away from the molecular plane are 0·027 and 0·020 e.Å^{-3} respectively. A search for bonding-electron effects, which may be of the order of 0·1 e.Å^{-3}, was thus amply justified.

Within the framework of the molecule the most significant peaks are at the bond centres, and are distributed roughly as expected from the work of O'Connell, Rae & Maslen (1966). However, the resolution is not as good, and the maximum densities, with the possible exception of the C(2)–N(2) bond, are not quite as high as expected for a well ordered structure. Outside the molecular framework there are significant features between the substituent oxygen O(2) and the nitrogen with two bonds N(1), and another significant peak on the other side of O(2) at the same radial distance as O(2) from the ring centre. It is readily seen that all the significant peaks can be generated by arranging the molecule with the central ring in very nearly the same orientation, but with the molecule as a whole having either opposite sense, and/or an orientation corresponding to a rotation of 60° about the threefold molecular axis. There are no significant features of the synthesis which cannot be explained on this basis, and one must conclude that, notwithstanding the low final R value of 4·0%, the structure is disordered. The amount of disorder is small, but is sufficient to preclude a detailed examination of the effects of the bonding electrons in the structure. It is to be expected that this disorder will have resulted in incorrect thermal parameters, especially for the outer atoms. It had already been noted by Cady, Larson & Cromer (1966) that the thermal parameters are not consistent with a rigid body model for the structure. This was attributed by these authors to flexibility in the furoxan rings, but in the light of the evidence from the difference map the effect of disorder provides a more probable explanation for this inconsistency.

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On the Accuracy of Electron-Density Distributions with Particular Reference to Structures with Non-Crystallographic Molecular Symmetry

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The effects of scale and phase angle errors on the accuracy of electron-density distributions are discussed. It is shown that scale factor errors may result in errors in the electron density at the atomic centres which are several times the standard deviations calculated by the normal method. The phase errors have a systematic effect on the difference density, which makes a quantitative analysis of the electron distribution impossible unless the structure is either centrosymmetric or phase-refined.

Introduction

Cruickshank (1949*a*,*b*; 1950*a*,*b*) has derived expressions for the standard deviation of the structural parameters and the electron-density distributions in crystal-structure analysis. In a more recent paper Cruickshank (1960) has used these expressions to determine the conditions necessary to attain certain desirable levels of precision in crystal-structure analysis. The standard deviations are related primarily to errors in the observed structure factors F_o. It is assumed that these errors are random, or may be treated as random for the parameter in question. In general this assumption appears to be satisfactory, although it has been shown on a number of occasions (*e.g.* O'Connell & Maslen, 1967) that the effects of systematic error may in some cases be considerably greater than those of random errors of similar magnitude. This has led some workers (*e.g.* Hamilton, 1965) to suggest the application of a correction factor to the calculated standard deviations in assessing their significance. The correction factor appears to be somewhat arbitrary, however, and a more systematic approach to the problem is to be preferred. Systematic errors invalidate the calculation of standard deviations only if they do not fulfil the conditions of the Central Limit Theorem (Cramér, 1946) which usually happens in one of two ways. Either the effects of the errors on the parameter being considered are largely cumulative, or the calculation is dominated by large inaccuracies in a small number of terms. It is important in assessing the validity of calculated standard deviations to test for effects of this kind. If such errors are present predictions based on the calculated standard deviations must be regarded with suspicion, and conversely.*

Scale errors

One factor which has a systematic effect on the electron-density distribution is the scale error in the observed structure factors. This does not occur directly in Cruickshank's standard-deviation formulae for the electron-density distribution. It is instructive to recalculate these formulae in a form which includes the scale and phase errors explicitly. The power of a beam reflected from a set of planes in a crystal is given by

$$P = vAyI_0Q \tag{1}$$

where v is the crystal volume
A is the absorption factor
y is a factor arising from extinction and multiple scattering
I_0 is the intensity of the incident beam

and

$$Q = \left|\frac{e^2F_o}{mc^2V}\right|^2 \lambda^3 Lp \tag{2}$$

e and m are the charge and mass of the electron
c is the velocity of light
V is the unit-cell volume
λ is the wave length of the radiation

and L and p are the Lorentz and polarization factors respectively.

