

References

- BARTELL, L. S., KUCHITSU, K. & DE NEUI, R. J. (1961). *J. Chem. Phys.* **35**, 1211–1218.
- BEEVERS, C. A., McDONALD, T. R. R., ROBERTSON, J. H. & STERN, F. (1952). *Acta Cryst.* **5**, 689–690.
- BERMAN, H. (1970). *Acta Cryst.* **B26**, 290–299.
- BERMAN, H., CHU, S. S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.
- BROWN, G. M. & LEVY, H. A. (1963). *Science*, **141**, 921–923.
- BROWN, G. M. & LEVY, H. A. (1964a). *J. Phys. Radium*, **25**, 469–473.
- BROWN, G. M. & LEVY, H. A. (1964b). *J. Phys. Radium*, **25**, 497–502.
- BROWN, G. M. & LEVY, H. A. (1965). *Science*, **147**, 1038–1039.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457–464.
- CHIDAMBARAM, R. & BROWN, G. M. (1972). *Cryst. Struct. Commun.* **1**, 269–272.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
- ELIEL, E. L. (1969). *Svensk kem. Tidskr.* **81**, No. 6-7, 22–27.
- FRIES, D. C., RAO, S. T. & SUNDARALINGAM, M. (1971). *Acta Cryst.* **B27**, 994–1005.
- FROST, A. & ROUSE, R. A. (1968). *J. Amer. Chem. Soc.* **90**, 1965–1969.
- HANSON, J. C., SIEKER, L. C. & JENSEN, L. H. (1973). *Acta Cryst.* **B29**, 797–808.
- HIROTA, E. & MORINO, Y. (1966). *J. Chem Phys.* **45**, 2326–2327.
- HOOG, A. J. DE, BUYS, H. R., ALTONA, C. & HAVINGA, E. (1969). *Tetrahedron*, **25**, 3365–3375.
- JEFFREY, G. A. & PARK, Y. J. (1972). *Acta Cryst.* **B28**, 257–267.
- JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794, (2nd rev.), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- KOETZLE, T. F. & HAMILTON, W. C. (1972). *Acta Cryst.* **B28**, 2083–2090.
- KUCHITSU, K. (1968). *J. Chem. Phys.* **49**, 4456–4462.
- LIDE, D. R., JR (1960a). *J. Chem Phys.* **33**, 1514–1518.
- LIDE, D. R., JR (1960b). *J. Chem. Phys.* **33**, 1519–1522.
- LIDE, D. R., JR & CHRISTENSEN, D. (1961). *J. Chem. Phys.* **35**, 1374–1378.
- NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* **A25**, 391–392.
- NEWTON, M. D., LATHAM, W. A., HEHRE, W. J. & POPLE, J. A. (1970). *J. Chem. Phys.* **52**, 4064–4072.
- PARK, Y. J., JEFFREY, G. A. & HAMILTON, W. C. (1971). *Acta Cryst.* **B27**, 2393–2401.
- ROHRER, D. C. (1972). *Acta Cryst.* **A28**, 425–433.
- SCHARPEN, L. & LAURIE, V. L. (1963). *J. Chem. Phys.* **39**, 1732–1733.
- SEQUEIRA, A., RAJAGOPAL, H. & CHIDAMBARAM, R. (1972). *Acta Cryst.* **B28**, 2514–2519.
- STRAHS, G. (1970). *Advanc. Carbohydrate Chem.* **25**, 53–107.
- Structure Reports* (1952). **16**, 483–484.
- SUNDARALINGAM, M. (1965). *J. Amer. Chem. Soc.* **87**, 599–605.
- SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.

Acta Cryst. (1973). **B29**, 797

Sucrose: X-ray Refinement and Comparison with Neutron Refinement

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The structure of sucrose has been refined with Mo $K\alpha$ diffractometer data collected from two crystals to a $\sin \theta/\lambda$ limit of 0.81 \AA^{-1} . 3280 reflections were measured of which 3098 were greater than 2σ . The structure has been refined with low-angle data ($\sin \theta/\lambda < 0.64 \text{ \AA}^{-1}$), high-angle data ($\sin \theta/\lambda > 0.64 \text{ \AA}^{-1}$) and all the data, and the results compared with the very precise neutron-diffraction results of Brown & Levy. The final R indices are 0.025, 0.029 and 0.029 respectively for the X-ray data. The C–O bond lengths from refinements of low-angle and all data are longer and thermal parameters greater than those from the neutron data. The thermal parameters for the nonhydrogen atoms obtained from the high-angle refinement, however, are not significantly different from the neutron values. Use of bonded hydrogen atom scattering factors of Stewart, Davidson & Simpson [*J. Chem. Phys.* (1965). **42**, 3175–3187] led to thermal parameters for hydrogen bonded to oxygen and for hydrogen bonded to carbon which were respectively $0.3(3) \text{ \AA}^2$ greater and $1.9(1) \text{ \AA}^2$ less than those from the neutron results. Residual electron-density maps based on neutron coordinates and X-ray data showed the expected bond and lone pair features much more clearly than maps based on the coordinates obtained from refinement of high $\sin \theta$ X-ray data.

Introduction

The structure of sucrose was solved by Beevers, McDonald, Robertson & Stern (1952), and subsequently

Brown & Levy (1963) carried out a highly precise refinement using neutron-diffraction data (see accompanying paper by Brown & Levy, 1973). This report describes a refinement based on X-ray data collected on

a four-circle diffractometer. Initially, the purpose was to compare the B values from a refinement in which scattering factors for the isolated hydrogen atom were used with B values from refinement of neutron data (Jensen & Sundaralingam, 1964; Mason, Phillips & Robertson, 1965). Several comparisons of results from neutron and X-ray data have been reported (Coppens, Sabine, Delaplane & Ibers, 1969; Coppens & Vos, 1971), but the number of hydrogen atoms involved was not large. In the sucrose structure, however, the number of hydrogen atoms in general positions should provide sufficient data for statistical comparisons. Moreover, reflections from sucrose can be observed well beyond the limit of the Cu sphere, so that parameters of the nonhydrogen atoms based on both low- and high-angle reflections can be determined and compared with neutron results. We also wanted to examine residual density maps obtained using the observed X-ray data and the coordinates derived from the neutron and X-ray data.

A preliminary account of the results reported here was given in the symposium on Experimental and Theoretical Studies of the Electron Densities in Crystals and Molecules at the Albuquerque ACA meeting, April, 1972 (Hanson, Sieker & Jensen, 1972).

Experimental

Crystals of sucrose were grown from a methanol-water solution by slow evaporation. Unit-cell parameters were determined from 2θ values for 27 reflections measured on a manually operated, four-circle diffractometer, both $+2\theta$ and -2θ being measured for each reflection. The following parameters were derived from a least squares fit of the data based on $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ and are tabulated along with the values determined by Brown & Levy (1973).

	This work	Brown & Levy (1973)
a	10.8648(15) \AA	10.8633(5) \AA
b	8.7028(12)	8.7050(4)
c	7.7578(11)	7.7585(4)
β	102.956(15) $^\circ$	102.945(6) $^\circ$

The agreement between these two sets of parameters is satisfactory, and they are not significantly different from the results of Beevers *et al.* (1952). The space group is $P2_1$.

Two crystals of approximate size $0.27 \times 0.32 \times 0.36 \text{ mm}$ and $0.32 \times 0.33 \times 0.38 \text{ mm}$ were used for the intensity data. The crystals were well within the intensity plateau of the beam (focal spot size, $0.8 \times 15 \text{ mm}$, take-off angle, 3° ; collimating apertures, 1.0 mm ; focal spot to crystal distance, 145 mm). Measurements were made by the $\omega/2\theta$ scan technique at a 2θ scan rate of 2° per min with Mo $K\alpha$ radiation filtered through 0.026 mm Nb foil. Scan ranges were variable as computed from the tangent relation of Alexander & Smith (1964), and backgrounds were measured for half the scan time at each limit of the scan range. All reflections with

$2\theta < 70^\circ$ ($\sin \theta/\lambda < 0.81 \text{ \AA}^{-1}$) were measured for both crystals.

