

from the plane of the three remaining axial carbon atoms increases linearly on going away from the ring; the maximum amount of this out-of-plane bending is 2.3° (plane III). The maximum displacement of the atoms defining the mean planes is less than 0.02 \AA .

The lengths and direction cosines of the principal axes of thermal vibration are given in Table 8. The anisotropy is particularly evident for the methyl carbon atoms.

A study of the possible rotation of the methyl groups around their axes was made by evaluation of the $H \cdots H$ interactions using Bartell's (1960) formula and considering only the atoms lying at a distance $r \leq r_0$ from the methyl hydrogen atoms, where r_0 is the abscissa of the minimum in the curve. The maximum height of the resulting barriers was only 22 cal.mole^{-1} . However, this fact cannot be taken as proof that the freedom of rotation of methyl groups shown in isolated molecules of methylbenzenes (Woolfenden & Grant, 1966) is maintained in our crystal; a more sophisticated calculation allowing $C \cdots H$ and $H \cdots H$ interactions both for the attractive and repulsive region might lead to a significant barrier height.

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Least-Squares Weighting Schemes for Diffractometer-Collected Data.

IV. The Effect of Random Errors in the Form Factors Resulting from Bonding

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An analysis is made of the random errors that are encountered in a diffractometer experiment. These are the result of counting statistics, random setting errors and random errors resulting from errors in the form factors caused by bonding between atoms. For the all-light-atom example considered this latter error is of the order of 3%. A schematic technique for obtaining absolute weights is indicated.

Introduction

Analysis of the weighting function for least-squares refinement derived on the basis of counting statistics

and random instrumental setting errors for a diffractometer experiment leads to an expression

$$1/w(\mathbf{h}) = \sigma_1^2(\mathbf{h}) + \sigma_2^2(\mathbf{h})$$

where $\sigma_1^2(\mathbf{h})$ is the variance of $|F(\mathbf{h})|$ resulting from counting statistics alone and $\sigma_2^2(\mathbf{h})$ the variance resulting from the random instrumental setting errors. It has been shown (Grant, Killean & Lawrence, 1969) that the form of $\sigma_2^2(\mathbf{h})$ is

$$\sigma_2^2(\mathbf{h}) = c^2 |F(\mathbf{h})|^2$$

where c is a constant which can be found approximately from the G factor.

This weighting scheme, although producing satisfactory refinement if the small structure factors are given zero weight, considerably underestimates the variance of these small structure factors and this paper is concerned with the random error which is predominant for these structure factors. It will be shown that inclusion of this error modifies the weights of all the structure factors and the value of c and leads to a weighting scheme which appears to allow the refinement of a structure without recourse to the use of artificial weights; the one exception to this being that it may be necessary to apply zero weight to any structure factor which is clearly affected by non-random errors such as extinction.

The modified weighting scheme

The error in the calculated value of a structure factor arises from (i) errors in the positional parameters, (ii) errors in the thermal parameters and (iii) errors in the scattering factor curves as a result of the use of an 'isolated atom' model to compute these curves. Errors (i) and (ii) do not contribute to the least-squares weight for a structure factor as these are the parameters in the least squares and hence (iii) is the only error to be considered.

The errors in the scattering-factor curves will be of two main types. The first error will have a systematic effect upon the structure factors and is a result of approximations in the 'isolated atom' model producing errors in the scattering factor curve. The second error will have a random effect upon the structure factors and is a result of each atom having its electron cloud distorted in a different way from the free-atom shape. This distortion is highly asymmetric and is caused by the bonding of each atom to other atoms.

Consider the structure-factor expression

$$F(\mathbf{h}) = \sum_j [f(\mathbf{h}) + \delta(\mathbf{h})] \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j,$$

where $f(\mathbf{h})$ is the 'isolated atom' scattering factor and $\delta(\mathbf{h})$ is the correction to be applied to $f(\mathbf{h})$ because of the bonding of the atom. Assume that

$$|\delta(\mathbf{h})| = k f(\mathbf{h}),$$

remembering that $\delta(\mathbf{h})$ unlike $f(\mathbf{h})$ can have both positive and negative values. Hence

$$F(\mathbf{h}) = \sum_j f(\mathbf{h}) \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j + \sum_j k s_j f(\mathbf{h}) \exp 2\pi i \mathbf{h} \cdot \mathbf{r}_j,$$

where s_j is ± 1 . Clearly the second term of this expression gives a variance

$$\sigma_3^2[|F(\mathbf{h})|] = k^2 \langle [\sum s_j f(\mathbf{h})]^2 \rangle = k^2 \langle |F(\mathbf{h})|^2 \rangle.$$

This is a measure of the variance of $|F(\mathbf{h})|$ resulting from the bonding of the atoms. The weight of a structure factor is now given by

$$\begin{aligned} 1/w(\mathbf{h}) &= \sigma^2(\mathbf{h}) = \sigma_1^2(\mathbf{h}) + \sigma_2^2(\mathbf{h}) + \sigma_3^2(\mathbf{h}) \\ &= \frac{K}{4 L_p} \cdot \frac{(I+B)}{(I-B)} + c^2 |F(\mathbf{h})|^2 + k^2 \langle |F(\mathbf{h})|^2 \rangle, \end{aligned}$$

where $\sigma_1^2(\mathbf{h})$ is described for a constant-time experiment and I is the integrated peak count and B is the background count.

It is important to note that k is the average fractional error in the scattering curves resulting from the environment of the atoms.

