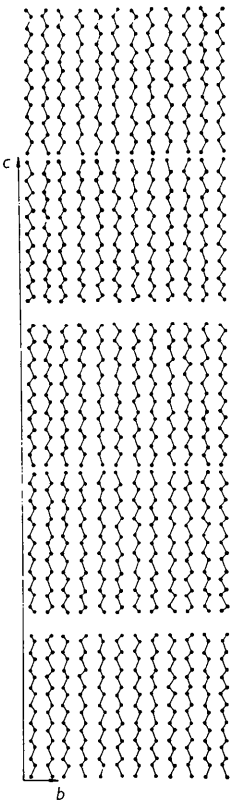

Fig. 4. Molecular arrangement as viewed along the *a* axis.

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The Required Precision of Intensity Measurements for Single-Crystal Analysis*

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A discussion is given of the requirements necessary for determining bond lengths crystallographically within a limit of error of 0·01 Å. A simple approximate formula is given relating the residual R to the co-ordinate estimated standard deviation.

The required standard of coordinate accuracy

The primary problem in single-crystal structure analysis is the determination of sufficiently accurate atomic coordinates. A great step forward in the detailed understanding of chemical valency would be possible if the accuracy were such that one could assert with confidence that *a measured difference of* 0·01 Å *between two bond lengths corresponded to a genuine difference.* Such a precision would allow the assignment of multiple bond orders within 0·05, would distinguish between the predictions of the molecular-

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orbital and valence-bond theories in aromatic hydrocarbons, and would make the accuracy of X-ray results for large molecules comparable with the best spectroscopic and electron-diffraction work for small molecules.

At the 0·1% level of significance, a difference must be 3·3 times the standard deviation to be accepted as genuine. Consequently a limit of error of 0·01 Å in the measurement of the difference between two bonds requires an estimated standard deviation (e.s.d.) of 0·003 Å or better. Since the e.s.d. of the bond difference is twice that of an atom in one of the bonds, the above criterion requires a *coordinate e.s.d.* $\sigma(x)$ *of* 0·0015 Å *or better*.

However, vibration effects often cause systematic errors which are much larger than this. In particular molecular angular oscillations sometimes cause apparent displacements of 0·02 Å at room temperature (Cruickshank, 1956*a*). As the corrections for this are somewhat approximate, it is desirable to reduce the effect by studying crystals at low temperatures. For molecular crystals held by van der Waals' forces the vibration square amplitudes, and hence the rotational corrections, drop to about a third at liquid nitrogen temperature (~ 90 °K.) and by a similar proportion again at liquid hydrogen or helium temperatures (Cruickshank, 1956*b*). Further reasons for working at low temperatures are to reduce any possible effects of vibration anharmonicity and, if the refinement is by Fourier methods, to reduce the back-shift corrections by utilizing data of high $\sin\theta/\lambda$. Consequently, the first practical requirement from theoretical considerations for an accurate structure determination of a molecular crystal is that

(I) *the crystal temperature must be* < 100 °K.

A simple formula for coordinate e.s.d.'s

The least-squares formula for coordinate e.s.d.'s, assuming that the off-diagonal terms in the normal equations are negligible, is

$$\sigma^2(x) = 1/\{\Sigma w(\partial|F|/\partial x)^2\}\ , \tag{1}$$

where w is the absolute weight* of an $|F|$, $w = 1/\sigma^2(F)$.

In the space group $P1$ with x in Å one can show (Cruickshank, 1949), for isotropic data, that the denominator of (1) has the approximate value

$$(2\pi^2/3)\Sigma wf^2s^2, \tag{2}$$

where f is the scattering factor including the vibrational exponent and $s = 2\sin\theta/\lambda$ is the reciprocal radius. Rounding-off the arithmetic we get approximately for $P1$

$$\sigma^2(x) \sim 1/\{6\Sigma wf^2s^2\}\ , \tag{3}$$

where the summation is over the independent reflexions observed.