Three reflections were chosen to monitor electrical and mechanical stability of the equipment and to check for crystal deterioration. They were measured at the beginning and end of each four-hour shift. In order to put all data on a common basis, the intensities collected during each shift were scaled by a factor based on the mean value of the monitor reflections bracketing the shift. For crystal 1, the range in scale factor was about 2%.

For crystal 2, it was observed that one of the monitor reflections, 200, increased in intensity during the first 32 hours of X-ray exposure, reaching a level of 1.1 times its initial value and then decreasing at essentially the same rate as the other two monitor reflections. The observed changes in this very intense reflection were interpreted in terms of increased mosaicity during the initial X-ray exposure which led to a decrease in secondary extinction. A similar observation has been reported by Delaplane & Ibers (1969). Only very small changes were observed in the other, less intense monitor reflections, and the range of scale factor based on them and applied to crystal 2 was about 3%. Reflection 200 had been used as a monitor in scaling the data from crystal 1, but the initial increase in intensity of this reflection noted for crystal 2 had not been ob-

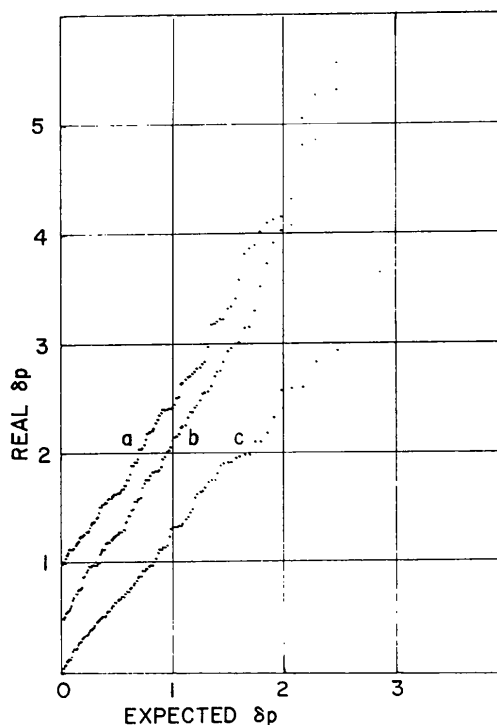


Fig. 1. Half-normal probability plots for x, y, z, U_{12}, U_{23} . Comparison of neutron parameters against (a) set I, points shifted 1.0 unit along y axis to separate plots; (b) set I+II, shifted 0.5 units along y axis to separate plots; (c) set II. A few points with $5 < \text{real } \delta\rho$ omitted from plot. $\delta_{\text{real}} = |P_x - P_N| / (\sigma_x^2 + \sigma_N^2)^{1/2}$.

served. This probably follows from the fact that crystal 1 had been exposed to the X-ray beam during the preliminary photographic observations and measurement of unit-cell parameters before initiating intensity data collection.

Intensities were corrected for coincidence loss as reported by Adman & Jensen (1970). The largest correction applied was 18%, a value which was 4% less than that obtained by measuring the same reflection at reduced X-ray tube current. The three most intense reflections were obtained from measurements at reduced current.

Standard deviations were estimated according to the equation $\sigma = (\sigma_c^2 + [0.022C]^2)^{1/2}$ where σ_c is the square root of the scan count plus the background counts and C is the net count of the reflection. The constant 0.022 was chosen so that sets of data grouped by intensity had deviations between observations approximating that to be expected from a normal distribution.

Three sets of data were collected. Two sets consisting of 3460 and 3047 measurements respectively were collected from crystal 1 and a single set of 3447 measurements was collected from crystal 2. These will be designated as sets 1, 2 and 3 respectively. In the course of collecting set 2, the characteristics of the pulse height analyzer changed enough to impair the quality of the data, and this set was used, therefore, only for checking purposes. All reflections for which the measurements had a range greater than 6σ were checked and observations were rejected if they differed from two more closely agreeing observations of the same reflection. Additional data designated set 4 were then collected

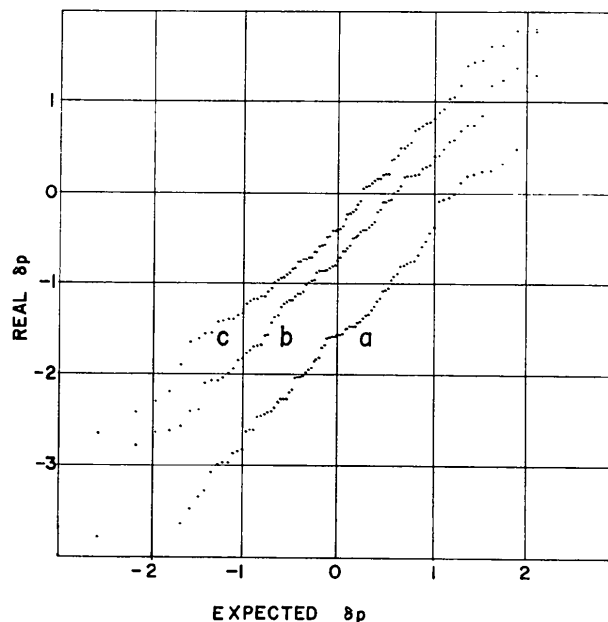


Fig. 2. Normal probability plot for $U_{11}, U_{22}, U_{33}, U_{13}$. Comparison of neutron parameters with (a) set I, (b) set I+II, (c) set II. A few points with $2 < \text{real } \delta p < -4$ omitted from plot. $\delta_{\text{real}} = (P_x - P_N) / (\sigma_x^2 + \sigma_N^2)^{1/2}$.

from crystal 2 for all reflections where the range was greater than 5σ or where only one observation remained from sets 1 and 3. A few low-order reflections where the backgrounds were questionable and intense reflections with counts greater than 5×10^5 were re-measured. 285 reflections were re-measured and 125 and 150 of the original observations in sets 1 and 3 respectively were rejected.

Scale constants of sets 3 and 4 relative to set 1 were determined and applied because different monitors had been used to scale the data within these sets. The scale constants k_3 and k_4 were adjusted so that the weighted sum of intensity ratios was equal to one. The resulting values were 0.949 and 0.988 relative to $k_1 = 1.000$. The intensity for each reflection was taken as the weighted average of all observations for that reflection. The standard deviations of the combined intensities were calculated according to the formula: $\sigma = (1/\sum 1/\sigma_i^2)^{1/2}$ where σ_i is the calculated standard deviation of measurement i .

As a measure of the agreement of observations within each set of data relative to the combined intensity, the average relative deviations from the mean, D , were calculated according to the equation:

$$D = \frac{\sum_b \sum_i |\bar{I}_h - I_{h,i}|}{\sum_b n_h \bar{I}_h}$$

where the sums are over all reflections in the set and over all observations i of those reflections. The values were 0.018, 0.018 and 0.013 for sets 1, 3 and 4 respectively. Using the 2746 pairs of reflections having only two observations, we find that differences between observations of each pair followed reasonably well a normal distribution. This conclusion is based on the distribution of $\sigma_{\text{ext}}/\sigma$ shown in Table 1.

Table 1. Distribution of $\sigma_{\text{ext}}/\sigma^*$

	Experimental	Theoretical
Fraction of data with $1 < (\sigma_{\text{ext}}/\sigma)$	0.33	0.32
Fraction of data with $2 < (\sigma_{\text{ext}}/\sigma)$	0.058	0.045

* $\sigma_{\text{ext}} = [(V_1/\sigma_1)^2 + (V_2/\sigma_2)^2]^{1/2} \sigma$, where $V_i = I - I_i$ and σ and σ_i are defined in text.

Of the 3280 reflections, 184 were found to be less than 2σ ; these were so coded and set equal to 2σ . Intensities greater than 2σ ranged from 66 to 3×10^6 counts and were converted to F^2 in the usual way with no corrections made for absorption ($\mu = 1.52 \text{ cm}^{-1}$). The 17 strongest reflections were coded extinct and weighted zero in the early stages of least squares refinement.

