

Packing arrangement

Fig. 2 shows the packing of the molecules in the lattice. The straight portions of the hydrocarbon chains are arranged in the triclinic form found in many other long chain compounds. The dimensions of the triclinic subcell ($T||$) are given in the experimental section; they are close to those observed by Lomer (1963) in lauric acid.

There are two short intermolecular distances:

Br \cdots C(1) at $010 + xyz$	3.60 Å
Br \cdots O(2) at $010 \times xyz$	3.21

No others (except those between carboxyl groups) are less than 3.8 Å.

The angle of tilt of the chain axes to the end group planes is 36° as compared to 46° in DL-2-methyloctadecanoic acid.

Thermal vibrations

The anisotropic thermal parameters, b_{ij} , were converted to mean square amplitudes of vibration in the directions of the principal axes of the hydrocarbon chain [C(4)–C(18) portion], and these are shown in Fig. 3. Although the estimated standard deviations of the b_{ij} parameters suggest that variations between neighbouring atoms are not significant, the general pattern is physically sensible. The perpendicular vibrations [Fig. 3(a)] increase considerably towards the C(18) end of the chain; the increase is particularly marked

from about C(14) onwards, *i.e.* for that part of the chain which is not flanked on all sides by other chains (see Fig. 2). The transverse vibrations [Fig. 3(b)] also increase towards the C(18) end, while the longitudinal vibrations [Fig. 3(c)] do not.

The initial calculations were done on the Saab D21 computer of the Institute of Medical Biochemistry, University of Göteborg. The remainder were done on the Atlas Computers at Manchester University and at the National Institute for Research in Nuclear Science in England. We are grateful to all these establishments and to the Edinburgh University Computer Unit for their cooperation, to Dr R. Diamand for his least-squares refinement program, and to Dr L. Hodgson for a bond-length and angle program. We also thank Mrs M. Innes, Mr U. Löfväs and Mr A. Westerdahl for technical assistance. Financial support has been obtained from the Swedish Natural Science and Swedish Medical Research Councils.

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An Experimental Determination of $\Delta f''$ for Iodine

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(Received 19 May 1964 and in revised form 28 May 1965)

The imaginary component of the anomalous contribution to the scattering factor ($\Delta f''$) of iodine for Cu $K\alpha$ radiation has been determined with the intensity data from the structure analysis of methyl melaleucate iodoacetate by Hall & Maslen (1965). The reliability of the calculation is shown to depend critically on the weighting of all terms, but particularly on those where the Bijvoet inequality is immeasurably small. A method for deriving the correct weighting scheme from an assessment of the errors is developed.

The results obtained are in reasonable agreement with those from theoretical calculations. The angular dependence of the $\Delta f''$ curve corresponds closely to that predicted. There is a small discrepancy in scale, but this may have resulted from an error in the experimental value.

Introduction

In recent years several experimental determinations of the anomalous dispersion corrections to the atomic scattering factors have been carried out. These were necessary both to confirm the theoretical values and

to investigate the dependence of $\Delta f''$ on the presence of more than one anomalous scatterer in the unit cell. In general the experimental zero Bragg angle values are in good agreement with values calculated by James (1954) from the wave mechanical theory of Hönl (1933) and by Dauben & Templeton (1955) and Cooper (1963) from the work of Parratt & Hempstead (1954) and Eisenlohr & Muller (1954). Recently the corrections at zero Bragg angle have been re-evaluated with the

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use of relativistic wave functions by Cromer (1965). Conflicting results have been reported for the dependence of $\Delta f''$ on the number of anomalous scatterers. Nevertheless recent work (Parthasarathy, 1962) suggests that this dependence is negligible, and some of the earlier results are presumably in error.

Little effort has been made however to determine experimentally the variation of the dispersion corrections with the Bragg angle, θ . The current theoretical method (Templeton, 1962) for estimating this angular dependence gives as the dominant factor the normal orbital transform of the appropriate electron energy states, such as those evaluated by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1959) and Veenendaal, MacGillavry, Stam, Potters & Römgers (1959). As pointed out by Templeton (1962), little reliability should be placed on these values in accurate work because of difficulties in assessing the accuracy of the angular dependent curves calculated in this way. However, since the orbital transforms of the inner, tightly bound electronic states contribute the major part of the anomalous dispersion correction, and these decrease slowly with θ , the angular dependence of $\Delta f'$ and $\Delta f''$ is only small, and in experimental investigations it has generally been considered to be of little importance. Recently, however, it has been possible to carry out far more accurate structural analyses in which this no longer applies. Moreover, in view of the power of anomalous dispersion techniques for the solution of structures, it is important to make an independent check of these theoretical values. For this reason an attempt was made to calculate the angular dependent values of $\Delta f''$ for iodine, using the intensities and structural parameters of methyl melaleucate iodoacetate (Hall & Maslen, 1965).