The values of e, m, c and λ are known accurately, and it is a comparatively trivial matter to reduce the uncertainties in the calculation of A, V, L and p to a level where they make no appreciable contribution to the error in P. The quantity vI_0 fulfils the role of a scale factor. In general it is difficult to estimate the form of the error in y, but if care is taken it is possible to avoid multiple scattering and to make a reasonably accurate correction for extinction (Zachariasen, 1967). Vainshtein & Kayushina (1966) have shown that the form of the electron-density distribution is determined primarily by the stronger terms, and in these circumstances the effects of a residual error in y should not be greatly different from those due to a residual error in scale. Let the scale factor as applied to the $\mathscr{F}^*$ values be denoted k. The $\mathscr{F}$ values, which are unscaled, are related to the corresponding F_o's by the relation

$$F_o = k\mathscr{F}\ . \tag{3}$$

The electron density at a point $\mathbf{r}$ in the cell is given by

$$\varrho(\mathbf{r}) = \frac{1}{V}\sum^{N} k\vec{\mathscr{F}}_n \exp\left(-2\pi i\mathbf{H}_n\,.\,\mathbf{r}\right). \tag{4}$$

Writing $\vec{\mathscr{F}}_n$ as $\mathscr{F}_n \exp(i\alpha_n)$, and following a development similar to that given by Cruickshank (1949*a*) one obtains

$$\sigma^2\{\varrho(\mathbf{r})\} = \frac{1}{V^2}\Big[\sum_3 k^2\sigma^2(\mathscr{F}_n)\Big\{\sum_{\text{form}}\cos\left(2\pi\mathbf{H}_n\,.\,\mathbf{r}-\alpha_n\right)\Big\}^2 + \sigma^2(\alpha_n)k^2\mathscr{F}_n^2\Big\{\sum_{\text{form}}\sin\left(2\pi\mathbf{H}_n\,.\,\mathbf{r}-\alpha_n\right)\Big\}^2\Big] + k^{-2}\sigma^2(k)\varrho(\mathbf{r})^2\,, \tag{5}$$

where $\sum_3$ is a summation over the independent reflections only and $\sum_{\text{form}}$ is a summation over all the symmetry equivalents. For a general position $\mathbf{r}$ in the cell, the values for the $\cos^2$ and $\sin^2$ functions may be replaced by the corresponding mean value for a randomly distributed argument. As has been shown by Cruickshank (1949*a*), (5) then reduces to

$$\sigma^2\{\varrho(\mathbf{r})\} = \frac{1}{V^2}\Big\{\sum^{\mathrm{N}} k^2\sigma^2(\mathscr{F}_n) + \sigma^2(\alpha_n)k^2\mathscr{F}_n^2\Big\} + k^{-2}\sigma^2(k)\varrho(\mathbf{r})^2\,. \tag{6}$$

These expressions differ from those given by Cruickshank by the inclusion of the term involving the standard deviation of the scale factor. In general this will be of importance only at or near the nuclear rest position, but it can be seen by taking examples from the literature that its contribution is far from trivial at these points. Typically it increases the calculated standard deviation $\sigma\{\varrho(\mathbf{r})\}$ by factors ranging from 1·8 to 4·0 at the atomic centres. The extra term applies only to the absolute value of $\varrho(\mathbf{r})$ and must be considered when comparing residual densities at similar sites in different structures, but not in the same structure. If $\varrho(\mathbf{r})$ is the same at both positions the errors due to the scale factor will be identical in the latter case and can be neglected in the comparison.

The effect of scale factor errors on the structural parameters is already incorporated in the normal method of least-squares refinement since the off-diagonal terms include the interaction of the scale factor and the other parameters.

Phase errors

Another important case of systematic error is the residual phase errors in non-centrosymmetric struc-

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* Alternatively, a lack of validity of predictions from standard deviation calculations may result from non-linearity of the residuals as functions of error over the range of errors present (Hamilton, 1965). For accurate work this is unlikely, and can usually be discounted.

* Throughout this paper the notation, other than that defined in the text, is as in Maslen (1968*a*).

tures. In evaluating electron-density distributions the phases are generally taken from a theoretical calculation of the structure factors, and thus include the effects of any shortcomings in the theoretical models for the atomic scattering and temperature factors as well as those of residual errors in the structural parameters. In centrosymmetric structures where the phases are restricted to 0 or π the probability of phase errors is small, but such errors occur invariably in non-centrosymmetric structures. Since the phases do not enter the refinement equations their associated errors are not calculated directly, and must be estimated by other arguments. Customarily they are calculated from the F_o *versus* F_c agreement. Consider Fig. 1. In general $\mathbf{F}_c$ is known exactly and F_o is known, but the phase error $\delta\alpha$ is indeterminate. However for small $\delta\alpha$ F_o-F_c is very nearly equal to the component of $\mathbf{F}_o-\mathbf{F}_c$ parallel to $\mathbf{F}_c$. For a random distribution of difference density the component perpendicular to $\mathbf{F}_c$ will have the same probability distribution so that to a good approximation

$$\sigma^2(\alpha_n)=\langle(F_n{}^o-F_n{}^c)^2\rangle/F_n^{2o} \qquad (7)$$

where the mean is taken over the appropriate range of F_o values.