Refinement

In order to be completely independent of the results based on neutron data, refinement was initiated with the positional parameters of Beevers *et al.* (1952). The scale factor and over-all thermal parameter were esti-

Table 2. *Observed and calculated structure factors*Each group of four columns contains respectively l , $10F_o$, $10F_c$, $100\sigma(F_o)$.

l	$10F_o$	$10F_c$	$100\sigma(F_o)$
100	100	100	100
200	200	200	200
300	300	300	300
400	400	400	400
500	500	500	500
600	600	600	600
700	700	700	700
800	800	800	800
900	900	900	900
1000	1000	1000	1000
1100	1100	1100	1100
1200	1200	1200	1200
1300	1300	1300	1300
1400	1400	1400	1400
1500	1500	1500	1500
1600	1600	1600	1600
1700	1700	1700	1700
1800	1800	1800	1800
1900	1900	1900	1900
2000	2000	2000	2000
2100	2100	2100	2100
2200	2200	2200	2200
2300	2300	2300	2300
2400	2400	2400	2400
2500	2500	2500	2500
2600	2600	2600	2600
2700	2700	2700	2700
2800	2800	2800	2800
2900	2900	2900	2900
3000	3000	3000	3000
3100	3100	3100	3100
3200	3200	3200	3200
3300	3300	3300	3300
3400	3400	3400	3400
3500	3500	3500	3500
3600	3600	3600	3600
3700	3700	3700	3700
3800	3800	3800	3800
3900	3900	3900	3900
4000	4000	4000	4000
4100	4100	4100	4100
4200	4200	4200	4200
4300	4300	4300	4300
4400	4400	4400	4400
4500	4500	4500	4500
4600	4600	4600	4600
4700	4700	4700	4700
4800	4800	4800	4800
4900	4900	4900	4900
5000	5000	5000	5000
5100	5100	5100	5100
5200	5200	5200	5200
5300	5300	5300	5300
5400	5400	5400	5400
5500	5500	5500	5500
5600	5600	5600	5600
5700	5700	5700	5700
5800	5800	5800	5800
5900	5900	5900	5900
6000	6000	6000	6000
6100	6100	6100	6100
6200	6200	6200	6200
6300	6300	6300	6300
6400	6400	6400	6400
6500	6500	6500	6500
6600	6600	6600	6600
6700	6700	6700	6700
6800	6800	6800	6800
6900	6900	6900	6900
7000	7000	7000	7000
7100	7100	7100	7100
7200	7200	7200	7200
7300	7300	7300	7300
7400	7400	7400	7400
7500	7500	7500	7500
7600	7600	7600	7600
7700	7700	7700	7700
7800	7800	7800	7800
7900	7900	7900	7900
8000	8000	8000	8000
8100	8100	8100	8100
8200	8200	8200	8200
8300	8300	8300	8300
8400	8400	8400	8400
8500	8500	8500	8500
8600	8600	8600	8600
8700	8700	8700	8700
8800	8800	8800	8800
8900	8900	8900	8900
9000	9000	9000	9000
9100	9100	9100	9100
9200	9200	9200	9200
9300	9300	9300	9300
9400	9400	9400	9400
9500	9500	9500	9500
9600	9600	9600	9600
9700	9700	9700	9700
9800	9800	9800	9800
9900	9900	9900	9900
10000	10000	10000	10000

Table 2 (cont.)

Table 2 (cont.) showing a grid of data points, likely structure factors or related parameters, organized in columns and rows. The data is presented in a dense, tabular format typical of scientific publications of this era.

mated from statistics (Wilson, 1942). Because of some large coordinate shifts found by Brown & Levy (1963), we initiated refinement by ΔF syntheses and reduced $R(= \sum |k|F_o| - |F_c| / \sum |F_o|)$ from 0.41 to 0.27. The carbon and oxygen scattering factors were those of Berg-huis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

The refinement of carbon and oxygen parameters (isotropic temperature factor) was continued by full-matrix least squares and R decreased to 0.11. The reflections coded as less than 2σ were used in the refinement only if $|F_c| > |F_o|$. The next cycle of refinement with anisotropic temperature factors reduced R to 0.06. A ΔF synthesis was computed and peaks ranging from 0.33 to 0.56 $e \text{ \AA}^{-3}$ were found for all the hydrogen atoms. One additional refinement cycle including hydrogen atoms reduced R to 0.036. For the remaining cycles, it was necessary to break each refinement cycle into two overlapping segments, one including all atoms of the pyranose ring plus C(2) of the furanose ring (see Fig. 3 for numbering of atoms) and the other segment including all atoms in the furanose ring plus atoms H(1), C(1) and O(1) in the pyranose ring.

At this point a plot based on the formulation of Zachariasen (1967) indicated that extinction was negligible, and it was determined that the strongest reflections which had been weighted zero to this point were not significantly affected by secondary extinction. These reflections were, therefore, included in the remaining refinement cycles. As an additional check, an isotropic extinction parameter value less than 0.5σ was obtained in a subsequent least-squares cycle with the final parameters.

One additional cycle decreased R to 0.030. To this point, the scattering factors of McWeeny (1951) for the isolated hydrogen atom were used because of our inter-

est in the effect of bonding on hydrogen atom thermal parameters. We now substituted the scattering factors of Stewart, Davidson & Simpson (1965) for bonded hydrogen, and two additional cycles of least squares were run with little change in R .

The standard deviation of an observation of unit weight (S) was 3.1, and this suggested either that the weights had been overestimated or that the model was deficient. Refinement of uracil (Stewart & Jensen, 1969), 6-mercaptapurine (Brown, 1969), thiocytosine (Furberg & Jensen, 1970) and cyanuric acid (Coppens & Vos, 1971) have shown that the refinement of a high angle data set leads to values of S close to the expected value of 1.0. Accordingly, the data for sucrose were divided into two sets: set I with $\sin \theta / \lambda < 0.64 \text{ \AA}^{-1}$, set II with $0.64 < \sin \theta / \lambda < 0.81 \text{ \AA}^{-1}$. For set I two cycles of refinement were done in the same manner as the final cycle of refinement of all data. For set II the hydrogen parameters were fixed at the values determined from the refinement with all data, and the remaining parameters were allowed to vary. Table 2 lists the observed and calculated structure factors ($\times 10$) and the standard deviations in the structure factors ($\times 100$).

Data pertinent to the refinement are listed in Table

Table 3. Summary data of refinements

	Set I	Set II	Set I+II
$\sin \theta / \lambda$ max	0.64	0.81	0.81
$\sin \theta / \lambda$ min	0.05	0.64	0.05
Total reflections	1666	1614	3280
Reflections $< 2\sigma$	40	144	184
$R \sum k F_o - F_c / \sum F_o $	0.025	0.029	0.029
$R_w = [\sum w(k F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.031	0.025	0.033
$S = [\sum w(k F_o - F_c)^2 / m - n]^{1/2}$	3.1	1.3	2.6
Scale for F_o	0.1102	0.1113	0.1117
Highest peak in ΔF map	0.18 $e \text{ \AA}^{-3}$	0.07 $e \text{ \AA}^{-3}$	0.3 $e \text{ \AA}^{-3}$
Av. shift/error last cycle	0.25	0.32	0.32

3. As expected, R for data set II is greater than that for set I. On the other hand, R_w is less for set II than it is for set I. Furthermore, S is much greater than the ideal value of the unity for set I, but only a little greater for set II. The contrast in behavior of R and of R_w and S suggests the presence of errors not properly covered by the weights. Although experimental error may account in part for the observations, neglect of the effects of bonding and lone pair electrons by use of spherically symmetrical scattering factors is probably responsible for the behavior of R_w and S . Indeed, a ΔF synthesis based on coordinates from the refinement of set I had peaks as high as $0.18 \text{ e } \text{Å}^{-3}$ which were interpretable in terms of residual electron density along bonds. A ΔF synthesis based on set II data and with parameters from the refinement of set II, on the other hand, showed no peaks higher than $0.07 \text{ e } \text{Å}^{-3}$.

Discussion

Comparison of parameters

Parameters from the refinement of data set I + II and set II are listed in Table 4. Parameters from set I have

not been tabulated because they are less accurate, but the results from all three refinements are included in the following comparisons which are made relative to the neutron parameters of Brown & Levy (1973).

Comparison of the parameters is based on normal or half-normal probability plots as described by Abrahams & Keve (1971). Such plots provide a convenient comparison of real differences in parameters relative to the values expected from the combined standard deviations of the parameters.

