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# Parameter Refinement for Tetrafluoroterephthalonitrile at 98 K: Making the Best of a Bad Job

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## Abstract

The effect of selectively excluding weak reflections from least-squares refinements of crystal structures has been examined. A systematic bias in the intensities of weak reflections may be introduced by improper treatment of prescan measurements. Omission of reflections with weak or negative measured intensity from high-order ($\sin \theta/\lambda > 0.85$ Å$^{-1}$) refinements has practically no effect on the positional or vibrational parameters provided that this bias is eliminated. However, substantial errors in the parameters may be introduced by refining with only low-order reflections or even with full data sets that include low-order reflections. These conclusions are based on calculations made with a reasonably accurate and extensive data set measured for tetrafluoroterephthalonitrile ($C_8F_4N_2$) at 98 K, including all 2378 reflections accessible out to $\sin \theta/\lambda = 1.15$ Å$^{-1}$.

## Introduction

Van Rij & Britton (1981) determined the crystal structure of tetrafluoroterephthalonitrile at room temperature and pointed out the suitability of this compound for a low-temperature charge-density study: the molecule contains no hydrogen, all its atoms have approximately the same scattering power for X-rays, and the molecular site symmetry in the crystal is $2/m(C_{2h})$. We decided to take up the problem where van Rij & Britton had left it. Preliminary results of our low-temperature study were reported at Ottawa (Dunitz, Schweizer & Seiler, 1981). The most remarkable feature of the deformation maps we obtained is the weakness of the bonding density in the carbon–fluorine bond relative to that in the other bonds and to the lone-pair density at the nitrogen atom. Some details of the work have been described by Dunitz, Schweizer & Seiler (1982, hereinafter DSS)

together with the possible implications of the results for bonding theories.

In this paper we wish to discuss more technical aspects: the effect of omitting various systematically chosen groups of reflections from the least-squares refinement of the atomic parameters. This question has been discussed many times before but usually from a theoretical point of view with an emphasis on the bias introduced by a particular kind of systematic error. Here we adopt an outspokenly empirical attitude. We had at our disposal a set of integrated intensities of better than normal quality and extending reasonably far in reciprocal space for an organic compound (to about $\sin \theta / \lambda \sim 1 \cdot 15 \text{ Å}^{-1}$). We recognize that any set of measured structure amplitudes is contaminated by many different kinds of experimental error and that it is very difficult to analyse their combined effect theoretically. Nevertheless, we can still use our imperfect measurements as a base for comparing the effect on structural parameters of the various ways that have been proposed for handling the data.

## Experimental information

All X-ray measurements were carried out on an Enraf–Nonius CAD4 diffractometer equipped with graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069 \text{ Å}$) and a modified Enraf–Nonius gas-stream low-temperature device. The temperature of the gas stream was kept constant at about 98 K by a feedback control system. Temperature fluctuations monitored by a PT100 resistor were less than $\pm 0 \cdot 5$ K during the experiment.

The compound was recrystallized by slow evaporation of an acetone solution at ca 253 K. The crystal selected for intensity measurements (dimensions ca $0 \cdot 45 \times 0 \cdot 35 \times 0 \cdot 3$ mm) had a mosaic spread smaller than the divergence of the primary beam ($<0 \cdot 2°$ peak-half-width at half-height for reflections with $\sin \theta / \lambda = s < 0 \cdot 15 \text{ Å}^{-1}$) and showed minimal intensity fluctuations when rotated round the diffraction vector **H** for several reflections.

Unit-cell dimensions were obtained by least-squares refinement of setting angles for 20 reflections with $2\theta$ values in the range 40 to 54°: orthorhombic, $Cmca$, $a = 7 \cdot 6848$ (4), $b = 9 \cdot 7350$ (6), $c = 9 \cdot 5549$ (7) Å, $V = 714 \cdot 8 \text{ Å}^3$, $Z = 4$, $D_x = 1 \cdot 790 \text{ Mg m}^{-3}$ (identical with values given in DSS).

Three standard reflections: $10,0,0 (s = 0 \cdot 651 \text{ Å}^{-1})$, 333 and 3$\bar{3}$3 ($s = 0 \cdot 294 \text{ Å}^{-1}$) were monitored 221 times at intervals of $15 \times 10^3$ s radiation time; they showed a slow intensity decrease amounting to about 8% at the end of the measurement period (about six weeks elapsed time). A correction was made to compensate for this slow intensity drift.

Integrated relative intensities were obtained by $\omega$, $\theta$ scans. All reflections within a limiting sphere of radius

$s = 1 \cdot 15 \text{ Å}^{-1}$ were measured, mostly in all symmetry-equivalent orientations, a total of 17 740 measurements. A variable scan width was taken from $2\theta(\alpha_1) - 1 \cdot 0°$ to $2\theta(\alpha_2) + 1 \cdot 0°$ for the peak plus a quarter of this scan width at each end for background measurement.*

The standard CAD4 data-collection software offers the possibility of an optional rapid prescan measurement for each reflection, designed to save measuring time in two opposite circumstances. For very strong reflections the prescan count is used to estimate the scanning rate required to achieve any desired precision in the normal slow scan. At the opposite extreme the slow scan can be omitted altogether if a reflection is judged too weak to yield a significant measurement in the maximum allotted time. Prescans are not regarded as part of the normal measurement routine:† in particular, for reflections remeasured in the slow-scan mode, the prescan counts are discarded.

For the present investigation, the desired relative precision for an individual slow-scan measurement was chosen to be 2% in the integrated intensity $I_i = P_i - 2B_i$, where $P_i$ = integrated peak counts, $B_i$ = sum of background counts, subject to a maximum scan time of 300 s. Weak reflections were rescanned only if the result of the prescan gave $I_i > 2\sigma(I_i)$. The prescan time was varied between 40 and 80 s depending on the scattering angle.