If the error in $F_n{}^o$ is also estimated from the F_o *versus* F_c agreement the standard deviations are then $\sqrt{2}$ times as great as those for a similar centrosymmetric structure. This treatment is valid only if the difference synthesis, and consequently the phase errors, are random. Real features in the difference synthesis will be altered by systematic phase errors by amounts given approximately by the n-shift rule (Shoemaker, Donohue, Schomaker & Corey, 1950). However, as shown in the preceding papers (Maslen, 1968*a,b*), the effect of the phase errors is not just a pure scaling down of the real features in the synthesis. There is also an appreciable drop in resolution, and in symmetrical systems such as benzene rings spurious features may occur in such a regular manner that they appear to be real. It is therefore unwise to attempt to analyse electron-density distributions quantitatively in $\mathbf{F}_c$ phased non-centrosymmetric structures.

Accuracy of phase-refined structures

For a phase-refined structure the phase-angle standard deviation may be assessed from equation (5) in Maslen (1967*a*) and the reasoning given in deriving (7) above to be

$$\sigma(\alpha_n)=\left(\frac{J}{J-1}\right)\sigma(F_n{}^o-|\mathbf{F}_n{}^c+\Delta\mathbf{F}_n|)/F_n{}^o\,. \qquad (8)$$

The standard deviation in the electron density may now be obtained by substituting this expression for $\sigma(\alpha_n)$ in equations (5) and (6) above. Moreover in a phase-refined structure the standard deviation in $\mathscr{F}_n$ can be calculated from the agreement between $F_n{}^o$ and $|\mathbf{F}_n{}^c+\Delta\mathbf{F}_n|$ by means of the expression

$$k^2\sigma^2(\mathscr{F}_n)=\left\langle\frac{J}{J-1}\,(F_n{}^o-|\mathbf{F}_n{}^c+\Delta\mathbf{F}_n|)^2\right\rangle \qquad (9)$$

so that (5) and (6) reduce to

$$\sigma^2\{\varrho(\mathbf{r})\}=\frac{1}{V^2}\sum_3 k^2\sigma^2(\mathscr{F}_n)\,[\{\sum_{\text{form}}\cos(2\pi\mathbf{H}_n\,.\,\mathbf{r}-\alpha_n)\}^2$$
$$+\{\sum_{\text{form}}\sin(2\pi\mathbf{H}_n\,.\,\mathbf{r}-\alpha_n)\}]^2+k^{-2}\sigma^2(k)\varrho(\mathbf{r})^2 \qquad (10)$$

and

$$\sigma^2\{\varrho(\mathbf{r})\}=\frac{2}{V^2}\sum^N k^2\sigma^2(\mathscr{F}_n)+k^{-2}\sigma^2(k)\varrho(\mathbf{r})^2 \qquad (11)$$

respectively.

However, $\sigma^2\{\varrho(\mathbf{r})\}$ can also be estimated directly from the electron-density distribution by comparing the difference density at chemically equivalent points. This yields

$$\sigma^2\{\varrho(\mathbf{r})\}=\frac{J}{J-1}\;\frac{\int\left\{\varrho(\mathbf{r})-\frac{1}{J}\sum^J\varrho(\mathbf{r}_j)\right\}^2d\tau}{\int d\tau} \qquad (12)$$

Relations (11) and (12) are alternative methods of calculating the standard deviations, which provide a check on their validity. Likewise (8) gives a check on the $\sigma(\mathscr{F}_n)$ obtained from counting statistics, or preferably from a comparison of equivalent reflexions (Ibers, 1967). Unlike the use of the F_o *versus* F_c agreement for this purpose this is largely independent of the reliability of theoretical models for atomic scattering and thermal motion. Molecular but non-crystallographic symmetry also provides a check on the validity of the standard deviations of the structural parameters, which may be compared by means of the multiparameter χ^2 significance test (*International Tables for X-ray Crystallography*, 1959). Such tests are a valuable guide to the reliability of the calculated standard deviations. It should be noted, however, that systematic errors which can be treated as random for one parameter cannot necessarily be treated as random for another. Thus a scale error may have a negligible effect on the positional parameters in a structure, a moderate influence on the thermal parameters, and a large effect