Three half-normal probability plots of x, y, z, U_{12} and U_{23} for the nonhydrogen atoms are displayed in Fig. 1. The plots labeled a, b , and c are for parameters from set I, set I + II, and set II respectively. In order to separate the plots, points for a have been increased by 1 unit in y , those for b have been increased by $\frac{1}{2}$ unit in y . It can be seen that for all three sets of parameters the plots have slopes different from unity suggesting that the standard deviations have been underestimated, but the slope of c , the set II plot, is closest to unity.

Fig. 2 shows three normal probability plots for U_{ii} and U_{13} , again a, b and c being the plots for set I, set I + II, and set II. The slopes are nearly ideal suggesting

Table 4. Fractional coordinates and anisotropic thermal parameters

(a) Nonhydrogen atom parameters from refinement set I + II followed by those from set II. Positional parameters are $\times 10^4$, thermal parameters $\times 10^4 \text{ Å}^2$. Thermal parameters defined by expression

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

Standard deviations in parentheses are to be multiplied by 1.03 for set I + II parameters and 1.06 for set II parameters to correct for the effects of refining in two passes.

C(1)	29986(10)	35792(14)	48521(14)	155(4)	159(5)	170(4)	5(4)	42(3)	0(4)
	29967(9)	35792(13)	48469(13)	155(3)	156(3)	169(3)	5(3)	42(3)	-3(3)
C(2)	31263(11)	47475(16)	63545(15)	170(4)	201(5)	188(5)	-17(4)	39(4)	-19(4)
	31260(12)	47490(17)	63604(17)	173(4)	192(4)	185(4)	-13(3)	37(3)	-19(3)
C(3)	29555(11)	63659(15)	56441(17)	187(5)	177(5)	285(5)	-6(4)	75(4)	-38(4)
	28554(13)	63699(17)	56413(21)	185(4)	167(4)	292(5)	-4(3)	79(4)	-30(4)
C(4)	37392(12)	67096(16)	44220(18)	230(5)	160(5)	298(6)	-4(4)	94(4)	16(5)
	37415(14)	67103(17)	44230(20)	225(5)	160(5)	287(5)	-8(4)	95(4)	13(4)
C(5)	35912(11)	55188(16)	29557(16)	186(5)	201(5)	235(5)	-11(4)	58(4)	30(4)
	35936(12)	55153(18)	29551(18)	183(4)	203(5)	227(4)	-10(4)	56(4)	22(4)
C(6)	45728(13)	57082(19)	18430(18)	292(6)	308(7)	255(6)	-63(5)	121(5)	8(5)
	45764(17)	57072(24)	18485(21)	286(6)	306(7)	252(5)	-63(5)	122(5)	11(5)
C'(1)	10322(12)	13101(16)	54340(15)	270(5)	223(6)	152(4)	-19(5)	66(4)	44(4)
	10306(13)	13160(15)	54366(14)	270(4)	219(4)	154(3)	-21(3)	68(3)	43(3)
C'(2)	12444(10)	19247(14)	36908(13)	181(4)	142(4)	135(4)	-4(4)	48(3)	2(4)
	12451(10)	19280(13)	36897(11)	181(3)	141(3)	126(3)	-2(3)	45(2)	8(2)
C'(3)	728(10)	19052(15)	21444(14)	164(4)	171(5)	145(4)	-13(4)	43(3)	9(4)
	715(9)	19078(13)	21460(12)	162(3)	167(3)	146(3)	-14(3)	41(3)	10(3)
C'(4)	6499(11)	16669(15)	5485(14)	202(5)	190(5)	141(4)	-28(4)	44(4)	-5(4)
	6491(11)	16686(13)	5477(12)	198(3)	188(4)	133(3)	-20(3)	43(3)	-2(3)
C'(5)	17628(11)	6119(15)	12843(15)	247(5)	173(5)	157(4)	5(4)	64(4)	-27(4)
	17643(11)	6149(14)	12856(13)	231(4)	173(4)	156(3)	11(3)	60(3)	-23(3)
C'(6)	29923(13)	8164(18)	4674(17)	271(6)	303(7)	246(5)	33(5)	123(5)	-19(5)
	29918(13)	8200(19)	4653(17)	262(5)	294(6)	238(4)	30(4)	117(4)	-20(4)
O(1)	17120(7)	34687(11)	39090(11)	151(3)	132(3)	162(3)	-6(3)	22(3)	10(3)
	17142(8)	34699(11)	39136(11)	151(3)	138(3)	182(3)	-8(2)	20(2)	8(2)
O(2)	22877(10)	43566(14)	74727(13)	275(4)	301(5)	192(4)	-18(4)	93(3)	-4(4)
	22907(13)	43571(18)	74747(16)	271(5)	293(5)	188(3)	-22(4)	88(3)	-7(3)
O(3)	30902(11)	74808(15)	70284(17)	332(5)	267(5)	498(6)	-105(5)	221(5)	-196(5)
	30844(17)	74825(20)	70307(28)	336(6)	256(5)	491(8)	-95(5)	214(6)	-184(6)
O(4)	34882(15)	81380(16)	35521(20)	628(8)	182(5)	477(7)	67(5)	249(6)	79(5)
	34954(30)	81462(21)	35589(35)	628(13)	173(5)	489(9)	71(6)	257(9)	83(6)
O(5)	37733(8)	39888(12)	36855(12)	185(4)	178(4)	240(4)	-0(3)	100(3)	1(3)
	37737(10)	39899(14)	36854(16)	185(4)	169(3)	246(4)	2(3)	97(3)	-5(3)
O(6)	58164(10)	54571(16)	28597(17)	232(4)	337(6)	432(6)	-50(4)	154(4)	-69(5)
	58175(15)	54543(22)	28643(26)	223(4)	330(6)	415(6)	-47(4)	144(5)	-66(5)
O'(1)	2997(10)	23560(15)	62074(12)	282(4)	337(5)	206(4)	-47(4)	131(3)	-17(4)
	2984(12)	23603(17)	62091(13)	280(4)	342(5)	203(3)	-47(4)	128(3)	-15(3)
O'(2)	21227(8)	9445(12)	31608(10)	225(4)	197(4)	148(3)	60(3)	31(3)	-18(3)
	21230(9)	9463(12)	31586(11)	228(3)	196(3)	153(3)	60(3)	34(2)	-18(2)
O'(3)	-7430(9)	31771(13)	20409(13)	195(4)	233(4)	257(4)	43(4)	55(3)	29(4)
	-7393(10)	31834(14)	20422(15)	195(3)	228(3)	255(3)	43(3)	55(3)	25(3)
O'(4)	-2176(9)	9715(15)	-8923(12)	298(5)	335(5)	149(4)	-70(4)	14(3)	-27(4)
	-2135(12)	9742(16)	-8943(12)	291(4)	326(5)	151(3)	-70(4)	15(3)	-27(3)
O'(6)	32654(10)	23865(16)	3981(14)	323(5)	360(6)	253(4)	-74(5)	115(4)	-5(4)
	32652(13)	23882(19)	4004(16)	317(5)	342(5)	246(4)	-65(4)	106(3)	-1(4)

Table 4 (cont.)

(b) Hydrogen atom parameters from refinement of set I+II. Positional parameters are $\times 10^4$, thermal parameters $\times 10^3 \text{ \AA}^2$. Thermal parameters defined by expression $\exp [8\pi^2 U(\sin^2 \theta/\lambda^2)]$. Standard deviations in parentheses are to be multiplied by 1.03 to correct for the effects of refining in two psases.