In applying (1) or (3) a satisfactory estimate of the total error can be obtained if the estimates for $\sigma(F)$ and hence of the absolute weights are based not merely on the random experimental errors but on the values of the ΔF's, since this procedure allows for some systematic experimental errors and for the imperfection of the model used in the structure-factor calculations. For order-of-magnitude purposes the expression for $\sigma^2(x)$ can be simplified still further by the following argument. Since the ordinary residual, $R = \Sigma|\Delta|/\Sigma|F|$, is approximately equal to the average proportionate error in an F, we have on average

$$\sigma^2(F) \sim \tfrac{1}{2}\pi R^2|F|^2, \tag{4}$$

where the factor $\frac{1}{2}\pi$ covers the transition from the square of an average error to a mean square error. If the unit cell contains N like atoms, the average value of $|F|^2$ at a given $\sin\theta$ is Nf^2, so that, within an order of magnitude,

$$1/w = \sigma^2(F) \sim \tfrac{1}{2}\pi R^2 N f^2. \tag{5}$$

Substituting (5) in (3), we obtain

$$\sigma^2(x) \sim R^2N/(4\Sigma s^2)\ . \tag{6}$$

In general we may derive a formula

$$\sigma(x) \sim \frac{R}{\bar{s}}\left(\frac{N}{4p}\right)^{\frac{1}{2}} \tag{7a}$$

for non-centrosymmetric space groups, or

$$\sigma(x) \sim \frac{R}{\bar{s}}\left(\frac{N}{8p}\right)^{\frac{1}{2}} \tag{7b}$$

for centrosymmetric space groups.* These formulae assume that the data are isotropic in three dimensions and that no atoms are in special positions. The symbols have the meanings:

R is the residual;
$\bar{s}$ is the r.m.s. reciprocal radius for the planes observed;
p is the difference between the numbers of independent planes observed and of parameters determined;
N is the number of atoms, similar to the one whose $\sigma(x)$ is in question, needed to give a scattering power at $\bar{s}$ equal to that of the asymmetric unit of the actual structure, i.e. $\Sigma_i f_i^2 \equiv Nf^2$.

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* If the intensity $I = L|F|^2$, then

$$w = (4LI)/\sigma^2(I)\ ;$$

so that w is constant if $\sigma^2(I) \propto I$, as in fixed-time methods, or $w \propto 1/I$ if $\sigma^2(I) \propto I^2$, as in fixed-count methods.

* There is no inconsistency between the fact that (7*a*) and (7*b*) differ by a factor of $\sqrt{2}$, whereas the non-centrosymmetric and centrosymmetric formulae for $\sigma(x)$ given by Cruickshank (1950) in terms of $(\Sigma h^2\Delta^2)^{\frac{1}{2}}$ differ by a factor of 2, since the latter formulae also show a factor of $\sqrt{2}$ when the average Δ^2 is approximated in terms of R and Nf^2.

Equations (7*a*) and (7*b*) are necessarily very approximate and are intended solely to give orders of magnitude. Their form is of some interest. Not surprisingly $\sigma(x)$ varies proportionally with R and inversely as $p^{\frac{1}{2}}$; it is improved by having reflexions of high reciprocal radius, and worsened if an atom contributes only a small part of the total scattering.

As a first example of the use of (7) consider the two sets of data for anthracene, which Sparks (1958) has refined by least-squares to give 64 parameters: (I) the 682 reflexions measured photographically (Mathieson *et al.*, 1950), and (II) the 245 reflexions measured by proportional counter by Arndt & Phillips. For (I), $R=0{\cdot}104$, $\bar{s}\sim 0{\cdot}8$ Å^{-1}, $p=618$ and $N=7$. For (II), $R=0{\cdot}036$, $\bar{s}\sim 0{\cdot}6$ Å^{-1}, $p=181$ and $N=7$. The simple formula (7*b*) gives $\sigma(x)=0{\cdot}0049$ and $0{\cdot}0044$ Å respectively, which are about 20% higher than the average carbon $\sigma(x)$ found by Sparks from the exact formula.