We had originally intended to use the stronger reflections, measured mainly in the slow-scan mode, for our deformation density study. Only when that study was reaching its final stages did we decide to use our data to examine the effect of including or excluding the weak intensities. Many of these include what we may call mixed-mode reflections; that is to say, within a group of symmetry-equivalent reflections, some measurements were made in normal slow-scan mode, others only in the prescan mode, depending on the result of the prescans.

In the initial data processing (DP1) individual intensity measurements, including mixed-mode reflections, were normalized to a standard scan speed of 2° min$^{-1}$ and corrected for the slow intensity drift. Multiple measurements were then averaged to give mean intensities $\langle I_H \rangle$ for all 2387 independent reflections within the limiting sphere. Absorption corrections were not applied ($\mu = 1 \cdot 92 \text{ cm}^{-1}$). The internal consistency of the multiple measurements can be

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* A list of intensities for dataset 2 with their SIGMAX weights has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39348 (15 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Except for reflections strong enough that the prescan measurement reaches the desired precision normally attained in the normal scan.

judged by the value of

$$R = \frac{\sum\limits_{H}\sum\limits_{N}|I_{H,i} - \langle I_H \rangle|}{\sum\limits_{H} N\langle I_H \rangle} = 0.016,$$

where $N$ is the multiplicity of the reflection **H**. DP1 corresponds to the procedure normally used in our laboratory and in many others for processing mixed-mode intensity measurements. At a later stage the data-processing program was altered so that for mixed-mode reflections prescan measurements were discarded. Mean intensities $\langle I_H \rangle$ for these reflections were then estimated from the slow-scan measurements only (DP2).

Standard deviations (s.d.'s) of the averaged intensities were estimated in two ways – from counting statistics and from the deviations of individual measurements from their respective means. For the first method we used the approximation

$$SIGSTAT = \{\sum(p_i + 4b_i + 0.0002I_i^2)\}^{1/2}/N, \quad (1)$$

where $p_i$ and $b_i$ are the normalized peak and background variances for individual measurements of a given reflection. Equation (1) is strictly valid only when the variances of the individual measurements are nearly equal, as they are in DP2. Otherwise SIGSTAT is estimated too high. For the second method we took

$$SIGDEV = \{\sum\limits_{N} (I_i - \langle I \rangle)^2/N(N-1)\}^{1/2}. \quad (2)$$

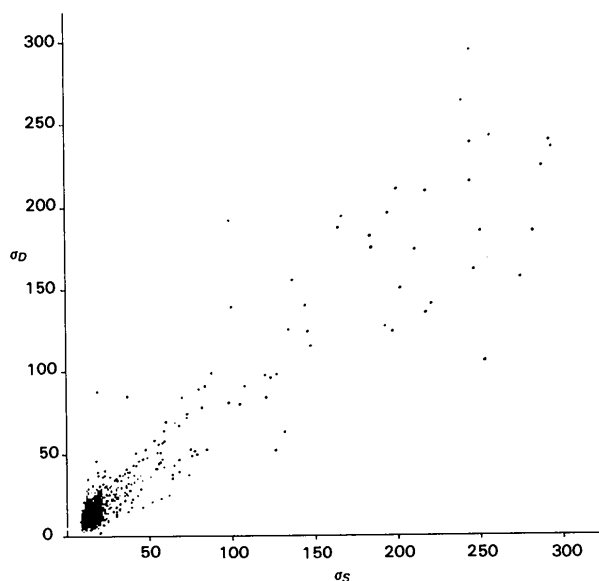The overall agreement between the two estimates for DP1 is indicated by Fig. 1, where values of SIGSTAT

are plotted against those of SIGDEV for general $hkl$ reflections measured in all eight orientations. For DP1 we took $\sigma(I) = $ SIGSTAT and for DP2 we took $\sigma(I) = $ SIGMAX the larger of the two estimates SIGSTAT and SIGDEV. From now on we drop the brackets indicating average values and write simply $I$ for $\langle I \rangle$, the average normalized intensity.

The dependence of $\sigma(I) = $ SIGSTAT on $I$ for general $hkl$ reflections in DP1 is shown in Fig. 2. For



Fig. 1. Scatter plot of SIGSTAT *versus* SIGDEV for general $hkl$ reflections measured in all eight orientations. SIGSTAT and SIGDEV are two estimates of $\sigma(I)$, the former based on counting statistics (equation 1), the latter on deviations of individual measurements from their respective means (equation 2).
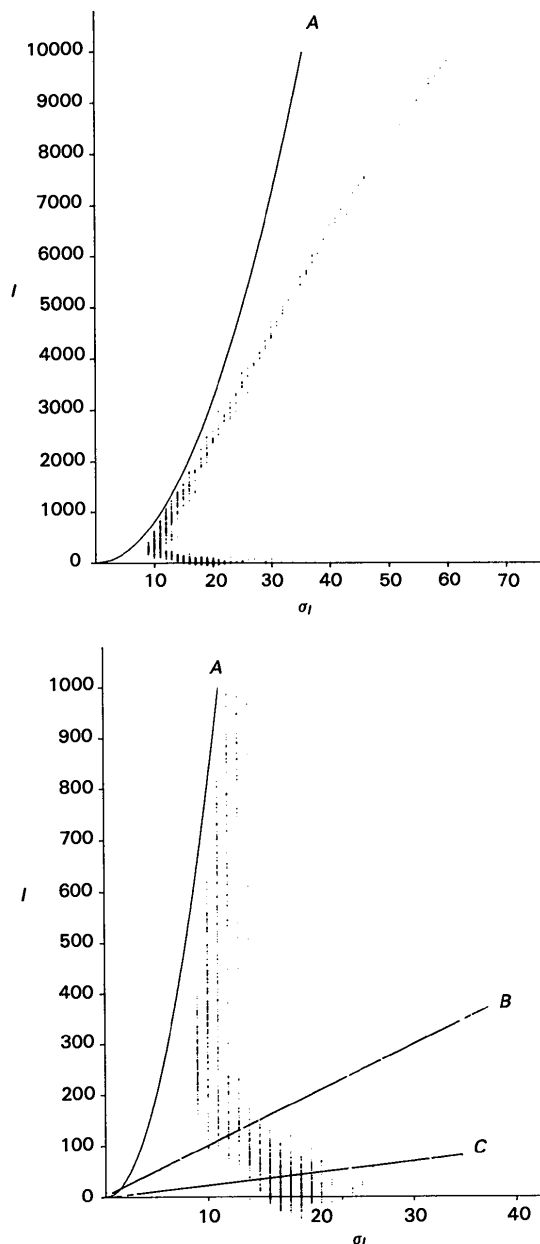