H(C1)	3274(13)	2621(19)	5306(18)	8(3)
H(C2)	3967(14)	4718(20)	7060(20)	17(4)
H(C3)	2001(15)	6409(21)	4985(20)	18(4)
H(C4)	4606(15)	6671(22)	5157(21)	19(4)
H(C5)	2754(14)	5651(20)	2178(19)	15(3)
H(C6)	4511(16)	6744(23)	1367(22)	23(4)
H'(C6)	4331(17)	4999(23)	779(24)	28(4)
H(C' 1)	600(13)	317(21)	5218(21)	17(4)
H'(C' 1)	1855(14)	1140(21)	6206(20)	19(3)
H(C' 3)	-434(14)	1036(21)	2269(20)	13(3)
H(C' 4)	886(14)	2585(21)	209(20)	16(3)
H(C' 5)	1462(14)	-439(21)	1117(21)	21(4)
H(C' 6)	3627(16)	209(22)	1155(23)	21(4)
H'(C' 6)	2690(14)	507(23)	-807(22)	24(4)
H(O2)	2645(21)	3776(33)	8251(33)	55(7)
H(O3)	2517(21)	7659(30)	7394(29)	43(7)
H(O4)	3430(27)	8680(37)	4078(37)	63(10)
H(O6)	5951(27)	4535(44)	2783(38)	69(10)
H(O' 1)	778(19)	3111(31)	6541(27)	40(6)
H(O' 3)	-423(19)	3922(29)	1817(27)	37(6)
H(O' 4)	-155(22)	1376(36)	-1705(30)	60(8)
H(O' 6)	3486(22)	2694(33)	1453(33)	54(7)

realistic standard deviations, but the intercepts are negative indicating systematic errors in these thermal parameters of 0.5 to 1.5 times the combined σ .

For hydrogen atom positional parameters, the half-normal probability plot (not shown) has a slope between 4.5 and 5. This is to be expected for hydrogen because of the very aspherical electron distribution for the bonded atom (Stewart *et al.*, 1965).

Comparison of bond lengths

In Fig. 3 the bond lengths are listed in the order set I, set II, set I+II, and neutron. In Table 5 the mean differences ($\bar{\Delta}$) between X-ray and neutron bond lengths of the various bond types are given. Also tabulated are the standard deviations in the mean difference (s) derived from sample variance and the standard deviations in the mean differences (σ) derived from the standard deviations of the least-squares refinement.

In Table 5 it is seen that the set II bond lengths agree most closely with the neutron values. This is to be expected because the contribution from aspherical electron densities is least for this set.

The C-C bond lengths do not differ significantly in any of the refinements. This is consistent with the assumption that the residual densities are nearly symmetric about the nuclear positions.

The 0.004(1) mean differences in the ether C-O bond lengths from set I and set I+II can be explained in terms of a shift of the oxygen atoms toward the lone-pair region (Dawson, 1964). For these bonds the 'spherical' model atom refines to balance the two bond densities and the lone-pair density. For the hydroxyl oxygen atoms the balance is between the C-O and O-H bond densities and the lone-pair density. In the latter case the shift is larger in the direction of the lone pairs and is greater than 3σ for all three refinements. The fact that even with the high-angle data of set II these bond lengths differ from the neutron values is consistent with the results of Coppens & Vos (1971) who suggest

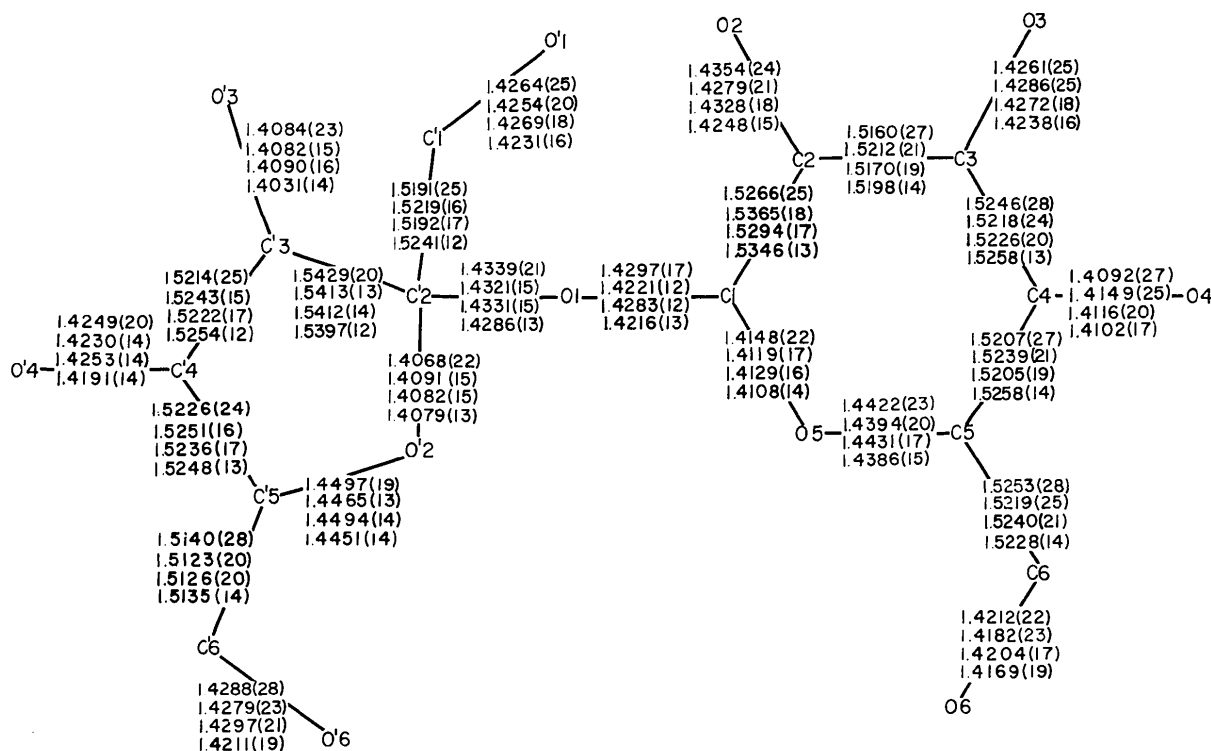


Fig. 3. Bond lengths and their standard deviations in the order set I, set II, set I+II, neutron.

that the contribution from the lone pair region of the oxygen atom is still significant in this $\sin \theta/\lambda$ range.

The most extreme shift along a bond is for the hydrogen atom because of the large aspherical distortion of the electron density toward the atom to which it is bonded (Cochran, 1956; Tomiie, 1958; Stewart *et al.*, 1965). A good comparison between X-ray and neutron

bond lengths for O-H and C-H is that of Hvoslef (1968) on ascorbic acid, who found the shift to be 0.09(3) Å for C-H and 0.18(3) Å for O-H. Our values are comparable, 0.13(1) Å and 0.18(2) Å respectively, the larger standard deviation of the O-H bond length difference being attributable to hydrogen bonding.

For the nonhydrogen atoms s and σ agree quite well

Table 5. Comparison of bond lengths

$\bar{\Delta}$ = (X-ray bond length - neutron bond length), s is standard deviation of mean difference based on sample variance, σ is standard deviation of mean difference based on e.s.d.'s of atomic parameters.

$\sin \theta/\lambda$ Bond	Set I 0.05-0.64			Set I+II 0.05-0.81			Set II 0.64-0.81		
	$\bar{\Delta}$	s	σ	$\bar{\Delta}$	s	σ	$\bar{\Delta}$	s	σ
C-C	0.0023 Å	0.0011 Å	0.0009 Å	-0.0024 Å	0.0008 Å	0.0007 Å	-0.0006 Å	0.0006 Å	0.0007 Å
C-O (hydroxy)	0.0048	0.0012	0.0010	0.0051	0.0009	0.0008	0.0040	0.0006	0.0009
C-O (ether)	0.0041	0.0012	0.0010	0.0037	0.0009	0.0008	0.0014	0.0004	0.0008
C-H	-0.13	0.01	0.005	-0.13	0.01	0.004	*	-	-
O-H	-0.17	0.02	0.011	-0.18	0.02	0.009	*	-	-

* Hydrogen parameters were not varied in refining with data set II.