Method for determining $\Delta f''$

The method for determining $\Delta f''$ from the intensity data and structural parameters of methyl melaleucate iodoacetate (referred to below as MMI) was necessarily different from that of previous determinations. In the structures used by Roof (1961, 1962) the analysis was considerably simplified because all atoms were at special positions in the unit cell. In any case no provision was made for angular variation. The procedure used by Parthasarathy (1962) is more general* both because it may be applied to structures with more than one scatterer per unit cell and because it permits the variation of $\Delta f''$ with θ to be studied.

The latter method uses the tabulated values of the real scattering factors f^0 and $\Delta f'$. These may be omitted from the determination, however, by means of the more concise relationships which may be derived from the general structure factor equations, as follows:

$$F_H = A' - B'' + i(A'' + B') \quad (1)$$

and

$$F_{\bar{H}} = A' + B'' + i(A'' - B') \quad (2)$$

where

$$A' = \sum_j^N (f_j^0 + \Delta f_j') \exp(-B_j) \cos 2\pi H \cdot x_j$$

$$B' = \sum_j^N (f_j^0 + \Delta f_j') \exp(-B_j) \sin 2\pi H \cdot x_j$$

$$A'' = \sum_j^N \Delta f_j'' \exp(-B_j) \cos 2\pi H \cdot x_j$$

$$B'' = \sum_j^N \Delta f_j'' \exp(-B_j) \sin 2\pi H \cdot x_j$$

for N atoms at positions x_j in the unit cell.

From the complex conjugates

$$F_H^* = A' - B'' - i(A'' + B') \quad (3)$$

$$F_{\bar{H}}^* = A' + B'' - i(A'' - B') \quad (4)$$

the relative difference of the hkl and $\bar{h}\bar{k}\bar{l}$ intensities is

$$F_H \cdot F_H^* - F_{\bar{H}} \cdot F_{\bar{H}}^* = \Delta F^2 = 4(A''B' - A'B'') \quad (5)$$

Assuming only one type of anomalous scatterer is present in the unit cell, equation (5) may be expanded in terms of the normal and anomalous scattering factors. For example

$$\begin{aligned} \sum_j^N (f_j^0 + \Delta f_j') \exp(-B_j) \cos 2\pi H \cdot x_j \\ = (f^0 + \Delta f'') \sum_j^M \exp(-B_j) \cos 2\pi H \cdot x_j \\ + \sum_j^{N-M} f_j \exp(-B_j) \cos 2\pi H \cdot x_j \end{aligned} \quad (6)$$

Similar expansions are possible for the other terms. The sum of the terms with coefficients $(f^0 + \Delta f'')$ cancel to give the expression

$$\begin{aligned} \Delta f'' = \Delta F^2 / 4 \sum_j^M \exp(-B_j) \cos 2\pi H \cdot x_j \sum_j^{N-M} f_j \exp(-B_j) \\ \sin 2\pi H \cdot x_j - \sum_j^M \exp(-B_j) \sin 2\pi H \cdot x_j \sum_j^{N-M} f_j \\ \exp(-B_j) \cos 2\pi H \cdot x_j \end{aligned} \quad (7)$$

For the sake of convenience equation (7) may be written

$$\Delta f'' = \frac{\Delta F^2}{4(A_a B_n - B_a A_n)} \quad (8)$$

This relationship enables the imaginary anomalous dispersion correction to be evaluated from a structure containing any number of one type of anomalous scatterer and any number of types of normal scatterer in the unit cell. Equation (8) is virtually* independent of the real anomalous contribution.

* Although Parthasarathy (1962) considered only centricly arranged anomalous scatterers a similar approach may be used when these atoms are placed acentricly.