As a second example consider the determination by Swallow & Truter (1960) of the carbon positions in a platinum complex $(PtO_2C_{12}H_{24})_2$. In this analysis $\bar{s}\sim 0{\cdot}9$ Å^{-1} and at this reciprocal radius the scattering from Pt is vastly greater than from all the light elements. With temperature factors of $B=3{\cdot}7$ Å^2 for Pt and $B=6{\cdot}4$ Å^2 for C, the scattering factors at $s=0{\cdot}9$ Å^{-1} are 22·5 and 0·50 respectively. Hence for platinum $N\sim 1$, and for carbon $N\sim(22{\cdot}5/0{\cdot}50)^2=2025$. Thus with $R=0{\cdot}076$ and $p=1400$, (7*b*) gives $\sigma(x, \mathrm{Pt})=0{\cdot}0008$ Å and $\sigma(x, \mathrm{C})=0{\cdot}036$ Å, which satisfactorily agree with the correct values of 0·0010 Å and 0·035 Å.

This last example emphasizes the difficulty of determining accurate carbon bond lengths in the ligands of metal complexes. Despite the superb accuracy of the Pt position, the accuracies of the O and C positions were insufficient even to settle whether a particular sequence of four bonds went double, single, single, double, or whether all four were of order 1·5.

The required precision for intensities

The earlier formula (3) shows that the planes which are worth measuring accurately are those with large f^2s^2 (see also Appendix). Fig. 1 shows the variation of f^2s^2 with a carbon atom with different temperature factors ($s=1{\cdot}30$ is the limit for Cu $K\alpha$ radiation). Since for a crystal held by van der Waals' forces, a B of 6 or 3 Å^2 at room temperature may be expected to drop to about 2 or 1 Å^2 at 90 °K., the figure shows that the use of low temperatures greatly increases the number of worthwhile reflexions.

We can now re-examine the anthracene problem to see what would have to be done to get $\sigma(x)=0{\cdot}0015$ Å. The observations must be made at, say, 90 °K. to reduce the vibrational effects. Before (7*b*) can be applied, it is necessary to make a prediction of the likely value of R at the low temperature. This is difficult to do and, for simplicity, we shall assume that R is unlikely to change much for a given technique. (Some experience in this laboratory suggests that this is a reasonable first approximation.) On this basis we find that $\sigma(x)=0{\cdot}0017$ Å if as many reflexions were to be measured by proportional counter, with $R=0{\cdot}036$, as had been measured photographically. This is effectively the desired level of accuracy.

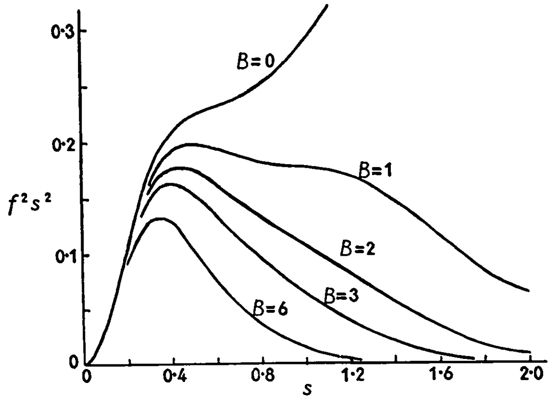

Fig. 1. The variation of f^2s^2 with s for a carbon atom.

For the platinum complex mentioned above the photographic technique used is obviously incapable of achieving $\sigma(x, \mathrm{C})\sim 0{\cdot}0015$ Å. This accuracy can be reached with $T=90$ °K. if 5000 reflexions are measured ($\bar{s}=1{\cdot}35$ Å^{-1}) and if the final $R\sim 0{\cdot}011$. Hence we may conclude that it should be possible to measure C–C, C–N, etc. bonds with a limit of error of 0·01 Å in complexes of any metal by measuring several thousand reflexions at low temperatures if we can achieve

(II) *a final R of* 1% .