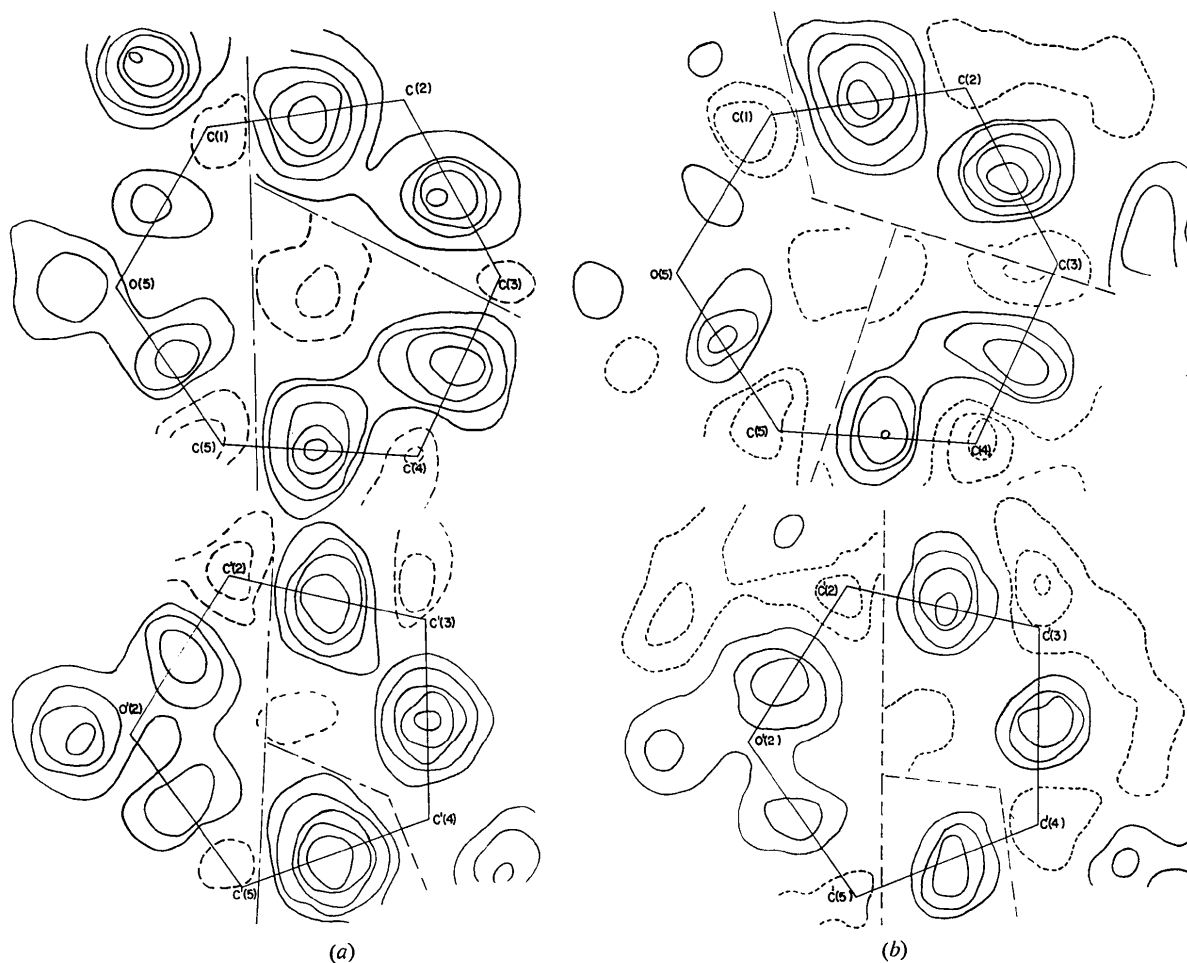


Fig. 4. Composite of sections from ΔF syntheses showing residual electron density. Each section of the composite defined by plane of three adjacent atoms and separated by ————. Contour levels at intervals of $0.05 \text{ e}\text{\AA}^{-3}$; solid lines, positive; dashed lines, negative; zero contours omitted. (a) X-ray neutron ΔF synthesis, (b) high-angle X-ray ΔF synthesis.

indicating that σ 's derived from least-squares calculations provide reasonable estimate of the scatter in the difference between the X-ray and neutron results. For the bond lengths involving hydrogen, however, σ is about one half s .

Comparison of thermal parameters

Recent work suggests that thermal parameters determined in the usual least-squares refinement of X-ray data are systematically in error. Stewart & Jensen (1969) found significant differences in thermal parameters obtained from refinements of low- and high-angle data for uracil; but O'Connell (1969) found no significant difference in thermal parameters obtained in a similar way for taurine, attributing this to the tetrahedral geometry of the atoms. Coppens (1967) and Coppens *et al.* (1969) demonstrated correlation of hybridization models by plotting the ellipsoids corre-

sponding to the differences in the thermal parameters obtained from refinements of the X-ray and neutron data.

In order to simplify the comparison of thermal parameters, B_{iso} is defined as the arithmetic mean of the three eigenvalues of the thermal ellipsoid tensor (Hamilton, 1959). B_{iso} , the mean difference between the X-ray and neutron B_{iso} , and the standard deviations of the mean differences are listed in Table 6.

It can be seen that the thermal parameters of the non-hydrogen atoms from set II data are not significantly different from those of the neutron refinement. This indicates that the effects of aspherical electron density are small enough for the X-ray and neutron results to be in close agreement. For set I the X-ray \bar{B}_{iso} are shifted to values significantly larger than the neutron values while for set I+II they are shifted in the same sense but by smaller amounts. This demonstrates the strong effects of high-order data in fixing thermal parameters.

The effects of error in the scattering factors of hydrogen on the temperature factors derived from the refinement have been discussed by Calder, Cochran, Griffith & Lowde (1962) who compared X-ray and neutron results to show that in crystals of LiH the hydrogen ion suffers contraction compared to the free atom. Jensen & Sundaralingam (1964) found evidence for contraction of the bonded hydrogen atom by comparing the isotropic thermal parameters of the hydrogen to B_{iso} of the atoms to which they are bonded. By comparing neutron and X-ray B values of hydrogen from different structures, Jensen (1965) estimated that the B 's derived from X-ray refinement were low by $2.5\text{--}3 \text{ \AA}^2$ if the scattering factors for the free atom were used in the model. Similar results were found independently by Mason, Phillips & Robertson (1965). Stewart *et al.* (1965) calculated scattering factors for atoms in the hydrogen molecule and predicted a change of 2.3 \AA^2 in the isotropic thermal parameters if the bonded atom scattering factors were used.

In comparing the X-ray and neutron thermal parameters in Table 6, we have tabulated the \bar{B} and $\bar{\Delta}$ obtained

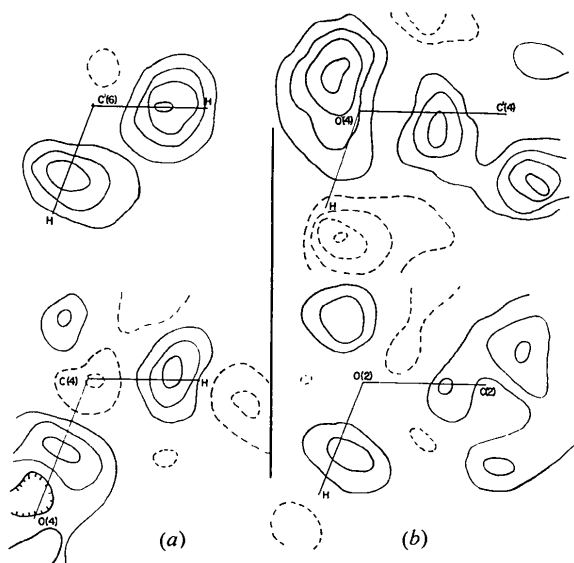


Fig. 5. Sections showing residual electron density through some C-H and O-H bonds, X-ray neutron ΔF syntheses.

Table 6. Comparison of thermal parameters from X-ray and neutron data

$B_{iso} = \frac{1}{3}(B_1 + B_2 + B_3)$ where B_i is an eigenvalue of the thermal parameter tensor. $\Delta = (\bar{B}_{iso} \text{ X-ray}) - (\bar{B}_{iso} \text{ neutron})$. Standard deviations in $\bar{\Delta}$ calculated from sample variance.