* Inaccuracies in f^0 and $\Delta f'$ may affect $\Delta f''$ indirectly through errors in the temperature factor of the anomalous scatterer. Such effects will, however, be small for a well refined structure.

Assessment of error

It is essential in the evaluation of $\Delta f''$ to consider carefully the effect of errors on equation (8). If the structure factors of methyl melaleucate iodoacetate were independent of systematic error the calculation of a mean $\Delta f''$ may be considered purely as a statistical problem. The physical sense of anisotropic thermal parameters and the low structure factor residual indicate that these errors are small. Even so, it is probable, in view of the restricted angular range of the intensity data, that the accuracy of the structure factor scale K is limited. The importance of an error in K is discussed later, but it suffices at present to ignore this source of error and consider each value of $\Delta f''$ according to its standard deviation in the calculation of a mean. In particular, with the method of least squares, reflexions should be weighted according to the inverse of the variance,

$$i.e. w = 1/\sigma^2(\Delta f''_{hkl}). \quad (9)$$

An analysis of errors therefore resolves itself into the problem of estimating the standard deviation of $\Delta f''$ for any given reflexion hkl . This may be derived by considering the individual errors in equation (8) due to the structure factor components A_a , B_a , A_n and B_n , and the intensity difference ΔF^2 . The variance of the denominator of equation (8) becomes

$$\sigma_D^2 = A_a^2 B_n^2 \left\{ \frac{\sigma^2(A_a)}{A_a^2} + \frac{\sigma^2(B_n)}{B_n^2} \right\} + A_n^2 B_a^2 \left\{ \frac{\sigma^2(A_n)}{A_n^2} + \frac{\sigma^2(B_a)}{B_a^2} \right\} \quad (10)$$

where $\sigma(A_a)$, $\sigma(B_a)$, $\sigma(A_n)$, and $\sigma(B_n)$ are the standard deviations in A_a , B_a , A_n and B_n respectively. Assuming that on the average $\sigma(A_a) \simeq \sigma(B_a)$ and $\sigma(A_n) \simeq \sigma(B_n)$, equation (10) simplifies to

$$\sigma_D^2 = (A_a^2 + B_a^2)\sigma^2(A_n) + (A_n^2 + B_n^2)\sigma^2(A_a). \quad (11)$$

Similarly the variance of the numerator of equation (8) may be expressed in terms of the relative intensity standard deviation as

$$\sigma_N^2 = \sigma^2(\Delta F^2) = 2\sigma^2(|F|^2). \quad (12)$$

Combining equations (11) and (12), the total variance becomes

$$\sigma^2(\Delta f'') = (\Delta f'')^2 \left\{ \frac{(A_a^2 + B_a^2)\sigma^2(A_n) + (A_n^2 + B_n^2)\sigma^2(A_a)}{16(A_a B_n - A_n B_a)^2} + \frac{2\sigma^2(|F|^2)}{(\Delta F^2)^2} \right\} \quad (13)$$

which, on expanding $\Delta f''$ in terms of equation (8), gives

$$\sigma^2(\Delta f'') = (\Delta F^2)^2 \left\{ \frac{(A_a^2 + B_a^2)\sigma^2(A_n) + (A_n^2 + B_n^2)\sigma^2(A_a)}{256(A_a B_n - A_n B_a)^4} + \frac{\sigma^2(|F|^2)}{8(A_a B_n - A_n B_a)^2} \right\} \quad (14)$$

Equation (14) provides a rigorous means of estimating the standard deviation of $\Delta f''$, and consequently the weight of each reflexion, provided the values of $\sigma(A_a)$, $\sigma(A_n)$ and $\sigma(|F|^2)$ are known.

A small alteration is necessary to equation (14) for certain reflexions if visually measured data are used in the determination, since a significant proportion of the relative intensity differences ΔF^2 are less than the incremental changes in intensity δI from one spot to the next on the calibrated intensity strip, and may therefore be regarded as immeasurably small. Because of the inability of the eye to measure to better than $\pm \delta I$, intensity differences less than $2\delta I$ have a high probability of being put to zero. In the $\Delta f''$ calculation these values give a result of zero. The reflexions of this type have a profound influence on the determination, and it is essential that they should be weighted correctly in the calculation. However, because the value of ΔF^2 is systematically forced to zero for these reflexions, the standard deviation estimated from equation (14) is incorrectly small. This may be overcome by estimating a value of ΔF^2 for use in equation (14) from the calculated components A_a , B_a , A_n and B_n and the theoretical $\Delta f''$ value in the expression

$$\Delta F^2 = 4\Delta f''_{\text{theor.}} \{A_a B_n - A_n B_a\}. \quad (15)$$

Using a theoretical value of $\Delta f''$ in equation (15) and the resulting ΔF^2 in equation (14) provides sufficiently reliable standard deviations for these reflexions.

