

the *Y* axis is in the *ab* plane normal to the *X* axis and the *Z* axis is normal to the *XY* plane. The deviations of the atoms from this plane are C(1), -0.002 Å; C(2), 0.022 Å; C(3), -0.002 Å; N, -0.010 Å

Intermolecular hydrogen bonding

A view of the structure projected down the *c* axis is shown in Fig. 5. The molecules in the lattice are held together by a three-dimensional network of hydrogen bonds. There are three protons available with the $-\text{NH}_3^+$ group. The nitrogen atom has three close neighbours and all of them are chloride ions. The distances from the nitrogen atom to Cl, Cl(I) and Cl(II) are 3.21, 3.25 and 3.20 Å respectively. The protons are oriented almost tetrahedrally towards these ions, with respect to the C(2)-N bond. The angles N-H...Cl indicate that these hydrogen bonds are fairly linear. The values of the hydrogen bond lengths and angles are given in Table 4.

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Table 4. *Hydrogen bonding distances and angles*

X-H...Y	X...Y	X-H	H...Y
N-H...Cl	3.21 Å	0.90 Å	2.32 Å
N-H...Cl(I)	3.25	1.15	2.11
N-H...Cl(II)	3.20	0.94	2.99
C(2)-N...Cl	102.8°	N-H(1)...Cl	170.6°
C(2)-N...Cl(I)	107.4	N-H(2)...Cl(I)	169.5
C(2)-N...Cl(II)	116.2	N-H(3)...Cl(II)	166.3
Standard molecule at	<i>x</i>	<i>y</i>	<i>z</i>
Molecule I	at <i>x</i>	1 + <i>y</i>	<i>z</i>
Molecule II	at 1 - <i>x</i>	1 - <i>y</i>	1 - <i>z</i>

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Least-Squares Weighting Schemes for Diffractometer-Collected Data.

II. The Effect of Random Setting Errors

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An analysis is made of the weighting function derived on the basis of counting statistics and random setting errors for a constant-time diffractometer experiment. It is shown that these two random errors must make a major contribution to the weighting function and a practical application of this function is discussed in detail.

Introduction

It has been shown (Killean, 1967*a*) that, on consideration of counting statistics alone, the weighting schemes

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for constant-count and constant-time experiments are very different, and that the weights obtained for the constant-time experiment are not suitable for a satisfactory least-squares refinement. These weighting

schemes take no account of other random errors and this paper shows that consideration of these errors modifies the previously obtained weights to give a satisfactory weighting scheme for the constant-time experiment.

The modified weighting scheme

Considering counting statistics alone, the variance of $F_o(\mathbf{h})$ is:

$$\sigma_1^2[F(\mathbf{h})] = \frac{K}{4 \text{Lp}} \cdot \frac{(I+B)}{(I-B)},$$

where I is the peak count and B is the background count for $F(\mathbf{h})$. Consequently the least-squares weight is

$$w(\mathbf{h}) = \frac{4 \text{Lp}}{K} \cdot \frac{(I-B)}{(I+B)}.$$

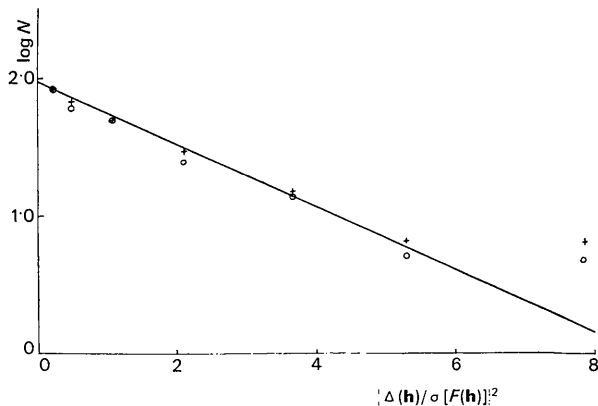


Fig. 1. Plot of $\log N$ against $\{\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]\}^2$ showing that $\log N = 1.976 - 0.227 \{\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]\}^2$ or $N = 94.6 \exp [-(1.05/2) \{\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]\}^2]$.