Atom	f	Set I		Set I+II		Set II		Neutron \bar{B}_{iso}
		\bar{B}_{iso}	$\bar{\Delta}$	\bar{B}_{iso}	$\bar{\Delta}$	\bar{B}_{iso}	$\bar{\Delta}$	
C	Berghuis <i>et al.</i>	1.703 \AA^2	0.157 (5) \AA^2	1.586 \AA^2	0.039 (5) \AA^2	1.558 \AA^2	0.012 (7) \AA^2	1.547 \AA^2
O	Berghuis <i>et al.</i>	2.165	0.112 (11)	2.097	0.044 (9)	2.076	0.023 (11)	2.054
Atom	f	\bar{B}	$\bar{\Delta}$	\bar{B}	$\bar{\Delta}$	\bar{B}	$\bar{\Delta}$	\bar{B}_{iso}
H (bonded to C)	SDS	1.25	-1.98 (15)	1.33	-1.90 (13)	-	-	3.23
	McW	*	-	-0.13	-3.36 (12)	-	-	
H (bonded to O)	SDS	4.15	0.31 (49)	4.15	0.31 (42)	-	-	3.84
	McW	*	-	2.15	-1.69 (33)	-	-	

* Set I data was not used to refine the hydrogen atoms with McWeeny f_H .

with the isolated atom scattering factors of McWeeny (1951) together with those of Stewart *et al.* (1965) for the bonded atom where refinement was carried out with both. We see that for sucrose the isolated atom scattering factors (McW) lead to \bar{B} values which are slightly negative for hydrogen bonded to carbon (set I+II). The magnitude of the mean difference (-3.36 \AA^2) is greater for these hydrogen atoms than for those bonded to oxygen (-1.69 \AA^2), but in both cases the thermal parameters are too low. This is consistent with the fact that the contraction of the electron density on bond formation has been ignored. By use of the bonded atom scattering factors (SDS) we found the \bar{B} values for hydrogen bonded to carbon still to be less than the neutron values, but they are greater than the neutron values for hydrogen bonded to oxygen. This suggests that the contraction of the electron density on bond formation is overestimated for hydrogen bonded to oxygen and underestimated for hydrogen bonded to carbon.

It should be noted that the standard deviations in the \bar{z} values in Table 6 for hydrogen bonded to oxygen are

much greater than those for hydrogen bonded to carbon. This could be caused by variable effects of hydrogen bonding on the electron distribution in oxygen.

Residual density maps

When refinement of a structural model is satisfactorily complete and all atoms are included, a ΔF synthesis (residual density map) with good data to the limit of Cu $K\alpha$ radiation will show density corresponding to bonding and lone-pair electrons (O'Connell, Rae & Maslen, 1966). Parameters for the spherical atoms usually assumed for the model, however, will have refined to positions tending to minimize the residual density. O'Connell (1969) and Hope & Kim (1971) have shown that improved residual density maps can be obtained if the parameters from a refinement based on high-angle data are used. This follows from the fact that the systematic shifts resulting from the bonding and lone-pair electrons in refinement with low-angle data tend to be reduced in refinement with high-angle data.

Coppens (1967, 1970) has shown that residual elec-

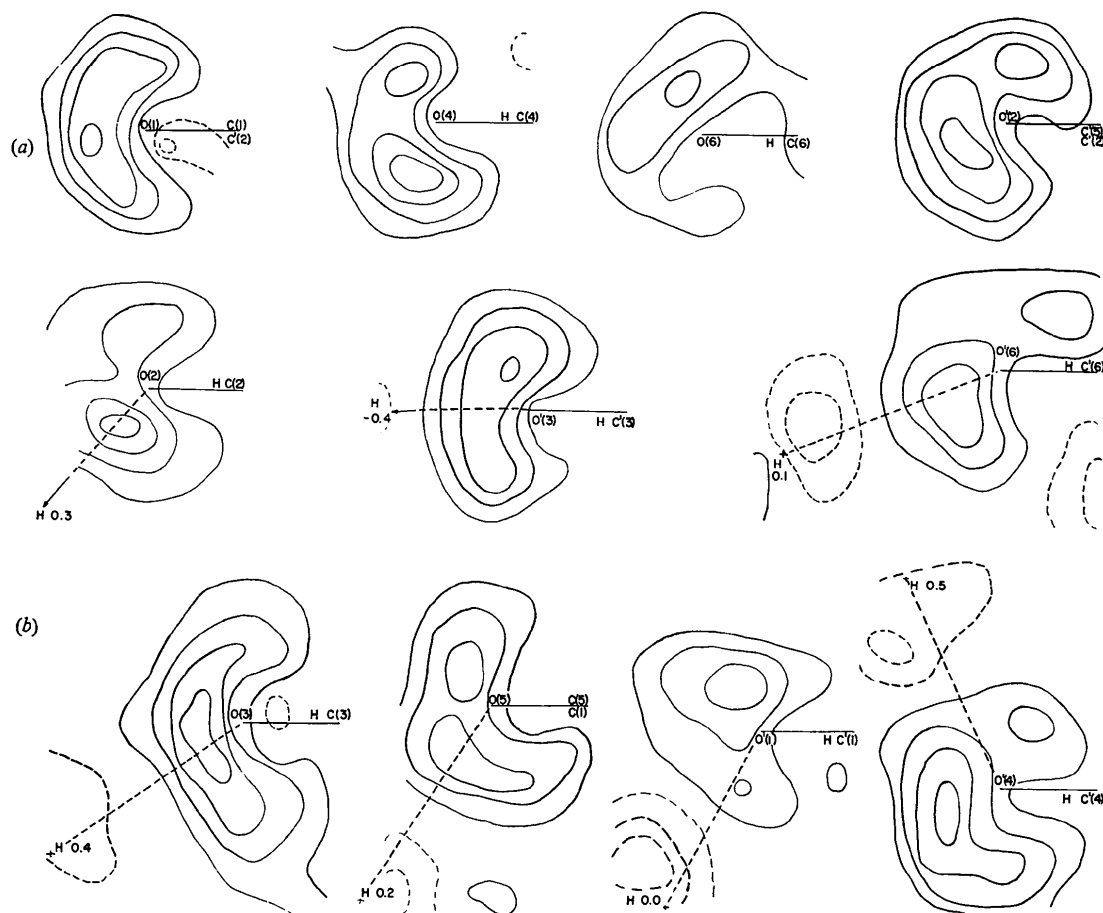


Fig. 6. Sections from X-ray neutron ΔF synthesis through oxygen lone-pair region. The x axis is the bisector of the angle formed by oxygen and the two atoms bonded to it, and the y axis is perpendicular to the plane defined by these three atoms. The projected position of the hydrogen atoms is shown and their distance from the plane of the figure indicated.

tron densities are shown to advantage by X-ray neutron ΔF syntheses. The coefficients in such a synthesis are $\Delta F e^{i\varphi_N}$ where

$$\Delta F = k|F_o| - |F_N|$$

k = scale factor

$|F_o|$ = observed structure amplitude

$|F_N|$ = structure amplitude calculated with neutron coordinates and scattering factors as used in X-ray calculations

φ_N = phase calculated with neutron coordinates.

For the X-ray neutron structure factor calculation, the scale factor, k , was within 0.5% of that derived from the refinement of all data. The R index was 0.037 compared to 0.029 for the refinement of all data, and the average difference in phase was 1.8° . The variation in $\Delta\varphi$ with $\sin\theta$ was small for $\sin\theta/\lambda < 0.3$ and ranged from 4.4 to 0.68 with increasing F_N . There was virtually no correlation with ΔF .

Fig. 4(a) is a composite of sections from the X-ray neutron ΔF synthesis showing the residual density in the pyranose and furanose rings. An average σ of $0.02 \text{ e } \text{\AA}^{-3}$ was calculated from estimated σ 's of the observed data (Cruickshank, 1949). All bonds show peaks in the range $0.12\text{--}0.27 \text{ e } \text{\AA}^{-3}$ with the residual density along C–C bonds considerably greater than that along C–O bonds. Similar sections from the high-angle X-ray ΔF syntheses are shown in Fig. 4(b). Again residual density appears in the bonds, but generally the peaks are somewhat less prominent than in the X-ray neutron maps.