Computation of c and k values

The G factor for a structure (Kitaigorodski, 1957) is defined as

$$G^2 = \frac{\sum_{\mathbf{h}} |A(\mathbf{h})|^2}{\sum_{\mathbf{h}} |F(\mathbf{h})|^2}.$$

Thus,

$$\begin{aligned} G^2 &= \frac{\sum_{\mathbf{h}} [\sigma_1^2(\mathbf{h}) + \sigma_2^2(\mathbf{h}) + \sigma_3^2(\mathbf{h})]}{\sum_{\mathbf{h}} |F(\mathbf{h})|^2} \\ &= S^2 + c^2 + k^2, \end{aligned}$$

or

$$G^2 - S^2 = c^2 + k^2 = M.$$

Since c and k have been taken to be constants it is necessary that $(G^2 - S^2)$ should have the same value, M , over ranges of θ . The weight of a structure factor is now given by

$$\frac{1}{w(\mathbf{h})} = \frac{K}{4 L_p} \cdot \frac{(I+B)}{(I-B)} + (M - k^2) |F(\mathbf{h})|^2 + k^2 \langle |F(\mathbf{h})|^2 \rangle.$$

Suppose that a structure has been refined by the use of any reasonable weighting scheme. In practice it appears to be sufficient to use the $|A(\mathbf{h})|$ from the last cycle of refinement and combine these with various sets of weights obtained by allowing k^2 to vary from zero to M . The value of k^2 which gives the minimum value of $\sum w(\mathbf{h}) |A(\mathbf{h})|^2$ at this stage may be used to continue the refinement with weights on the absolute scale. Clearly if G^2 alters significantly during this subsequent refinement a new value of k^2 should be computed.

At the conclusion of refinement, if $\sigma_1(\mathbf{h})$, $\sigma_2(\mathbf{h})$ and $\sigma_3(\mathbf{h})$ are an accurate estimate of the random errors present, then

$$\frac{\sum w(\mathbf{h}) |A(\mathbf{h})|^2}{m - n} \rightarrow 1,$$

where m is the number of independent structure factors and n is the number of parameters being refined. However, small positive departures of the value from unity can be expected because of systematic errors in the data.

An example

An accurate set of data for α -glucose monohydrate was collected (Rogers & Hough, 1968) on a Siemens diffractometer and the approximate coordinates previously obtained from visual data (Killean, Ferrier & Young, 1962) were used as a starting point for refinement. The details of the refined structure will be published elsewhere.

The weighting scheme used initially was with $k^2=0$ and gave

$$\frac{\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2}{m-n}$$

equal to 2.4. It was particularly noticeable that $|\Delta(\mathbf{h})|/\sigma(\mathbf{h})$ was large for most small structure factors indicating that $\sigma(\mathbf{h})$ for these structure factors was severely underestimated. The reciprocal space was divided up into annuli each containing the same number of structure factors and the mean value of G^2 was 0.00142 with a standard deviation of 0.00013 and no systematic trend in G^2 . Because of the high counts obtained from the diffractometer experiment S^2 for each annulus was negligibly small.

Values of $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2$ were then calculated for values of k^2 between 0.00142 and 0.0:

k^2	$\frac{\sum w(\mathbf{h}) \Delta(\mathbf{h}) ^2}{m-n}$
0.0	2.40
0.00026	1.70
0.00045	1.44
0.00064	1.30
0.00083	1.24
0.00101	1.23
0.00120	1.27
0.00140	1.39

The value of k^2 which gave the minimum value of $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2/(m-n)$ was found to be 0.00096 and further refinement with this value of k^2 reduced $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2/(m-n)$ to 1.14.

As a check that a minimum value had been obtained the refinement was repeated with $k^2=0.00142$ and 0.00041. These gave

$$\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2/(m-n)$$

equal to 1.28 and 1.49 respectively.

Since k has been defined as the average fractional error in the scattering curves resulting from bonding,

a value of k^2 of 0.00096 suggests an error of the order of 100%, i.e. a 3% error for this structure in the scattering curves of 'light' atoms.

In this example, the variances of the observed structure factors resulting from counting statistics were negligible since very high counts were recorded. In view of the large value obtained for k^2 , it is obvious that thoroughly acceptable results could be achieved with appreciably smaller numbers of total counts and, therefore, a faster counting rate (Killean, 1967).

Conclusion

It has been shown that consideration of the weighting scheme necessary for satisfactory minimization of $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2$ leads to a measure, k , of the fractional error in the scattering factor curves resulting from bonding. For the example considered this error was of the order of 3%.

The procedure for obtaining the weighting scheme is:

- (1) refine with any weighting scheme;
- (2) compute $M=G^2-S^2$ and check that M is constant for ranges of θ ;
- (3) compute $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2$ for various values of k with $M \geq K \geq 0$ with

$$\frac{1}{w(\mathbf{h})} = \frac{K}{4 \text{Lp}} \cdot \frac{(I+B)}{(I-B)} + (M-k^2)|F(\mathbf{h})|^2 + k^2 \langle |F(\mathbf{h})|^2 \rangle;$$

- (4) continue refinement with the value of k that gives the minimum $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2$;
- (5) if necessary, recompute from (2) above.

The final value of $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2/(m-n)$ should approach unity. If it does not a search should be carried out for systematic errors in the data.

It should be emphasised that in the use of this weighting scheme all measured structure factors are used in the refinement process and recourse does not have to be made to omitting the small structure factors in order to get a satisfactory refinement. It is of course formally invalid to systematically omit a subset of the data.

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