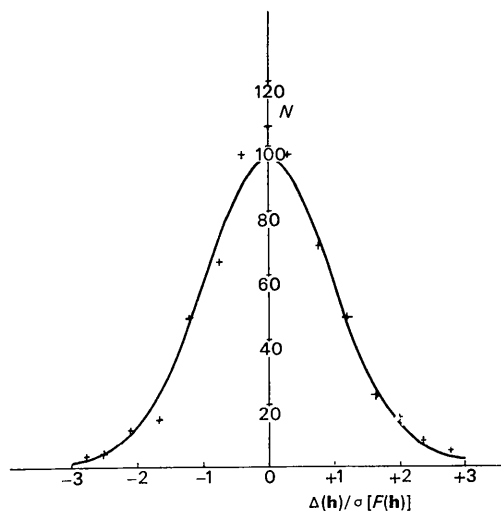


Fig. 2. The frequency distribution of $\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]$ compared with $N = 94.6 \exp [-(1.05/2) \{\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]\}^2]$, the continuous curve.

It is well known that for several random, but uncorrelated, errors in a measurement,

$$\sigma^2[F(\mathbf{h})] = \sum_i \sigma_i^2[F(\mathbf{h})].$$

It is likely that in a diffractometer experiment these errors have a major contribution $\sigma_2[F(\mathbf{h})]$ from small random setting errors resulting from the reflexion being measured off peak-centre. To a reasonable approximation, for a given crystal the peak shape near the track through the centre is the same for all reflexions. This implies that $\sigma_2[F(\mathbf{h})]$ has the form

$$\frac{\sigma_2[F(\mathbf{h})]}{|F(\mathbf{h})|} = c,$$

where c is a constant for a given crystal. Since, owing to setting errors, the measured intensity is always less than that measured through the peak centre the consequential errors will appear not to be distributed about this maximum intensity. However, it must be remembered that the same empirical scale factor, K , is applied to all intensities and hence the distribution of these errors may be considered to be symmetrical about the presumed maximum intensity. Consequently, an improved weighting scheme is given by

$$\sigma^2[F(\mathbf{h})] = \sigma_1^2[F(\mathbf{h})] + \sigma_2^2[F(\mathbf{h})]$$

$$\sigma[F(\mathbf{h})] = \left[\frac{K}{4 \text{Lp}} \cdot \frac{(I+B)}{(I-B)} + c^2|F(\mathbf{h})|^2 \right]^{1/2},$$

which gives a better approximation for $w(\mathbf{h})$ as

$$\frac{1}{w(\mathbf{h})} = \frac{K}{4 \text{Lp}} \cdot \frac{(I+B)}{(I-B)} + c^2|F(\mathbf{h})|^2.$$

The problem now consists in determining c so that numerical values can be given to the weights of $|F(\mathbf{h})|$.

It has been shown that the theoretical obtained R index can be calculated as a function of $\sigma[F(\mathbf{h})]$ (Killean, 1967*b*), and consideration of the distribution function for $|F(\mathbf{h})|$ gives

$$R = \frac{2}{\pi} \frac{\sum_{\mathbf{h}} \left[\frac{K}{4 \text{Lp}} \cdot \frac{(I+B)}{(I-B)} + c^2|F(\mathbf{h})|^2 \right]^{1/2}}{\sum |F(\mathbf{h})|}.$$

Using a sensible weighting scheme (e.g. Hughes, 1941), this theoretical R index can be approached by least-squares refinement, and the theoretical R index based only on the counting statistics calculated. Unfortunately, owing to the form of the equation for R , it is very difficult to compute the value of c . This difficulty can be resolved by using the G factor, defined by Kitai-gorodski (1957), as a measure of goodness-of-fit.

$$G^2 = \frac{\sum_{\mathbf{h}} |\Delta(\mathbf{h})|^2}{\sum_{\mathbf{h}} |F(\mathbf{h})|^2} = \frac{\sum \sigma^2[F(\mathbf{h})]}{\sum |F(\mathbf{h})|^2}$$

$$= \frac{\sum \sigma_1^2[F(\mathbf{h})]}{\sum |F(\mathbf{h})|^2} + c^2.$$

The value of c^2 can be obtained from this equation by using the value of G^2 obtained experimentally. Individual weights for each of the m structure factors can then be computed and it should be possible to obtain, after minimizing with respect to the n parameters, a value for $\sum w(\mathbf{h})|\Delta(\mathbf{h})|^2$ close to its theoretical limit of $(m-n)$, provided other errors, e.g. errors in atomic form factors, are small (*Computing Methods in Crystallography*, 1965).