Fig. 2. Scatter plots of $\sigma(I) = $ SIGSTAT *versus* $I$ for general $hkl$ reflections measured in all eight orientations. The upper figure shows the complete range of data, the lower one shows the lower region on an expanded scale. The smooth curve $A$ is the function $\sigma(I) = (I/8)^{1/2}$, curves $B$ and $C$ are the functions $I = 10\sigma(I)$ and $I = 2.5\sigma(I)$, respectively.

large $I$, the influence of the background is negligible, and the $I^2$ term dominates SIGSTAT, so that $\sigma(I)$ is effectively proportional to $I$ (equation 1). A minimum value of $\sigma(I) \sim 9$ is reached for $I \sim 200$–300 counts. The sharp increase in $\sigma(I)$ as $I$ approaches zero is a result of the decrease in measurement time for weak reflections measured only in prescan mode. The effect of cutting the data at various $I/\sigma(I)$ levels is also shown in Fig. 2. It is evident that reflections with $I \sim 0$ and those with $I < 0$ have $\sigma(I)$ of about 15–20, i.e. they have an exceedingly low signal-to-noise ratio. These reflections have scaled background $(2B)$ in the range 600–1000 counts {for $2B \sim 600$, $[(P + 4B)/8]^{1/2} \sim 15$}.

In the subsequent least-squares calculations involving minimization of $\sum \omega_I (I - I_c)^2$, weights $\omega_I$ were assumed to be inversely proportional to the variances, that is, to $\sigma^2(I)$. From Fig. 2 it is easy to see how these weights will behave: they will be small for large $I$ and for $I \sim 0$, and they will be nearly uniform over quite a large range of $I$, say from $I \sim 100$ to $I \sim 1000$.

The influence of a correlation between weights and intensities on derived least-squares parameters has been discussed by Wilson (1976), who assumed that the variance in $I$ should be a linear function of $I$, corresponding to $\sigma(I) \sim (a + bI)^{1/2}$. Fig. 2 shows that, at least for our data, this would be a good approximation only for a small fraction of the measured reflections. Other analytical expressions have been proposed by various authors (Huml, 1980). However, it is clear that no simple weighting formula in which the background is supposed to be negligible or constant can possibly account for the observed type of dependence of $\sigma(I)$ on $I$ shown in Fig. 2.

## Omitting weak reflections is wrong

Largely because of their suitability for automatic iterative computer operation, least-squares methods have practically displaced all other methods in the refinement of crystal structures. The function minimized is usually taken as

$$\sum \omega_F (|F_o| - |F_c|)^2, \qquad (3)$$

but many authors have urged that

$$\sum \omega_{F^2} (F_o^2 - F_c^2)^2 \qquad (4)$$

or

$$\sum \omega_I (I_o - I_c)^2 \qquad (5)$$

be used instead. Indeed, $F$ refinements can be criticized on the grounds that they are less closely related to the experimental observations and that reflections with negative net $I$ or $F^2$ have to be omitted. Since weights $\omega_F$ taken as reciprocals of the variances of $\Delta F$ are in any case small for small $F$ values because of the relationship

$$\sigma^2(F) \sim \sigma^2(F^2)/4F^2; \qquad (6)$$

the obvious solution would seem to be to omit the weak 'unobserved' reflections altogether, those with negative or even those with small $F^2$ values. However, it has been argued, notably by Hirshfeld & Rabinovich (1973), that selective exclusion of weak (or negative) intensities leads to a bias in the remaining experimental data towards too high $F^2$ (or $I$) values and thus to systematic errors in the refined parameters. On the other hand, even if the errors in measurement of $F^2$ (or $I$) are random, a statistical bias towards too low $\langle F \rangle$ values is introduced when $F$ is estimated as $(F^2)^{1/2}$ (Ibers & Hamilton, 1964; Rees, 1977; Wilson, 1979). Nevertheless, it is easily shown (see, for example, Wilson, 1973) that refinements based on (3) or (4) lead to essentially the same results provided they are based on the same set of observations and provided weights are assigned inversely proportional to variances estimated in the usual way from (6). The argument depends on the approximation $(F_o^2 - F_c^2)/2F_c \simeq F_o - F_c$, which is valid when $F_o - F_c$ is small compared with $F_c$. Similarly, there is no difference between the results of $F^2$ and $I$ refinements provided the relative weights are properly assigned.

In spite of injunctions to the contrary, the vast majority of X-ray crystallographers continue to use $F$ refinements in which weak reflections are omitted according to some selection procedure or other, and for this they have recently drawn a stern rebuke from Schomaker (1982).

## But does it matter?

Even if the arguments against the use of $F$ refinements with rejection of weak reflections are accepted in principle, there is still the question of how serious the errors introduced by such malpractices actually are. In this work we have tried to provide a partial answer by ascertaining how much estimates of atomic positional and vibrational parameters actually differ when obtained from our experimental data by different kinds of refinement with different criteria for selecting the weak reflections.