The evaluation of the individual standard deviations $\sigma(A_n)$, $\sigma(A_a)$ and $\sigma(|F|^2)$ may now be considered in turn.

(i) $\sigma(A_n)$

Parthasarathy (1962) has shown that the standard deviation of a structure factor component $|A|$ of a non-centrosymmetric crystal, assuming that on the average $|A| = |F|/\sqrt{2}$, is given by

$$\sigma(|A|) = \left\{ \frac{\pi^2 N}{3} \right\}^{\frac{1}{2}} \cdot \frac{\int \bar{\sigma}(r)}{d}. \quad (16)$$

In the structure of MMI the average atomic coordinate standard deviation $\sigma(x)$ for the normal scatterers is approximately 0.02 Å so that $\sigma(r) \simeq 0.035$ Å. The mean atomic scattering factor was calculated according to the relative contributions of the oxygen, carbon and hydrogen atoms in 0.1 intervals of $\sin \theta$. These values were applied to equation (16) to give the variation of $\sigma(A_n)$ with $\sin \theta$ which are listed in Table 1(a) and graphed in Fig. 1(a).

(ii) $\sigma(A_a)$

Because the component A_a is independent of an atomic scattering factor, the standard deviation $\sigma(A_a)$ estimated from equation (16) varies linearly with $\sin \theta$. The atomic coordinate standard deviation of the iodine atom in the structure of MMI is 0.002 Å, giving $\sigma(r)$ as 0.0035 Å.

Table 1. Standard deviations $\sigma(A_n)$, $\sigma(A_a)$ in electrons

(a)		
$\sin \theta$	f	$\sigma(A_n)$
0.000	4.27	0.00
0.077	4.10	0.44
0.154	3.71	0.79
0.308	2.70	1.16
0.463	1.93	1.24
0.617	1.47	1.26
0.771	1.21	1.29
0.925	1.08	1.38
(b)		
$\sin \theta$	f	$\sigma(A_a)$
0.000	1.00	0.0000
0.154	1.00	0.0025
0.308	1.00	0.0051
0.463	1.00	0.0076
0.617	1.00	0.0102
0.771	1.00	0.0127
0.925	1.00	0.0152

Although $\sigma(A_a)$ is much smaller than $\sigma(A_n)$ the effect on the total standard deviation of these values is quite similar, since in equation (14) $\sigma(A_a)$ is multiplied by the usually large value of $(A_n^2 + B_n^2)$, whereas $\sigma(A_n)$ is multiplied by the smaller value of $(A_a^2 + B_a^2)$. The variation of $\sigma(A_n)$ with $\sin \theta$ is shown in Table 1(b) and Fig. 1(b).

(iii) $\sigma(|F|^2)$

It is convenient to express $\sigma(|F|^2)$ in terms of the observed structure factor $|F_o|$ and its standard deviation $\sigma(|F|)$. These are related by the expression

$$\sigma^2(|F|^2) = 2F_o^2 \sigma(|F|). \quad (17)$$

Methods of estimating the accuracy of $|F_o|$ have been considered by Abrahams (1955) and Ibers (1956) using observed structure factors of common reflexions collected about different axes. This was found to be a reliable method of evaluating $\sigma(|F|)$ provided that a significant proportion of the data was collected about two or more axes, and suitable corrections were made to remove systematic errors due to absorption and extinction. Cruickshank (1949) and Ibers (1956) have suggested an alternative approach whereby an estimate of $\sigma(|F|)$ may be derived from the difference between the observed and calculated structure factors $||F_o| - |F_c||$. Although this introduces errors arising from structural parameters, these should be small for a well refined structure, and the major part may be attributed to observational errors. Because of the limited number of common Hkl and hkL^* reflexions available in the intensity data of MMI both methods were used to estimate $\sigma(|F|)$ for this determination.