Clearly, if a large change in R and, consequently, the G factor results, it may be necessary to recompute c^2 . Now that an absolute value of $\sigma[F(\mathbf{h})]$ has been obtained, it is possible, before further refinement, to give zero weight to those values of $|F(\mathbf{h})|$ which are obviously subject to non-random errors.

Application to a crystal structure

Trichlorotrimethylaminealuminum(III) crystallizes in a monoclinic space group with

$$a = 6.81 \pm 0.02, \quad b = 10.66 \pm 0.03, \quad c = 7.31 \pm 0.02 \text{ \AA}$$

$$\beta = 118^\circ 0' \pm 5'$$

$$Z = 2.$$

Systematic absences $0k0$ for $k = 2n + 1$.

The space group is either $P2_1$ or $P2_1/m$ with, in the latter case, half the molecule forming the asymmetric unit. Inspection of the Patterson function indicates a mirror plane for the heavy atoms making it difficult to determine which of the space groups is correct. Indeed it is possible by least-squares refinement using a Hughes scheme to obtain an R value of approximately 0.08 in either space group with, in $P2_1$, a significant departure of the atoms from their mirror positions. The value of the constant c was computed as 0.075 from equation (1). The individual weight for each structure factor was calculated from

$$\frac{1}{w(\mathbf{h})} = \frac{K}{4 \text{ Lp}} \cdot \frac{(I+B)}{(I-B)} + 0.0056|F(\mathbf{h})|^2$$

and from this the individual standard deviation for each reflexion was obtained. The structure was refined in both space groups and gave:

Space group $P2_1/m$

$$R = 0.086; \quad \sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2 = 823; \quad m - n = 565$$

$$\frac{\sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2}{m - n} = 1.46.$$

Space group $P2_1$

$$R = 0.082; \quad \sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2 = 713; \quad m - n = 535$$

$$\frac{\sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2}{m - n} = 1.33.$$

The deduction made from the values $\sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2 /$

$(m-n)$ is that, provided the weights $w(\mathbf{h})$ are absolute, then the structure in space group $P2_1$ is to be preferred. The value of $\sum w(\mathbf{h}) |\Delta(\mathbf{h})|^2 / (m-n)$ for the space group $P2_1$ is in itself evidence for supposing the weights to be absolute. A further check on the absoluteness of the weights was made by computing the distribution of $\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]$ and obtaining the best-fit Gaussian curve from the constants obtained from Fig. 1. Fig. 2 shows the Gaussian curve and the experimental points. It is clear that apart from close to the origin of $\Delta(\mathbf{h})/\sigma[F(\mathbf{h})]$ the fit is good. The standard deviation of the best-fit curve departs from the theoretical value by less than 2.5%. There are nine structure factors with $\Delta(\mathbf{h})/\sigma[F(\mathbf{h})] > 3$ and most of them are probably subject to non-random errors.

These nine structure factors were given zero weight and the structure refined again in $P2_1$. The R value, including these nine terms, was reduced to 0.078 but more significantly $\sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2 / (m-n)$ was now 1.04,

justifying the choice of space group and the relevance of the weighting scheme.

Conclusions

It has been shown that a reasonable estimate of $\sigma_2[F(\mathbf{h})]$ is given by

$$\sigma_2[F(\mathbf{h})] = c|F(\mathbf{h})|,$$

which, when combined with $\sigma_1[F(\mathbf{h})]$, gives a value of $\sum_{\mathbf{h}} w(\mathbf{h}) |\Delta(\mathbf{h})|^2$ approximately equal to $(m-n)$ and a dis-

tribution of

$$\frac{\Delta(\mathbf{h})}{\left\{ \sum_i \sigma_i^2[F(\mathbf{h})] \right\}^{1/2}}$$

which conforms to that theoretically expected.

The weight of a structure factor is

$$w(\mathbf{h}) = \{ \sigma_1^2[F(\mathbf{h})] + \sigma_2^2[F(\mathbf{h})] \}^{-1},$$

where $\sigma_1[F(\mathbf{h})]$, in this paper, is that for a constant-time experiment, but is easily calculated for other types of diffractometer experiment (Killean, 1967a).

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