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The Influence of Profile Analysis on Structural Parameters and Deformation Density Distributions

By Hanno R. van der Wal, J. L. de Boer and Aafje Vos

Laboratorium voor Chemische Fysica, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 *AG Groningen, The Netherlands*

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Abstract

Nett X-ray diffraction intensities have been determined from measured step-scan profiles of deuterated 2,5-dimethyl-3-hexyne-2,5-diol by four different profile-analysis procedures. Least-squares refinements based on the different sets of F values showed that variations in profile analysis method may change the coordinates by 1·5 times the σ of $0{\cdot}8 \times 10^{-4}$ Å and the thermal parameters by twice the σ of $1{\cdot}4 \times 10^{-5}$ Å^2. The change in scale factor is 1·2% or 4σ. A correct choice of refinement procedure, in which full-angle data are used for the determination of the scale, turned out to be more important for the calculation of reliable deformation densities than the choice of profile-analysis method.

Introduction

Different profile-analysis methods have been described to deduce nett X-ray or neutron diffraction intensities from reflection profiles. For neutron diffraction data, for instance, Lehmann & Larsen (1974) have developed the $\sigma(I)/I$ minimum algorithm. Blessing, Coppens & Becker (1974) noticed that for X-ray data this algorithm makes the peak region too narrow. This is not too surprising as the $\sigma(I)/I$ method is correct only for profiles based on one simple distribution function, which is certainly not true in the X-ray case (α_1–α_2 splitting).

In the present paper we describe the results of four methods used for the analysis of the reflection profiles measured by Helmholdt (1975) for 10 829 independent reflections of deuterated 2,5-dimethyl-3-hexyne-2,5-diol. Details of the measurements have been reported (Helmholdt & Vos, 1977). Changes in structural parameters due to a change in profile-analysis method were found by least-squares refinements for the four different sets of F values. Also, for all four cases, deformation maps were computed to study the influence of profile analysis on experimental deformation density distributions.

Profile analysis methods

The nett intensity is given by

$$I(\text{nett}) = \sum_{i=n_1+1}^{n_2-1} Y(i) - \frac{m_p}{m_b}\left[\sum_{i=1}^{n_1} Y(i) + \sum_{i=n_2}^{n(\max)} Y(i)\right]. \quad (1)$$

$Y(i)$ is the intensity measured for each profile step. The peak region extends from steps $n_1 + 1$ to $n_2 - 1$, and the background regions contain the steps 1 to n_1 and n_2 to $n(\max)$. For all reflections $n(\max) = 96$. The numbers of steps m_p and m_b for peak and background regions respectively are given by

$$m_p = n_2 - n_1 - 1, \quad (2)$$

$$m_b = n_1 + (96 - n_2 + 1). \quad (3)$$

Four methods were used to find the location of n_1 and n_2:

(I) *Predetermined reflection width*

For the reflection width we have adopted the formula

$$R(\mathbf{H}) = A(\hat{\mathbf{H}}) + B \operatorname{tg} \theta. \quad (4)$$

$\hat{\mathbf{H}}$ is a unit vector in the direction $\mathbf{H}$. The anisotropic quantity $A(\hat{\mathbf{H}})$ is controlled mainly by the mosaic spread of the crystal and B depends on the wavelength spread in the incident beam (for further factors influencing $A(\hat{\mathbf{H}})$ and B, see Keulen, 1969; Alexander & Smith, 1962). The points n_1 and n_2 are taken at a distance of $\pm R(\mathbf{H})/2$ from the center of gravity of the peak. For the determination of $A(\hat{\mathbf{H}})$ and B the widths $Rg(\mathbf{H})$ of 38 reflections with $\sigma(I)/I < 0{\cdot}05$ and spread over eight directions were deduced from the formula

$$Rg(\mathbf{H}) = SM \times Rg[\mathbf{H}, TH \times Y(\max)]. \quad (5)$$

$Rg[\mathbf{H}, TH \times Y(\max)]$ is the width of the peak base at threshold TH times the maximum height $Y(\max)$, and SM scales $Rg[\mathbf{H}, TH \times Y(\max)]$ to the real Bragg reflection width. SM is determined by inspection of the profiles of a series of low-order reflections. For the present case we found $SM = 3{\cdot}5$ for TH set at 0·2. If three or more $Rg(\mathbf{H})$ values were available for a certain