For this purpose we chose to look first at high-order refinements (reflections with $0.85 < s < 1.15$ Å$^{-1}$) which should be relatively unaffected by valence-electron scattering. We began by analysing results of refinements made with DP1 and examined how the parameters varied as we went in stages from the canonical $I$ refinement including all 1406 reflections measured in this range (166 with zero or negative intensities) towards $F$ refinements with increasingly stringent inclusion criteria [$I > 2\sigma(I)$, 414 reflections]. An isotropic extinction correction was estimated using the full data set and held constant in the high-order refinements (and similarly for the subsequent refinements using DP2).

Table 1. *Results of six high-order refinements* $(0.85 \leq \sin \theta/\lambda \leq 1.15 \text{ Å}^{-1})$ *based on data set* 1 *(including mixed-mode reflections and with SIGSTAT weights)*

$U$ values are in units of $10^{-5} \text{ Å}^2$. Bond distances for these refinements are constant throughout and are within $1\sigma$ of those listed in Table 2.

| | A1 | B1 | C1 | D1 | E1 | F1 |
|---|---|---|---|---|---|---|
| Number of reflections | 1406 | 1240 | 1240 | 771 | 527 | 423 |
| Inclusion criterion | None | $I > 0$ | $I > 0$ | $I > 3\sigma(I)$ | $I > 10\sigma(I)$ | $I > 20\sigma(I)$ |
| Type of refinement | $I$ | $I$ | $F$ | $I$ | $F$ | $F$ |
| Scale factor | 0.2191 (6) | 0.2191 (6) | 0.2193 (6) | 0.2192 (7) | 0.2197 (7) | 0.2198 (7) |
| C(1) $U_{11}$ | 992 (5) | 991 (5) | 989 (5) | 989 (6) | 984 (6) | 982 (6) |
| $U_{22}$ | 959 (5) | 959 (6) | 958 (6) | 959 (6) | 957 (7) | 957 (7) |
| $U_{33}$ | 1072 (5) | 1071 (5) | 1070 (5) | 1071 (6) | 1069 (6) | 1068 (6) |
| C(2) $U_{11}$ | 1137 (8) | 1136 (8) | 1133 (8) | 1138 (10) | 1135 (10) | 1134 (10) |
| $U_{22}$ | 825 (7) | 825 (7) | 823 (7) | 824 (8) | 817 (9) | 817 (9) |
| $U_{33}$ | 930 (8) | 930 (8) | 929 (8) | 930 (9) | 925 (9) | 918 (10) |
| C(3) $U_{11}$ | 1758 (10) | 1758 (10) | 1757 (10) | 1761 (11) | 1756 (11) | 1753 (12) |
| $U_{22}$ | 948 (8) | 947 (8) | 944 (8) | 947 (9) | 939 (9) | 936 (10) |
| $U_{33}$ | 1068 (8) | 1068 (8) | 1065 (8) | 1066 (10) | 1062 (10) | 1063 (10) |
| F(1) $U_{11}$ | 1082 (5) | 1082 (5) | 1081 (5) | 1081 (6) | 1078 (6) | 1076 (6) |
| $U_{22}$ | 1666 (6) | 1666 (7) | 1665 (7) | 1665 (7) | 1663 (8) | 1661 (8) |
| $U_{33}$ | 1805 (7) | 1805 (7) | 1803 (7) | 1803 (8) | 1801 (9) | 1805 (9) |
| N(1) $U_{11}$ | 2968 (18) | 2967 (18) | 2962 (19) | 2962 (21) | 2958 (21) | 2954 (21) |
| $U_{22}$ | 1242 (9) | 1241 (9) | 1240 (9) | 1241 (10) | 1238 (10) | 1234 (10) |
| $U_{33}$ | 1574 (10) | 1574 (10) | 1570 (10) | 1571 (12) | 1559 (11) | 1554 (12) |
| Goodness of fit | 1.287 | 1.294 | 1.337 | 1.477 | 1.438 | 1.427 |
| $\sum w\Delta_i^2$ | 2267 | 2014 | 2150 | 1602 | 1013 | 807 |
| $R(F)$ | 0.087 | 0.067 | 0.067 | 0.028 | 0.013 | 0.010 |
| $R(I)$ | 0.056 | 0.047 | 0.047 | 0.032 | 0.020 | 0.017 |
| $R_H(F)$ | 0.017 | 0.017 | 0.017 | 0.015 | 0.012 | 0.011 |

The positional parameters obtained through these refinements are essentially the same as those published in DSS. They change from refinement to refinement by not more than $2 \times 10^{-4} \text{ Å}$ (about $0.5\sigma$) from their mean values and show no systematic variation; the corresponding changes in molecular geometry (see Fig. 3) lie below the threshold of physical significance. In contrast, the changes in the scale and temperature factors, although small, were systematic. Table 1 shows that as more and more weak reflections are excluded the atomic vibrational parameters show a slight systematic decrease. In accord with the strong correlation between scale and overall temperature
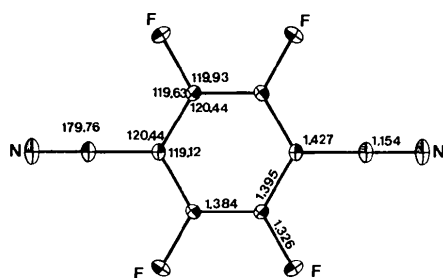


Fig. 3. Molecular geometry (bond lengths in Å, angles in °) and 50% vibration ellipsoids at 98 K from refinement A2. Standard deviations are about 0·0003 Å (see Table 2) in bond length and 0·03° in bond angle, so on purely statistical grounds it would seem justifiable to add another significant figure to the values shown in the diagram. However, since the bond lengths are complicated averages over many vibrational states the physical meaning of the extra significant figure would be questionable. Libration corrections for the various bond lengths amount to 0·001–0·002 Å [see Dunitz, Schweizer & Seiler (1982) for thermal motion analysis].

factors, the scale factor* increases slightly. On going from refinement A1 (all 1406 reflections) to refinement D1[771 reflections with $I > 3\sigma(I)$] there is very little change. The excluded reflections have such little weight that they make hardly any difference to the parameters.† Exclusion of weak reflections is carried to an extreme in refinement F1[423 reflections with $I > 20\sigma(I)$] but the total proportional increase in the scale factor is only about 0·3%, while the corresponding average decrease in a $U_{ii}$ component is less than $1 \times 10^{-4} \text{ Å}^2$ (or about $1\sigma$).