The residual† of common reflexions calculated in the initial correlation of the MMI data was 0.07 giving an average value of 0.07 $|F|$ for $\sigma(|F|)$, which is comparable to the value of 0.07 $|F|$ obtained by Abrahams (1955) from intensity data measured visually four times. This assumes a linear relationship with the observed structure factor F_o . However, recent evidence (Marsh, 1956; Donohue & Marsh, 1962; Watson, 1963) indic-

ates that this is not necessarily correct for all visual data. A graph of the mean values of ΔF with $|F_o|$ showed [Fig. 1(c)] not a simple straight line but a plot which could be best described as a two-stage linear relationship. This agreed closely with the mean values of $\sigma(|F|)$ estimated from the two sets of common reflexions according to the expression of Ibers (1956)

$$\sigma(|F|) = 0.89 \{ ||F_o(Hkl)| - |F_o(hkL)| \}. \quad (18)$$

The average standard deviation $\sigma(|F|)$ estimated from Fig. 1(c) is best described by the expression

$$\sigma(|F|) = a(|F_o| - b) \quad (19)$$

which, with equation (17) gives

$$\sigma^2(|F|^2) = 2a^2 F_o^2 (|F_o| - b)^2, \quad (20)$$

where for $0 < |F_o| < 70$ electrons, $a = 0.035$ and $b = -45.0$ electrons and for $70 < |F_o| < 300$ electrons, $a = 0.100$ and $b = +33.0$ electrons.

* The capital letter indicates the rotation axis.

† The residual in this case was

$$\frac{\sum ||F_o(Hkl)| - |F_o(hkL)||}{\sum |F_o(Hkl)|}$$

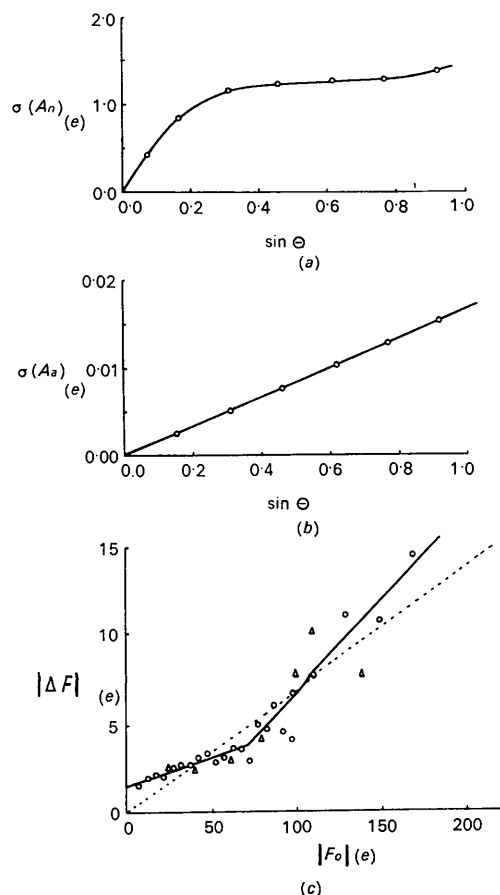


Fig. 1. Graphs showing the variation of (a) $\sigma(A_n)$ with $\sin \theta$, (b) $\sigma(A_a)$ with $\sin \theta$, (c) ΔF with $|F_o|$. Circles indicate $\Delta F = |F_o - F_c|$. Triangles indicate $\Delta F = 0.89 |F_o(Hkl) - F_o(hkL)|$. The dashed line is $\Delta F = 0.07 |F_o|$.

The larger values of $\sigma(|F|^2)$ given by equation (20) for high $|F_0|$ values may be expected to result from the effect of film factor errors on the high intensities. Of the two variations of $\sigma(|F|^2)$ with $|F_0|$, the one below 70 electrons corresponds to the region where the intensities were obtained from the first pack of films, and the film factors are known quite accurately. That above 70 electrons involves measurements from successive packs of films which are subject to the large probable errors in the statistical estimation of film factors.

