, *
      1 10H COMPLETED , 24X, @
      2 7HTIME = , F10.2 ) *
24  CALL PLOT ( X, 0.0, -3 )
      JINIT = LIMIT(IPARTS)
      IF (INPUT1 .GT. 1) REWIND INPUT1
15  REWIND INPUT
275  CONTINUE
      CALL SYMBOL ( STALAB, 0.0, 0.28, 17HEND OF ALL PASSES, THETA1, 17 )
      IF (IPASS .EQ. 1) GO TO 52 21
21  CALL PLOTND @
      TOTAL = 37.5 * TOTAL
      I = TOTAL
      IHR = I / 60
      IMN = I - IHR * 60
      PRINT 124, IHR, IMN
124  FORMAT (/// 1X, 45HAPPROXIMATE TIME NEEDED FOR PLOTTING ABOVE IS,
      1 14, 4H HR., 15, 5H MIN. )
      STOP
238  PRINT 114 $
114  FORMAT ( 81H ERROR..... TWO PASSES ARE INCAPABLE OF BEING JOINED I$
      1N ANY MANNER BY THIS PROGRAM ) $
      STOP
239  PRINT 115 @
115  FORMAT ( 56H ERROR..... SECTIONS IN CONTUR AND IN FOURIE ARE NOT SA@
      1ME ) @
      STOP
237  PRINT 116 @
116  FORMAT ( 43H ERROR..... CONTOURS NOT IN INCREASING ORDER )
      STOP $
      END
$IBMAP UTV DECK FTL27890
      ENTRY UTVAR. FTL27900
      EXTERN ERLOC. FTL27910

```


*				FTL27911
*	MACRO FOR GENERATING VARIABLE UNITS TABLE			FTL27912
*	AND CORRESPONDING EXTERNS			FTL27913
*				FTL27914
UNITS	MACRO	A		FTL27915
CNT	SET	0		FTL27916
	IRP	A		FTL27917
	DUP	1,@A@-CNT		FTL27918
	PZE			FTL27919
	PZE	FIL@A@.		FTL27920
	EXTERN	FIL@A@.		FTL27921
CNT	SET	@A@+1		FTL27922
	IRP			FTL27923
	ENDM			FTL27924
*				FTL27925
*ENTRY	FROM MAIN PROGRAM TO DEFINE A VARIABLE UNIT			FTL27930
*				FTL27940
UTVAR.	SXA	UTVX,4	SAVE RETURN INDEX	FTL27950
	LAC	UTVX,4		FTL27960
	SXA	ERLOC.,4		FTL27970
	LXA	UTVX,4		FTL27980
	LAS	NFILES	STOP IF LOGICAL TAPE NUMBER EXCEEDS	FTL27990
	TRA	USTOP	NUMBER OF FILES IN TABLE.	FTL28000
	NOP			FTL28010
	PAC	,4		FTL28020
	CLA	IOU,4	PICKUP ADDRESS OF FCB POINTER	FTL28030
	PAX	,4		FTL28040
	TXL	USTOP-2,4,0	STOP IF UNIT IS UNDEFINED	FTL28050
UTVX	AXT	**,4	RESTORE RETURN INDEX	FTL28060
	STO	2,4	SET LOCATION OF FCB	FTL28070
	TRA	1,4	RETURN TO MAIN PROGRAM	FTL28080
*				FTL28090
	LXA	UTVX,4		FTL28100
	CLA*	-1,4	RESTORE UNIT DESIGNATION	FTL28110
USTOP	TSL	FEXEM.	ERROR, ILLEGAL UNIT REQUESTED.	FTL28120
	PZE	EXIT,,32	NO OPTIONAL RETURN	FTL28130
*				FTL28140
*INPUT-OUTPUT	LOGICAL UNIT TABLE			FTL28150
*				FTL28160
*ADDITIONS OR DELETIONS SHOULD BE MADE TO CARD IOU FOLLOWING				FTL28170

	*				FTL28180
	IOU	UNITS	(01,02,03,04,11,12,13,14)		
	NFILES	PZE	*-IOU-1		FTL28270
	*		FTL28280
		EXTERN	FEXEM.,EXIT		FTL28300
		END			FTL28310
	\$IBFTC	ALT 2	DECK		
		SUBROUTINE	ALTZ		
		DIMENSION	RHO(31, 31, 8), LAXI(3)		
		COMMON	INPUT, NPASS, NEWZ, RHO		
		INTEGER	OUTPUT		
		DATA	LAXI / 18HX AXISY AXISZ AXIS /		
		REWIND	INPUT		
		REWIND	1		
		DO 1	L = 1, NPASS		
		REWIND	13		
		REWIND	14		
		READ (INPUT)	IX10, IX20, IX30, IDX1, IDX2, IDX3, IP1, IP2, IP3,		
		1	II, JJ, KK		
		IF (NEWZ .NE. II)	GO TO 14		
		PRINT 15, LAXI(NEWZ)			
15		FORMAT (// 16H WARNING...	THE , A6, 32H IS ALREADY THE AXIS OF SE		
		CTIONS / 50H THE PROGRAM CONTINUES WITHOUT ALTERATION OF AXES)		
		RETURN			
14		IP11 = IP1 / 2			
		IP12 = IP1 - IP11			
		IP120 = IP11 + 1			
		DO 16	IK = 1,2		
		LIM = IP11			
		IF (IK .EQ. 2)	LIM = IP12		
		ITAPE = 13			
		IF (IK .EQ. 2)	ITAPE = 14		
		DO 2	K = 1, LIM		
10	2	READ (INPUT)((RHO(I, J, K), J = 1, IP2), I = 1, IP3)			
9	3	IF (NEWZ .NE. JJ)	GO TO 5		
8		DO 6	J = 1, IP2		
7	6	WRITE (ITAPE)((RHO(I, J, K), K = 1, LIM), I = 1, IP3)			
6		GO TO 16			
5	5	IF (NEWZ .NE. KK)	GO TO 9		
4		DO 10	I = 1, IP3		
3					

```

10  WRITE (ITAPE)((RHO(I, J, K), J = 1, IP2), K = 1, LIM )
16  CONTINUE
    REWIND 13
    REWIND 14
    IF (NEWZ .NE. JJ) GO TO 17
    WRITE ( 01 ) IX20, IX10, IX30, IDX2, IDX1, IDX3, IP2, IP1, IP3,
1    JJ, II, KK
    DO 18 K = 1, IP2
    READ (13)((RHO(I,J,1), J = 1, IP11), I = 1, IP3)
    READ (14)((RHO(I,J,1), J = IP120, IP1), I = 1, IP3)
18  WRITE(01)((RHO(I,J,1), J = 1, IP1), I = 1, IP3)
    GO TO 11
17  WRITE ( 01 ) IX30, IX20, IX10, IDX3, IDX2, IDX1, IP3, IP2, IP1,
1    KK, JJ, II
    DO 19 K = 1, IP3
    READ (13)((RHO(I,J,1), J = 1, IP2), I = 1, IP11)
    READ (14)((RHO(I,J,1), J = 1, IP2), I = IP120, IP1)
19  WRITE (1)((RHO(I,J,1), J = 1, IP2), I = 1, IP1)
11  PRINT 7, LAXI(NEWZ)
7   FORMAT (5X, 6H (THE , A6, 30H IS NOW THE AXIS OF SECTIONS) )
1   CONTINUE
    REWIND INPUT
    INPUT = 1
    RETURN
9   PRINT 4, NEWZ
4   FORMAT ( 13H ERROR--AXIS , I2, 15H DOES NOT EXIST )
    STOP
    END
$ENTRY

```