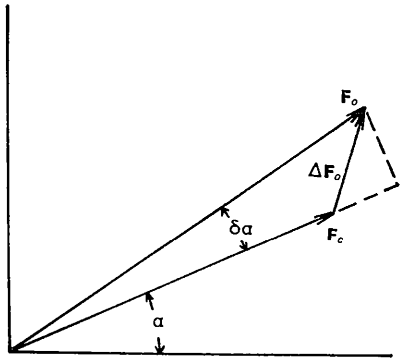

Fig. 1. Phase diagram of the observed and calculated structure factors.

on the electron density near the centres of the heavier atoms. Separate checks are necessary for each type of parameter.

For many purposes chemically equivalent parameters or regions of electron density may be averaged, and the standard deviations are a factor of $\sqrt{J}$ lower than those on the individual values. This frequently provides an improvement in accuracy which would be difficult to achieve by increasing the precision in the intensity data.

Criteria for accuracy in structure analysis

Cruickshank (1960) has determined the conditions necessary to attain the following desirable levels of precision in crystal structure analysis:

(i) A coordinate standard deviation of 0·0015 Å.
(ii) Thermal parameters to 1% precision.
(iii) A study of the bonding-electron distributions.

The requirements are problem-dependent, and Cruickshank has chosen the structures of anthracene (Sparks, 1958), and a platinum complex $(PtO_2C_{12}H_{24})_2$ (Swallow & Truter, 1960) to represent different degrees of difficulty. For the latter structure

(I) a crystal temperature < 100°K,
(II) a final R of 1%,
(III) three-dimensional data gathered completely out to $2 \sin \theta/\lambda \simeq 1{\cdot}2$ Å and at random out to 1·8 Å^{-1},
(IV) data free from errors systematic with θ, and
(V) an absolute scale of the $|F_o|$ determined experimentally

are necessary for the levels of precision stated. (For the anthracene structure an R value of $3\frac{1}{2}$% will give sufficient accuracy.) It is assumed that all errors may be treated as random and, for attaining level (iii), that the phases are absolutely correct. This is equivalent to regarding the study of bonding electrons as possible only for centrosymmetric structures.

Since 1960 more information on accurate structure analysis has become available, and it is possible to review Cruickshank's criteria in the light of more recent experience. In view of the pronounced effect of scale errors on the electron-density distribution it is necessary to consider requirement (IV) in more detail. The features associated with bonding electrons in final difference densities generally attain peak values of around 0·2 e.Å^{-3}. In order to make meaningful analyses of these features a standard deviation of approximately one sixth of this amount, *i.e.* 0·03 e.Å^{-3}, is necessary. The mean isotropic temperature factor coefficient for a crystal structure conforming to Cruickshank's criteria will be approximately 1 Å^2, and the peak heights at a carbon and a platinum position will be approximately 12 e.Å^{-3} and 600 e.Å^{-3} respectively. For the scale-factor error contribution to the electron density to be less than 0·03 e.Å^{-3} at a carbon and a platinum position, $k^{-1}\sigma(k)$ must be less than 0·25% for carbon and 0·005% for platinum.

This emphasizes the difficulty of making precise measurements of the electron density at the atomic positions, which has been noted recently by Stewart (1967).

A further factor which must be considered is the errors in positional and thermal parameters which result from the use of spherically averaged isolated atom ground-state wave functions in the refinement process. For hydrogen, which is the most extreme example, the error in the atomic position is approximately 0·07 Å (Stewart, Davidson & Simpson, 1965) but even for a nitrogen atom the error may be as large as 0·02 Å (Dawson, 1964). The mean isotropic temperature factor errors for hydrogen and for an sp^2 carbon with one hydrogen substituent have been estimated to be 2·3 Å^2 and 0·15 Å^2 respectively (Stewart, Davidson & Simpson, 1965; O'Connell, Rae & Maslen, 1966) while strongly anisotropic errors are expected for a terminal nitrogen atom (Dawson, 1964).

The precise magnitudes of these corrections are uncertain, however, and until more reliable bonded-atom wave functions are available it appears preferable to determine the positional and thermal parameters by neutron, rather than X-ray diffraction.

Finally, for an analysis of the electron-density distribution, it is necessary that the structure should be either centrosymmetric or phase-refined.

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