Table 4. *Deviations from planarity*

C_5 = −0·006 Å	C_{11} = +0·014 Å	C_1 = +0·069 Å
C_6 = −0·001	C_{12} = −0·012	C_2 = +0·055
C_7 = −0·005	C_{13} = −0·031	C_3 = +0·062
C_8 = +0·023	C_{14} = +0·012	C_4 = −0·062
C_9 = +0·014	O_{15} = −0·007	N_{17} = +0·096
C_{10} = +0·027	O_{16} = −0·009	

C_1', C_2', C_3', and C_4' are similarly displaced from plane (ii).

The dimensions of the molecule (Fig. 3) are generally consistent with the normally accepted values. The two C–N bonds have both the same length of 1·39 Å. Similar shortenings of the normal C–N single bond lengths of 1·47 Å have been found in other heterocyclic compounds and have been listed by Brown (1949). Of the two C=O bond lengths C_9–O_{15} is 1·21 Å and C_{10}–O_{16} is slightly longer at 1·23 Å. The four single C–C bonds, C_{10}–C_{14}, C_{10}–C_{13}, C_9–C_{11}, C_9–C_{12}, have lengths 1·49, 1·50, 1·48, and 1·50 Å respectively. The nitrogen atom is intramolecularly hydrogen-bonded to the adjacent oxygen atom, the N–H bond length being 1·01 Å as deduced from the hydrogen position measured from the [*b*] difference synthesis.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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On the treatment of unobserved reflexions in the least-squares adjustment of crystal structures.

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In the refinement of crystal structures by the least-squares method, the problem is often complicated by the question of what is the proper way to deal with unobserved reflexions, i.e. reflexions for which $0 \leqslant F^2 < F^2_{\text{min.}}$. It is obvious that an observation that a particular reflexion has a value in a certain range, in particular the range above, may be fully as important in the determination of a structure as observations of a more precise nature. It is the purpose of this note to point out a method of dealing with unobserved reflexions which is demanded by the spirit of least-squares adjustments.

Now the problem of least squares is to find (under the minimum variance criterion) the expected values for a set of parameters under the condition that a set of linear combinations of these parameters (the observables) have been observed to have certain values. These values are by their very nature unprecise; else there would be no need to call on the least-squares procedure. Actually, we may generalize the statement to say that we observe certain conditions which the observables must satisfy. The solution of the least-squares problem tells us that the best values of the parameters are given by the solutions of the *normal equations* with the value of each observable being taken as its *expected value* or *mean* (μ) under the conditions which the observations impose, together with any conditions we may assume about its possible value, and weighted inversely proportional to its variance (σ^2) under these conditions.[†]

The application of this point of view to observed reflexions is straightforward, the mean value of the distribution of the corresponding observable being simply the observed value.[‡] The weights are chosen by a more or less direct analysis of the experimental errors, usually combined with some scheme which contributes computational simplicity.

For unobserved reflexions, the best procedure is to determine the mean value and variance of an observation in the unobservable range, assuming that the probability distribution is the theoretical one for the space group under consideration (in the later stages of refinement, for the actual structure). Howells, Phillips & Rogers (1950) have derived the distributions for the space

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[†] The case of correlated observational errors and the consequent non-diagonal weight matrix will not be discussed here. However, see W. C. Hamilton & Verner Schomaker, *The Method of Least Squares in Electron Diffraction* (to be published) for a more detailed discussion of some of these points.

[‡] This is the case if an observation yields a definite *number*. If the intensities are visually estimated to lie in a certain range, the analysis below might well be more suitable.

groups $P1$ and $P\bar{1}$, and their results will be used below. In the following formulae, $z = I_{\text{min.}}/I_{\text{av.}} = F^2_{\text{min.}}/F^2_{\text{av.}}$ is the ratio of $I_{\text{min.}}$ to the average I over a shell of constant $\sin^2\theta$, and $N(z)$ is the cumulative distribution function.

$$P1$$

$$\begin{aligned}
N(z) &= \int_0^z e^{-t}dt \\
\mu(z) &= \int_0^z te^{-t}dt/N(z) \\
&= 1-ze^{-z}/N(z) \\
&\approx z/2 \\
\sigma^2(z) &= \int_0^z t^2e^{-t}dt/N(z)-\mu^2 \\
&= 2\mu-\mu^2+z(\mu-1) \\
&\approx z^2/12
\end{aligned}$$

$$P\bar{1}$$

$$\begin{aligned}
N(z) &= \text{erf}\,(z/2)^{\frac{1}{2}} \\
&= \frac{1}{\sqrt{(2\pi)}}\int_0^z e^{-\frac{1}{2}t}t^{-\frac{1}{2}}\,dt \\
\mu(z) &= \frac{1}{\sqrt{(2\pi)}}\int_0^z e^{-\frac{1}{2}t}t^{\frac{1}{2}}\,dt/N(z) \\
&= \sqrt{\left(\frac{2}{\pi}\right)}\,z^{\frac{1}{2}}e^{-\frac{1}{2}z}/N(z) \\
&\approx z/3 \\
\sigma^2(z) &= \frac{1}{\sqrt{(2\pi)}}\int_0^z e^{-\frac{1}{2}t}t^{3/2}dt/N(z)-\mu^2 \\
&= 3\mu-\mu^2+z(\mu-1) \\
&\approx 4z^2/45
\end{aligned}$$

From the definition of z we have $\mu(I_{\text{min.}}) = I_{\text{av.}}\mu(z)$ and $\sigma^2(I_{\text{min.}}) = I^2_{\text{av.}}\sigma^2(z)$, and thus, for the two cases above, we have approximately

$P1$	$P\bar{1}$
$\mu \approx I_{\text{min.}}/2$	$\mu \approx I_{\text{min.}}/3$
$\sigma^2 \approx I^2_{\text{min.}}/12$	$\sigma^2 \approx 4I^2_{\text{min.}}/45$

For practical purposes, these values may be taken as the proper ones for all acentric and centric space groups for all but the very finest refinements.*

Each unobserved reflexion must, to be consistent with the least-squares motivation, be entered into the refinement with its appropriate mean value and weight, as determined from the theoretical distribution. It is a mistaken notion that only those unobserved reflexions which have $F^2_{\text{calc.}} > F^2_{\text{min.}}$ at a particular refinement stage should be entered in the succeeding refinement. Even in the event that all the calculated structure factors are less than the minimum observable values, these reflexions must properly be included in the next refinement to obtain reliable estimates of error, which is one of the most useful features of the least-squares procedure.

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* The average intensity for a group of special reflexions may differ by an integral multiple from that for general (*hkl*) reflexions. These multiples depend on the symmetry elements present and may be as great as twelve; a table of their values for all the space groups is given by Rogers (1950). For such reflexions, z must accordingly be defined with the local average being taken over the group characterized by the same multiple, or, better, as the appropriate multiple times the local average for the non-special reflexions. However, to the approximation considered above, this factor does not enter the expressions for the mean values or variances of the *intensities*. For example, the next term in the series expansion for the variance in the acentric case is $-z^4/240$, so that the variance of the intensity to this degree of approximation is $I^2_{\text{min.}}/12-z^2I^2_{\text{min.}}/240$. In the present application, z will invariably be considerably less than unity, so that the second term is very unimportant. In the very rare case where it is large enough to be significant, use of the correct multiple is of course necessary.

Notes and News

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