Calculation of $\Delta f''$

Two methods were used to evaluate the angular dependence of $\Delta f''$. The first was to include all reflexions in a weighted least-squares calculation for the best linear relation between $\Delta f''$ and $\sin \theta$ by minimizing the function

$$\sum_{hkl} w \{ \Delta f''_{hkl} - m \sin \theta - \Delta f''_0 \}^2 \quad (21)$$

where m is the slope of the linear plot and $\Delta f''_0$ the zero angle value of $\Delta f''$. The results obtained were $\Delta f''_0 = 6.3$ electrons and $m = -0.4$, which differ slightly but not significantly from Templeton's theoretical values of 7.2 and -0.4 . This approach assumes, however,

that $\Delta f''$ varies linearly with $\sin \theta$, an assumption which may well be incorrect. An alternative was to calculate the mean $\Delta f''$ for discrete ranges of $\sin \theta$ by plotting the distributions of the weight w versus $\Delta f''$. The distribution of the weight w and the number of reflexions n with $\Delta f''$ in 0.1 intervals of $\sin \theta$ are shown in Figs. 2 and 3 respectively. The former distributions were used to evaluate the experimental curve shown in Fig. 5. In addition to allowing for different types of $\Delta f''$ angular dependence this approach provides a reasonable estimate of standard error of the mean $\Delta f''$ values. The normal procedure of evaluating the standard error $D(\Delta f'')$ requires that the w distributions be normal. A χ^2 test showed that the distributions may be considered normal to the 0.01 level of significance. Using large sampling theory the standard error of the mean was calculated as

Table 2. Mean values of $\Delta f''$, $\sigma(\Delta f'')$ and $D(\Delta f'')$ in ranges of $\sin \theta$ calculated from w distributions (Fig. 2)

$\sin \theta$	$\Delta f''$	$\sigma(\Delta f'')$	N	$D(\Delta f'')$
0.250	6.7	2.0	35	0.33
0.350	6.5	3.2	85	0.35
0.450	6.2	3.6	134	0.31
0.550	6.0	4.0	181	0.30
0.650	6.0	3.5	206	0.25
0.750	6.1	4.0	104	0.40

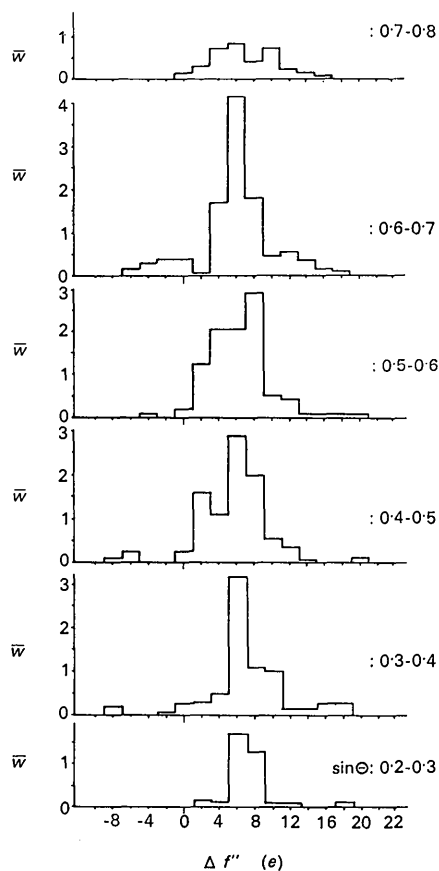


Fig. 2. The distribution of weight \bar{w} with $\Delta f''$ in intervals of $\sin \theta$.

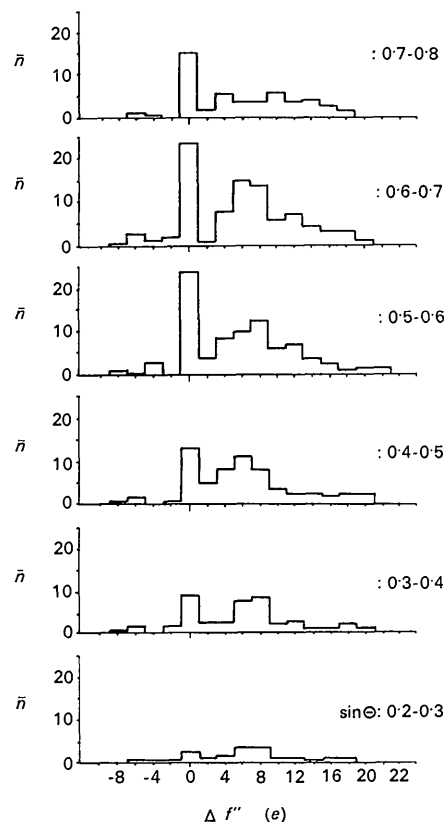


Fig. 3. The distribution of number of reflexions \bar{n} with $\Delta f''$ in intervals of $\sin \theta$.

$$D(\Delta f'') = \frac{\sigma(\overline{\Delta f''})}{\sqrt{N}}, \quad (22)$$

N being the number of reflexions within each 0.1 interval of $\sin \theta$. These values are listed in Table 2.