The slight systematic decrease in the temperature factors obtained by rejecting weak reflections is not due to the statistical bias discussed by Hirshfeld & Rabinovich (1973) but rather to a different kind of systematic error which is described in the following section.

The change from $I$ refinement to $F$ refinement also produces only trifling changes. In the XRAY system $\sigma^2(F)$ is estimated as

$$\sigma^2(F) = [(F^2)^2 + \sigma^2(F^2)/2]^{1/2} - F^2, \qquad (7)$$

which is smaller than the estimate given by (6) when $|F|$ tends to zero. The corresponding weights are then larger. However, in spite of this overweighting of the weak reflections the bias (Wilson, 1979) towards too

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* This is the factor by which relative values of $F_o$ are multiplied to bring them to the scale of $F_c$. It is thus the inverse of the factor that is actually adjusted in the least-squares refinement.

† Of course, this conclusion would not apply to any type of calculation where the reflections are assigned equal weights, e.g. a Fourier synthesis.

low $\langle F \rangle$ values that is introduced when $F$ is estimated as $(F^2)^{1/2}$ apparently has practically no effect on the parameters.

## A systematic error!

It is noticeable in Table 1 that the scale factor stays roughly constant from refinement $A1$ to $D1$ and from $E1$ to $F1$. The main change occurs between $D1$ and $E1$ just about the point where the $\sigma(I)/I$ ratio turns sharply upward (compare with Fig. 2). Besides the selection process involved in excluding the weak reflections as we go from refinement $A1$ to $F1$, we have to consider also another selection process, the one involved in the decision whether a given reflection should be remeasured in the slow scan mode or not. Recall that reflections identified as weak in the prescan were not remeasured (see *Experimental* section) although the corresponding counts (normalized) were included in the estimates of $\langle I \rangle$ in DP1. The inclusion of these prescan measurements (or rather the rejection of the high prescan counts) will have the effect that mixed-mode reflections, those with prescan intensities in the critical range $I_i \sim 2\sigma(I_i)$, are systematically too weak.* In fact, a simple statistical argument shows that in the critical range three quarters of the measured reflections will be weaker than the true $I$. The bias occurs because reflections in this critical range which happen to be measured too strong in the prescan receive the benefits of the longer scan time, whereas such reflections which happen to be measured too weak in the prescan are deprived of any chance to recover counts. Instead of being subjected to a second measurement the reflection intensity is simply multiplied by a factor to compensate for the smaller scan time. The contributions of the prescan measurements to mixed-mode reflections thus tend to bias the average intensity towards too low values. Inclusion of such reflections in the refinement should therefore lead to systematic errors in scale and overall temperature factors. This systematic error would not occur if the prescan counts were added to the slow-scan counts for reflections measured in the normal mode. In the standard CAD4 software, however, this is not done.†

In the present study the weak high-order reflections were measured for about $8 \times 80$ s each, the others for considerably longer. If in our experiment we had allotted approximately equal measuring time to all accessible reflections, the systematic underestimation of the mixed-mode reflections would disappear. Also, the sharp increase in the variance of the very weak

reflections (see Fig. 2) would be much less pronounced. For a given total measurement time, however, any increase in the time spent on the very weak reflections would obviously have to be paid for at the cost of time spent on the others.

Table 2 shows results of refinements made with DP2 in which prescan measurements were discarded for mixed-mode reflections and the larger of the two estimates SIGSTAT and SIGDEV for $\sigma(I)$ was used. The elimination of the prescan contributions to mixed-mode reflections has two effects. (1) The mean intensities $I$ of these reflections will tend to increase; this tendency will give a less biased estimate of $\langle I \rangle$ provided the reflections remeasured in the normal scan do not suffer from a larger opposite systematic positive bias. In fact, a statistical test based on repeated measurements of one reflection in the critical $I_i \sim 2\sigma(I_i)$ region indicates that any such bias would be at least an order of magnitude smaller. (2) SIGDEV should decrease and SIGSTAT should increase slightly. [Actually, because of the approximation involved in (1) the SIGSTAT estimate can decrease when prescan contributions are discarded from mixed-mode reflections.] The net result is that $\sigma(I)$ estimates are on the whole larger in DP2 compared with DP1.

The slight trend in scale factor (and overall temperature factor) that was apparent in Table 1 disappears when the prescan measurements are omitted from mixed-mode reflections (Table 2). Now the results of all refinements from $A2$ (all 1406 reflections, parameters given in Table 3) to $F2$ [436 reflections with $I \geq 20\sigma(I)$] are practically the same and are very similar to those of refinement $F1$ of Table 1, the one with the most stringent inclusion criterion. In agreement with the results obtained with DP1, the comparison of results of refinements $A2$ (all 1406 reflections) and $B2$ (1238 reflections with $I \geq 0$) confirms that the effects of omitting negative intensities are undetectable. Similarly, the effects of switching from $I$ refinement ($B2$) to $F$ refinement ($C2$) are negligible; the scale factor increases by 0·1% and the $U_{ii}$ components drop by $2 \times 10^{-5}$ Å$^2$ on average.

The slight increase of 0·2% in scale factor on going from refinement $F1$ (Table 1) to $F2$ (Table 2) is due mainly to the change in the estimation of $\sigma(I)$ and thus of the weights.