Typical sections through hydrogen atoms from the X-ray neutron ΔF syntheses are shown in Fig. 5. Sections through three C–H bonds [Fig. 5(a)] show residual density peaks shifted toward the hydrogen nuclear positions with heights of about $0.2 \text{ e } \text{\AA}^{-3}$. The residual density in the O–H bonds tends to be more diffuse with peak heights averaging about $0.1 \text{ e } \text{\AA}^{-3}$. In Fig. 5(b) the peak along the O(2)–H bond is localized, but in the O'(4)–H bond there is no localized density, and the hydrogen atom is located at the edge of a rather deep negative region. H(O'4) is involved in the shortest

hydrogen bond in the crystals, and the bonding density may be distorted as a result.

Cross sections through all oxygen atoms are shown in Fig. 6(a), (b). Here the x axis is the bisector of the angle formed by the oxygen and the two atoms bonded to it, and the y axis is perpendicular to the plane defined by these three atoms. For example, the section through O(1) shows the perpendicular bisector of the angle C(1)–O(1)–C'(2) as the x axis, the normal to the plane of these three atoms as the y axis.

The atoms O(1), O(4), O(6) and O'(2) [Fig. 6(a)] are the only oxygen atoms that are not acceptors in hydrogen bonds and their densities are more or less crescent shaped in the lone-pair region. The other seven oxygen atoms [Fig. 6(b)] in the structure are all acceptors in hydrogen bonds. The projected positions of the hydrogen atoms are shown, and their distances from the section indicated. In some instances the residual density is distorted toward the proton as might have been anticipated, but the opposite appears to be the case in at least two of the sections in Fig. 6(b).

Comparison of sections in common to Figs. 3, 5 and 6 of the preliminary paper (Hanson *et al.*, 1972) and Figs. 4(a), 5 and 6 of this paper will show the essential features to be similar. At the atomic sites, however, the earlier maps are more negative about $0.1 \text{ e } \text{\AA}^{-3}$ than the present ones. The difference stems from the use of a 0.1113 scale factor based on least-squares with unit weights used in the earlier work and the 0.1123 scale factor based on least-squares with statistical weights used in the present work.

Fig. 7 shows sections from the high-angle X-ray ΔF synthesis through three oxygen atoms corresponding to three of the sections in Fig. 6. Although, the same features are present, the peaks are much lower than in the X-ray neutron sections. Evidently the effects of the lone-pair electrons in the high-angle X-ray data causing an average change of only 0.004 \AA in the C–O bond lengths is sufficient to appreciably affect the residual density.

The computer programs used were from the *XRAY*

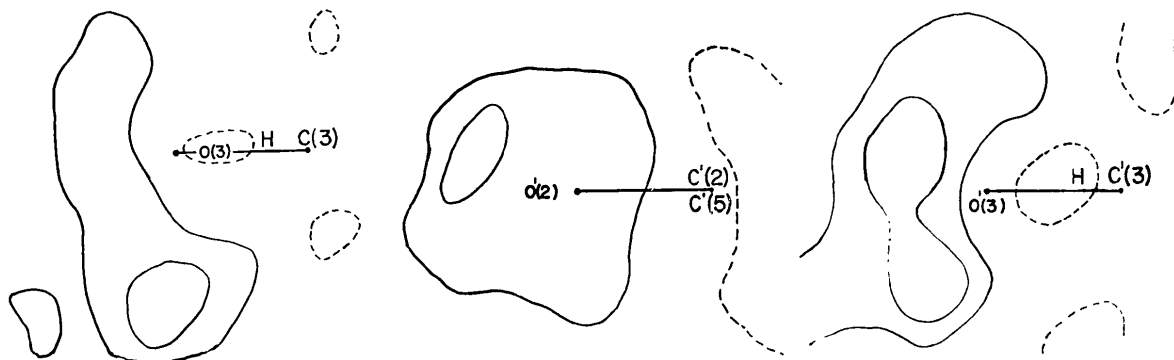


Fig. 7. High-angle X-ray ΔF synthesis through some oxygen lone-pair regions. Plane of sections same as corresponding ones in Fig. 6.

System (Stewart, Kundell & Baldwin, 1970), except for the Fourier retrieval programs which were written by Schilling & Nordman (1969). Support under USPHS Grant GM-10828 from the National Institutes of Health is gratefully acknowledged.

References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- ADMAN, E. & JENSEN, L. H. (1970). *Acta Cryst.* **B26**, 1326–1334.
- ALEXANDER, L. E. & SMITH, G. S. (1964). *Acta Cryst.* **17**, 1195–1201.
- BEEVERS, C. A., McDONALD, T. R. R., ROBERTSON, J. H. & STERN, F. (1952). *Acta Cryst.* **5**, 689–690.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478–483.
- BROWN, G. M. (1969). *Acta Cryst.* **B25**, 1338–1353.
- BROWN, G. M. & LEVY, H. A. (1963). *Science*, **141**, 921–923.
- BROWN, G. M. & LEVY, H. A. (1973). *Acta Cryst.* **B29**, 790–797.
- CALDER, R. S., COCHRAN, W., GRIFFITH, D. & LOWDE, R. D. (1962). *J. Phys. Chem. Solids*, **23**, 621–632.
- COCHRAN, W. (1956). *Acta Cryst.* **9**, 924–928.
- COPPENS, P. (1967). *Science*, **158**, 1577–1579.
- COPPENS, P. (1970). In *Thermal Neutron Diffraction*, pp. 82–100. Oxford Univ. Press.
- COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451–2458.
- COPPENS, P. & VOS, A. (1971). *Acta Cryst.* **B27**, 146–157.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65–82.
- DAWSON, B. (1964). *Acta Cryst.* **17**, 997–1009.
- DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2423–2437.
- FURBERG, S. & JENSEN, L. H. (1970). *Acta Cryst.* **B26**, 1260–1268.
- HAMILTON, W. L. (1959). *Acta Cryst.* **12**, 609–610.
- HANSON, J. C., SIEKER, L. H. & JENSEN, L. H. (1972). *Trans. ACA*, **8**, 133–153.
- HOPE, H. & KIM, N. E. (1971). *ACA. Abs.* p. 22. Winter Meeting, Columbia, S. C.
- HVOSLEF, J. (1968). *Acta Cryst.* **B24**, 23–35.
- JENSEN, L. H. (1965). *ACA. Abs.* p. 12. Winter Meeting, Suffern, N.Y.
- JENSEN, L. H. & SUNDARALINGAM, M. (1964). *Science*, **145**, 1185–1186.
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513–519.
- MASON, R., PHILLIPS, D. C. & ROBERTSON, G. B. (1965). *Mol. Phys.* **9**, 277–279.
- O'CONNELL, A. M. (1969). *Acta Cryst.* **B25**, 1273–1280.
- O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208–219.
- SCHILLING, J. W. & NORDMAN, C. E. (1969). Stored function retrieval program.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). *The XRAY System of Crystallographic Programs*, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STEWART, R. F. & JENSEN, L. H. (1969). *Z. Kristallogr.* **128**, 133–147.
- TOMIE, Y. (1958). *Proc. Phys. Soc. Japan*, **13**, 1030–1037.
- WILSON, A. J. C. (1967). *Nature, Lond.* **150**, 151–152.
- ZACHARIASEN, W. H. (1942). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1973). **B29**, 808.

The Crystal Structure of Twinned $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, 'Cadmium Chlorapatite'

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Twins of synthetic 'cadmium chlorapatite' were used for crystal-structure determination. The space group $P6_3/m$ is confirmed; $a = 9.633 \pm 0.004$ and $c = 6.484 \pm 0.004$ Å; $Z = 2$. The material is isostructural with fluorapatite. The volume ratio (0.35) of the crystals in the twin, and the usual structural detail have been obtained from X-ray data in which every observed reflection is the superposition of two reflections, one from each crystal in the twin. First the volume ratio and then the other parameters were adjusted in each cycle of least-squares refinement. The final R values are 5.6 and 5.5% for the two crystals in the twin.

Introduction

The members of the apatite group represented by the general formula $A_5(\text{MO}_4)_3\text{X}$ form a wide range of substitution solid solutions by partial or complete re-

placement of one kind of ion by another, with $A =$ alkaline earths, alkali metals, rare earths, Cd, Pb, Mn, etc.; $M =$ P, As, V, Si, Al, S, B, etc.; and $X =$ F, Cl, OH, O, Br, I or vacancies (Wondratschek, 1972). No complete crystal-structure investigation has been at-