Discussion

The theoretical curve of Templeton (1962), Cromer's (1965) zero Bragg angle value and the experimental $\Delta f''$ curve for iodine and Cu $K\alpha$ radiation found in this analysis are compared in Fig. 5. The distributions of weight w and the number of reflexions n with $\Delta f''$ in 0.1 intervals of $\sin \theta$ are shown in Figs. 2 and 3 respectively. The former distributions were used to evaluate the experimental curve shown in Fig. 5.

According to the standard error of the mean $D(\Delta f'')$ the experimental $\Delta f''$ curve does not differ to a very high level of significance from the theoretical values, but the zero Bragg angle value is considerably closer to that of 6.68 electrons by Cromer. However, the experimental values are consistently less than those from both theoretical calculations. It seems probable that the difference from Templeton's curve is real. If this is so it is a contributing factor in explaining why reliable estimates of the structure factor phases were obtained when an incorrect scale was used in the anomalous phase calculation in the solution of the structure of MMI (Hall & Maslen, 1965). The F_A' value in this calculation would have been overestimated and this would compensate for the effect of the scale on the numerator.

This independent agreement with the experimental $\Delta f''$ curve is not sufficient, however, in view of the large $D(\Delta f'')$ values, to state conclusively that the theoretical values are overestimated. Moreover it is possible that there is an additional systematic error caused by inaccuracy in the structure factor scale. Although the scales of the MMI data evaluated both from Wilson plot and internal scaling methods agree, they cannot be considered absolute because of the limited angular range of these data. Cruickshank (1960) and Dawson (1961) have stressed that significant errors may

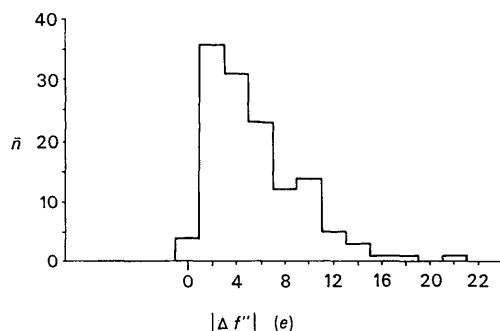


Fig. 4. The distribution of number of reflexions \bar{n} with $|\Delta f''|$ over all $\sin \theta$ for reflexions where ΔF^2 is given as zero from the visual measurements. (See text for the method of estimating $|\Delta F^2|$.)

arise in the scale calculated from low angle data owing to the effect of aspherical charge distributions, secondary extinction, and inaccurate hydrogen parameters. This was exemplified in the refinement of orthonilic acid (Hall & Maslen, 1966) when the scale obtained by refining the structure with data above $\sin \theta/\lambda = 0.4 \text{ \AA}^{-1}$ was 5% greater than that using all the data. It is likely that in the larger, less accurate structure of MMI there is a similar discrepancy.

A comparison of the n distributions and the w distributions (Figs. 2 and 3) illustrates the importance of weighting each reflexion correctly in the evaluation of $\Delta f''$, a point that most previous investigators have not fully appreciated. This is particularly important when visual data are used since systematic errors arising from the omission of reflexions with immeasurable ΔF^2 values from the n distributions give a positive angular dependence of $\Delta f''$, which is in contrast to the theoretical curve. This positive slope is due to a marked skewness of the n distribution from the normal towards the upper $\sin \theta$ regions. The absence of the immeasurable ΔF^2 values is the prime cause of this skewness, as was clearly shown by a simple test. Assuming that the measurable limit of the intensity difference by visual methods is $2\delta I$ (see above) all values with immeasurable differences were given the average value of $\Delta F^2 = |\delta I|$, representing the modulus of the most probable value of the intensity difference. This in turn enabled the most probable value of $\Delta f''$ for these reflexions to be estimated. The distribution of n versus $\Delta f''$ (Fig. 4), as expected, shows a maximum at about 2.5 electrons. Because the majority of the reflections would give positive values of $\Delta f''$ the inclusion of these terms