## Inclusion of low-order reflections

In contrast to the relatively trivial consequences of omitting weak or imprecisely measured reflections in a given data set, the effect of changing the $\sin \theta / \lambda$ limits for the refinement can be considerable. This is shown by the comparison in Table 2 between refinement $A2$ (all data, $0·85 \leq s \leq 1·15$ Å$^{-1}$, 1406 reflections) and refinement $G2$ (all data, $s \geq 0$, 2387 reflections). Not only are the changes in

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* After our DP1 data had been sent to Professor F. L. Hirshfeld for calculation of a static deformation density map, he drew our attention to a systematic error in the weak reflections. We are grateful to him for his persuasive persistence that we should look for the origin of this error.

† We are informed that Enraf–Nonius is taking steps to deal with this problem.

Table 2. *Results of refinements based on data set 2 (excluding prescan contributions to mixed-mode reflections and with SIGMAX weights)*

$A2$, $B2$, $C2$, $F2$ are high-order refinements $(0.85 \le \sin\theta/\lambda \le 1.15\,\text{Å}^{-1}$, as Table 1), $G2$ includes all accessible reflections out to $\sin\theta/\lambda = 1.15\,\text{Å}^{-1}$, $H2$ all accessible reflections out to $\sin\theta/\lambda = 0.65\,\text{Å}^{-1}$ (low-order refinement). $U$ values are in units of $10^{-5}\,\text{Å}^2$, bond distances in Å.

| | A2 | B2 | C2 | F2 | G2 | H2 |
|---|---|---|---|---|---|---|
| Number of reflections | 1406 | 1238 | 1238 | 436 | 2387 | 431 |
| Inclusion criterion | None | $I > 0$ | $I > 0$ | $I > 2\sigma(I)$ | None | $I > 0$ |
| Type of refinement | $I$ | $I$ | $F$ | $F$ | $I$ | $I$ |
| Scale factor | 0·2200 (6) | 0·2200 (6) | 0·2202 (6) | 0·2202 (7) | 0·2225 (3) | 0·2181 (9) |
| C(1) $U_{11}$ | 982 (5) | 981 (5) | 979 (5) | 978 (6) | 963 (10) | 1069 (50) |
| $U_{22}$ | 956 (5) | 956 (5) | 955 (5) | 955 (7) | 941 (11) | 1211 (53) |
| $U_{33}$ | 1069 (5) | 1068 (5) | 1067 (5) | 1067 (6) | 1045 (11) | 1094 (47) |
| C(2) $U_{11}$ | 1133 (8) | 1132 (8) | 1128 (8) | 1134 (10) | 1157 (16) | 1409 (66) |
| $U_{22}$ | 818 (6) | 817 (7) | 816 (7) | 813 (8) | 784 (15) | 920 (63) |
| $U_{33}$ | 918 (7) | 919 (8) | 919 (8) | 918 (10) | 891 (15) | 912 (63) |
| C(3) $U_{11}$ | 1743 (9) | 1744 (10) | 1742 (10) | 1746 (12) | 1651 (21) | 1497 (68) |
| $U_{22}$ | 937 (7) | 936 (7) | 933 (7) | 931 (9) | 1008 (18) | 1346 (73) |
| $U_{33}$ | 1060 (7) | 1059 (8) | 1057 (8) | 1061 (10) | 1041 (17) | 1113 (63) |
| F(1) $U_{11}$ | 1076 (5) | 1077 (5) | 1076 (5) | 1074 (6) | 1062 (9) | 1164 (35) |
| $U_{22}$ | 1654 (6) | 1653 (6) | 1653 (6) | 1658 (8) | 1611 (11) | 1728 (38) |
| $U_{33}$ | 1805 (7) | 1804 (7) | 1802 (7) | 1802 (9) | 1813 (12) | 1902 (39) |
| N(1) $U_{11}$ | 2966 (17) | 2963 (18) | 2958 (17) | 2956 (21) | 2769 (27) | 2742 (72) |
| $U_{22}$ | 1235 (8) | 1235 (9) | 1233 (9) | 1235 (11) | 1328 (19) | 1570 (66) |
| $U_{33}$ | 1553 (9) | 1553 (9) | 1551 (9) | 1552 (12) | 1540 (20) | 1619 (61) |
| Goodness of fit | 1·106 | 1·084 | 1·120 | 1·307 | 4·764 | 8·483 |
| $\sum \omega \Delta_i^2$ | 1674 | 1412 | 1506 | 682 | 53310 | 28350 |
| $R(F)$ | 0·081 | 0·060 | 0·060 | 0·010 | 0·055 | 0·028 |
| $R(I)$ | 0·052 | 0·042 | 0·042 | 0·017 | 0·045 | 0·041 |
| $R_H(F)$ | 0·016 | 0·016 | 0·016 | 0·011 | 0·037 | 0·035 |
| C(1)–C(2) | 1·3950 (3) | 1·3951 (3) | 1·3951 (3) | 1·3950 (3) | 1·3918 (5) | 1·3911 (12) |
| C(1)–F(1) | 1·3264 (3) | 1·3264 (3) | 1·3262 (3) | 1·3264 (4) | 1·3313 (5) | 1·3345 (11) |
| C(1)–C(1′) | 1·3841 (2) | 1·3841 (3) | 1·3841 (3) | 1·3841 (3) | 1·3814 (5) | 1·3768 (14) |
| C(2)–C(3) | 1·4270 (4) | 1·4270 (4) | 1·4270 (4) | 1·4270 (5) | 1·4322 (7) | 1·4366 (19) |
| C(3)–N(1) | 1·1538 (4) | 1·1538 (5) | 1·1537 (5) | 1·1537 (6) | 1·1489 (8) | 1·1432 (19) |