This requirement is, of course, not merely a demand on the accuracy of the intensity measurements, but also on the accuracy of the absorption and extinction corrections and of the theoretical scattering factors, including especially the anomalous dispersion allowance, etc.

The accuracy of vibration parameters

The accurate determination of vibration parameters can be discussed similarly. For instance, the e.s.d. of the isotropic mean-square vibration amplitude U for an atom in a centrosymmetric space group is

$$\sigma(U)\sim\frac{R}{\overline{s^2}}\left(\frac{N}{320p}\right)^{\frac{1}{2}}, \qquad (8)$$

where $\overline{s^2}$ is the r.m.s. value of s^2. Reflexions of high s are thus particularly valuable. For either of the existing sets of data for anthracene this gives $\sigma(U)\sim 0{\cdot}001$ Å^2. As the average U in anthracene at room temperature is about 0·04 Å^2, the proportionate error is about $2\frac{1}{2}$%. A serious study of the variation of the U's with temperature would require $\sigma(U)<0{\cdot}01U$, so that higher accuracy or more data are required. (The accuracy would have to be improved still further if the anisotropic motion were being studied.)

Equation (8), however, neglects the very serious correlation between the scale parameter of the $|F_o|$ and the vibration parameters. Typically the correlation coefficient between the scale and the average $\overline{U}$ for the whole structure is $\sim 0{\cdot}85$, so that the correct $\sigma(\overline{U})$ is about twice the value given by the simple formula [(8) without the N], and the individual $\sigma(U)$ have to be increased correspondingly.

Accuracy in the study of valence electrons

The study of valence electrons is notoriously much more difficult than the study of coordinates or vibrations, both because the effects are small and because systematic errors are likely to be serious. One typical problem is the determination of the number n of electrons in a given 'orbit'. The simple least-squares approach leads to an e.s.d.

$$\sigma(n) = 1/(\Sigma w f^2)^{\frac{1}{2}}, \tag{9}$$

where f is the scattering factor for the orbit. Since f usually decreases sharply with s, the reflexions of low order are of chief importance.

In another approach the valence electrons are studied by a difference map from which all electrons not involved in covalent bonding have been subtracted. However, satisfactory results can be obtained only if the atomic-vibration parameters are determined in a manner independent of any assumptions about the valence electrons. This can be done if the vibrations are determined from reflexions with $s > 1{\cdot}2$ Å^{-1}, for which the scattering from the valence electrons is negligible. Further, since a chemical bond is essentially three-dimensional, three-dimensional data are required for its effective study. In summary therefore the study of valence electrons requires

(III) *data gathered three-dimensionally out to* $s \sim 1{\cdot}8$ Å^{-1}.

If this maximum reciprocal radius would involve more reflexions than are needed for the necessary coordinate accuracy, then a *random* selection of reflexions within this radius may be made. Such a random selection will be preferable to data gathered only in the principal zones.

Since the vibrations are determined from reflexions of high s, while the valence electrons are revealed with those of low s,

(IV) *the data must be free from errors systematic with* s.

This requirement is also vital when the vibrations alone are studied.

Although the $|F_o|$ scale can be determined by least-squares alone, it is most desirable that

(V) *the absolute scale of the* $|F_o|$ *should be determined experimentally,*

as the comparison between the two determinations provides some check on the errors referred to in (IV).

APPENDIX

As a very simple example of how equation (3) may influence the strategy of an experiment, suppose that the intensities are measured by a counting technique in which, if C is the total number of counts, $\sigma(C) \propto C^{\frac{1}{2}}$. Then if t is the time spent measuring the intensity $\sigma(I) \propto (I/t)^{\frac{1}{2}}$, since $C \propto It$. Hence $w(F) \propto I/\sigma^2(I) \propto t$. Thus the weight of a reflexion is proportional to the time spent measuring it and is independent of the magnitude of F, so that it is most profitable to spend time on reflections with large f^2s^2 and of these we may as well spend equal time on all whether strong or weak.

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