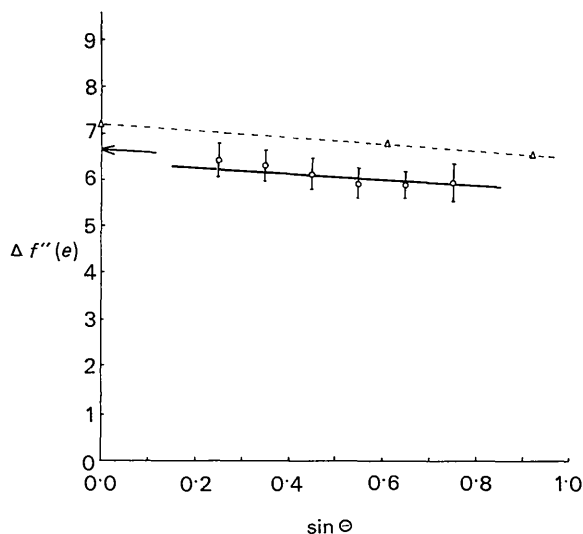


Fig. 5. A graph of $\Delta f''$ versus $\sin \theta$. The dashed line indicates the theoretical curve (Templeton, 1962) and the full line the experimental curve calculated from a weighted least-squares analysis. Cromer's (1965) zero angle value is indicated by the arrow. The circles and limits represent the mean values of $\Delta f''$ and their standard errors estimated from the weighted distributions (see Fig. 2.)

should largely correct for the skewness of the n distributions.

A second factor influencing the normality of the n distributions is the tendency for errors in the denominator* of equation (8) to cause larger errors in high rather than low $\Delta f''$ values. This is best illustrated by a simple example; if the numerator of equation (8) is 10.0 and the denominator is 2.0 ± 1.0 , $\Delta f''$ will have the value 5.0 and the error limits of 3.3 and 10.0. The difference of -1.7 and 5.0 of these limits from the mean indicates the degree to which errors in the values of A_a , B_a , A_n and B_n influence the value of $\Delta f''$ in either direction. This effect is worsened by the fact that high values of $\Delta f''$ generally arise from small denominators in equation (8). Because of this some care must also be taken with 'rounding off' the generally small components A_a and B_a , since incorrect procedures can cause severe errors in the value of $\Delta f''$.

Both sources of error contribute to the increase in the skewness of the n distributions at high angles, since the average structure factor $[N^{\frac{1}{2}} f \exp(-B \sin^2 \theta / \lambda^2)]$ decreases as θ becomes larger. The average ΔF^2 therefore decreases, and there is a higher probability of this value being immeasurable. This effect is particularly severe in the intensity data of MMI owing to the large overall temperature factor. Nevertheless the values obtained from this determination must be considered among the most reliable obtained experimentally to date. The accuracy would have been greatly enhanced if accurate high angle intensity data had been available, since this, in addition to providing more accurate values of ΔF^2 and the structure factor scale K , would have permitted better refinement of the structure, and consequently lower standard deviations for the structural parameters. The use of a smaller structure would allow a further improvement in accuracy. The determination is, however, sufficient to show a general agreement between the theoretical and the experimental $\Delta f''$ curves for iodine as well as providing a test of the general method and weighting scheme derived above. There appears little doubt from this study that equations (8) and (14) may be used with confidence to obtain reliable ex-

* The numerator will also decrease when the denominator is small but the effect of these errors is symmetrical, and does not influence the normality of the distribution.

perimental values of $\Delta f''$ where there is one type of anomalous scatterer in the cell. For structures with a higher number of types of anomalous scatterer more complex expressions are necessary.

In conclusion it is worth noting that in agreement with Parthasarathy (1962) and Bijvoet (1962) these results indicate that the value of $\Delta f''$ is unaffected by more than one anomalous scatterer per unit cell. However, because of the large number of non-anomalous scatterers in the unit cell of MMI this evaluation should not be considered a rigorous test for this interaction.

The authors wish to thank a referee for helpful advice which resulted in a substantial revision of this work. One of us (SRH) acknowledges receipt of a Commonwealth Postgraduate Award.

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