Table 3. *Positional and vibrational parameters ($\text{Å}^2$) (all $\times 10^5$ with s.d.'s in parentheses) from high-order refinement A2 (all reflections with $s \ge 0.85\,\text{Å}^{-1}$ including negative intensities)*

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 15650 (3) | 5913 (2) | 4020 (2) | 982 (5) | 956 (5) | 1069 (5) | −85 (4) | −44 (5) | −80 (3) |
| C(2) | 0 | 11980 (3) | 8083 (3) | 1133 (8) | 818 (6) | 918 (7) | 0 | 0 | −77 (5) |
| C(3) | 0 | 24199 (3) | 16333 (3) | 1743 (9) | 937 (7) | 1060 (7) | 0 | 0 | −189 (5) |
| F(1) | 30608 (2) | 11526 (2) | 7930 (2) | 1076 (5) | 1654 (6) | 1805 (7) | −365 (4) | −202 (4) | −284 (5) |
| N(1) | 0 | 34106 (3) | 22962 (4) | 2966 (17) | 1235 (8) | 1553 (9) | 0 | 0 | −562 (7) |

the scale factor and vibrational parameters much greater than those in the $A2$–$F2$ comparison, there are now also quite perceptible changes in the atomic positions and hence in the molecular dimensions (Fig. 4).

For a simple model structure, Ruysink & Vos (1974) have shown that inclusion of low-order reflections in the least-squares refinement led to significant deviations of positional and vibrational parameters from their true values. In our case we do not know the 'true' values of the parameters, but we can believe they are indeed closer to those of refinement $A2$ than $G2$, at least for the positional parameters.

As far as the changes in vibrational parameters are concerned it is harder to come to any decision, for these parameters are notoriously sensitive to many kinds of systematic error. For example, neglect of thermal diffuse scattering tends to lead to a general underestimation of the overall temperature factor (Feil, 1977), whereas truncation errors (Denne, 1977)

and neglect of deformation density terms, *i.e.* use of free-atom scattering factors in the least-squares refinement, have the opposite effect (Hirshfeld, 1976). In any case, the overall temperature factor often appears to vary somewhat from one crystal specimen to another and to increase with prolonged exposure of the crystal to X-radiation (Seiler, unpublished results). The behaviour of the present crystal in this respect was not studied in detail, although an intensity decrease of about 8% was observed for the 10,0,0 reflection over the measurement period.

In spite of these uncertainties, Hirshfeld's (1976) rigid-bond test provides a fairly clear-cut decision. Differences between mean-square vibrational amplitudes of bonded pairs of atoms along their respective interatomic vectors amount to at most $7 \times 10^{-4}\,\text{Å}^2$ for the results of refinements $A2$ to $F2$, whereas refinement $G2$ gives a difference of $20 \times 10^{-4}\,\text{Å}^2$ for the bond C(2)–C(3). Likewise, for the non-bonded pairs, the largest differences are $8 \times 10^{-4}\,\text{Å}^2$ for refinements

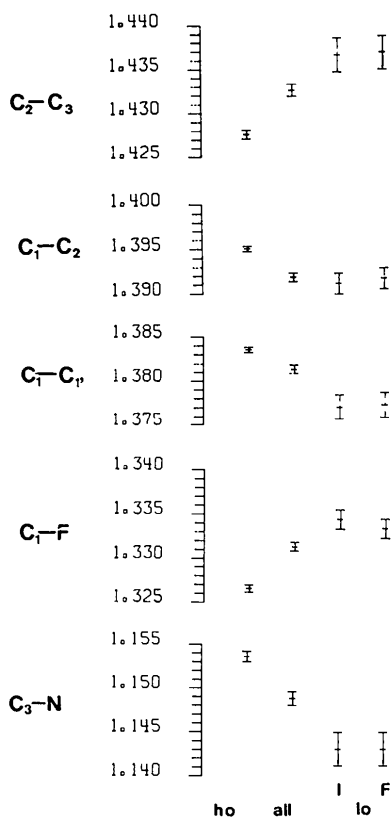Fig. 4. Comparison of interatomic distances (Å) obtained by high-order refinement (ho) $(s > 0.85 \text{ Å}^{-1})$, all-reflection refinement (all), and low-order refinement (lo) $(s < 0.65 \text{ Å}^{-1})$ on $I$ and $F$.

$A2$ to $F2$ and $25 \times 10^{-4} \text{ Å}^2$ for refinement $G2$. The librational and translational tensors for the molecular rigid-body motion are not greatly affected by these changes. In agreement with the results of others (see Coppens, 1977), we conclude that the results of refinement $G2$ are perceptibly contaminated by the valence-

electron distribution and are inferior to those of the high-order refinements $A2$ to $F2$. These are, among themselves, practically identical.

### Exclusion of high-order reflections

Most routine X-ray analyses are based on room-temperature intensity data that do not extend much past $s = 0.65 \text{ Å}^{-1}$ ($\theta = 27°$ for Mo $K\alpha$, $\theta = 90°$ for Cu $K\alpha$ radiation). In addition to the vibration parameters, positional parameters obtained by least-squares refinement of such low-order data sets may also be considerably in error because of the inadequacy of the free-atom scattering factors for low-order reflections.

For comparison with results obtained from high-order refinements, Fig. 4 also shows interatomic distances calculated from the low-order data with $s \leq 0.65 \text{ Å}^{-1}$ using both $I$ refinements (including reflections with negative intensities) and $F$ refinements (excluding them). It clearly makes very little difference which kind of refinement is made; the results of the $I$ and $F$ refinements agree very closely with one another, but there are discrepancies of more than $0.01 \text{ Å}$ between bond lengths obtained from these low-order refinements and the high-order ones mentioned earlier. The largest discrepancies occur for the exocyclic $C(2)-C(3)$ bond, which is too long, and for the $C(3)-N$ bond, which is too short; in the low-order refinement the $C(3)$ and N atoms are drawn towards the deformation density of the triple bond which is the strongest feature of the charge-density difference map (Fig. 5).

Refinements made on the low-order data with exponentially modified weights, $\omega_M = \omega_{exp}(as^2)$ (Dunitz & Seiler, 1973), lead to atomic positions and bond distances closer to the high-order values, as
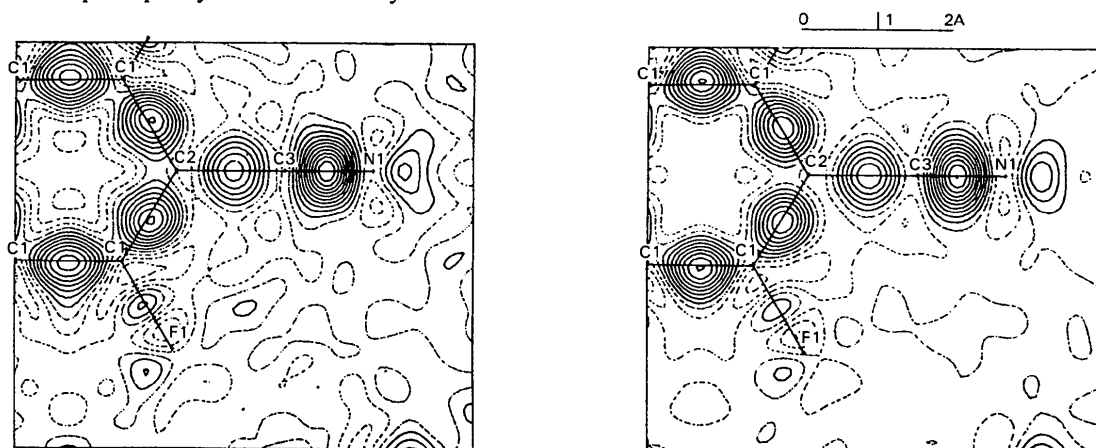


Fig. 5. Charge-density difference maps in the molecular plane based on high-order refinement $A2$ (Table 2). Maps based on the other high-order refinements of Tables 1 and 2 are practically indistinguishable. Contours are drawn at intervals of $0.075 \text{ e Å}^{-3}$, positive contours full lines, negative contours dashed, zero contour dotted. Left: calculated with all 981 reflections out to $\sin \theta / \lambda = 0.85 \text{ Å}^{-1}$ with $I \geq 0$. Right: calculated with 795 reflections in the same $\sin \theta / \lambda$ range with $I \geq 5\sigma(I)$. The standard deviations in the densities are $0.040 \text{ e Å}^{-3}$ and $0.011 \text{ e Å}^{-3}$, respectively.

expected. With $a \simeq 10 \text{ Å}^2$ the quantity $\langle \omega_M (\Delta F)^2 \rangle$ is approximately equal in different ranges of $s$, and the resulting atomic parameters are about halfway between the low-order values and those of refinement $G2$ (all reflections out to $s = 1 \cdot 15 \text{ Å}^{-1}$). No further improvement can be obtained by additional sharpening.

It is a pleasure to thank Professors F. L. Hirshfeld and V. Schomaker for their comments on a preliminary draft of this paper.

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# Book Reviews

*Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.*

**Intercalation chemistry.** Edited by M. S. WHITTING-HAM & A. J. JACOBSON. Pp. xvi + 595. London: Academic Press, 1982. Price £57.00, US$ 87.50.

In this book, all of the chapters are independent except for the first, written by one of the Editors, which gives an introduction to intercalation phenomena. The reader can therefore study at his choice. Because intercalation chemistry is growing significantly and extending into many scientific disciplines, the Editors decided to draw together into this volume related areas in which the host lattice maintains its essential structural features during host–guest reaction – as can be seen from the contents. The book aims to introduce specialist readers to the breadth of intercalation chemistry, and also to acquaint newcomers with the diverse research opportunities and challenges that there are in synthetic and reaction chemistry. Thus, the experimental details and theoretical background are not given. However, the reader can refer to original papers listed at the end of each contribution, and cited almost up to 1980. The book includes a subject index.

Each contribution describes the objective of its field. Many contributors recognize that work on intercalation has been deficient in regard to determination of the structure of the reaction products. However, crystallographic-shear structures, which are not usually considered as related to intercalation compounds, have important similarities in their structures, imposing constraints on the reactions that take place; and these are being studied by determining their structures (ch. 15). Some of the intercalates are now being studied crystallographically (ch. 3). Discussion of intercalation in the context of biological systems indicates an intercalation model compound (ch. 14).

Although the phenomenon of intercalation was first observed in the nineteenth century, detailed studies began only in the past two decades, and practical applications, and explanations of external appearances, preceded chemical investigations. This volume might stimulate wider interactions, not only among researchers in intercalation chemistry itself but among those in the various materials-science disciplines.

In this connection, a question arises in the mind of the reviewer. Why should a lengthening of the axis perpendicular to the host layer be an indicator of the occurrence of intercalation? In many cases, it is not at all clear what factors decide the length and direction of the axis perpendicular to the host layers in the intercalates, even if the host crystals were set in the appropriate orientation before the host–guest reaction. In practice, the lengthening of the crystal lattice is always detected by an X-ray powder pattern, from which, however, we can only know that the periodicity of the compound changes from one dimension to another; and this cannot mean that the periodic axis is retained. X-ray powder diffraction patterns in which faint peaks are hidden in the background could often be indexed with somewhat longer cell dimensions. Thus, it should be confirmed *by another technique* whether the host layered lattice is maintained or not. This point should be connected with the fact that the bonds between the host and guest molecules are not clearly understood, except in simple ionic cases. (This is a natural consequence of the fact that the structures of intercalated compounds are still scarcely known.) To solve these questions much effort is needed to seek further detailed knowledge.

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