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direction, a least-squares fit was made to determine $A(\hat{\mathbf{H}})$ and B. The values obtained are $A(\hat{\mathbf{H}}) = 0{\cdot}60$–$0{\cdot}71$ and $B = 0{\cdot}9$. The experimental B value deduced from a $\theta/2\theta$ scan with narrow slit width at $\theta = 40{\cdot}0°$ is $1{\cdot}0$ for monochromatized Mo radiation as used for the collection of the present data.

(II) *Standard Nonius CAD4F procedure*

The *CAD4F* program applies the θ dependence of (4) for the calculation of the scan width, but uses isotropic values for $A(\hat{\mathbf{H}})$. n_1 is taken as 16 and n_2 as 81. This implies that for isotropic $A(\hat{\mathbf{H}})$ and the use of suitable values for the constants A and B, the *CAD4F* procedure gives the same nett intensities as (I).

(III) *Profile analysis after smoothing of the profile dump*

Helmholdt & Vos (1977) have described a method (here to be referred to as III) for the determination of n_1 and n_2 after smoothing of the measured profile. For the stronger reflections only the outer parts of the profile were smoothed. Details can be found in Helmholdt (1975).

(IV) *Profile analysis without smoothing the profile dump*

First we checked the applicability of the Lehmann & Larsen $\sigma(I)/I$ method for X-ray diffraction by applying the method to a series of model X-ray profiles. These profiles consist of two Gaussian lines in proportion 2:1 with peak separation corresponding to $\lambda(\text{Mo } K\alpha_1) - \lambda(\text{Mo } K\alpha_2)$ and are superimposed on different backgrounds B. For $B/I(\text{max}) < 0{\cdot}05$ correct intensities were obtained. For increasing values of $B/I(\text{max})$ the peak region gradually becomes too small.

In view of the above results we have used the $\sigma(I)/I$ method only to obtain a lower estimate of the reflection width. Say that the $\sigma(I)/I$ reflection bounds are given by n_H and n_L. Starting from n_H and n_L and going outwards, a search is made for a region of ten points for which the profile is flat within experimental error. To this end, for the high-n side, a least-squares line,

$$Y_{J+i}(\text{calc}) = ax_{J+i} + b \quad (i = 1, 10), \tag{6}$$

is fitted to $Y_{J+i}(\text{obs})$. For x_{J+1} to x_{J+10} the values of 1 to 10 are taken. Successive trials with $J = n_H + k$ (k running integer index) are made. The criteria for a flat profile are $|a| < 0{\cdot}1$ and

$$\sum_i [Y_{J+i}(\text{calc}) - Y_{J+i}(\text{obs})]^2 = \sum_i Y_{J+i}(\text{obs}). \tag{7}$$

The point $n_H + k$ with smallest k which obeys the criteria is taken as n_2. An analogous procedure is followed for n_1. For low backgrounds with small random fluctuations, as is the case for the present profiles measured with monochromatized radiation, (IV) is analogous to (III).

Influence on structure factors

The structure factors $F_M(\mathbf{H})$ deduced from the nett intensities of method M (M = II, III, IV) have been compared with the structure factors $F_{\text{I}}(\mathbf{H})$ of (I). Fig. 1 shows Wilson-like plots of

$$\ln \frac{\langle |F_M(\mathbf{H})| \rangle}{\langle |F_{\text{I}}(\mathbf{H})| \rangle} \textit{ versus } (\sin\theta/\lambda)^2.$$

The plots indicate that for (III) and (IV), the $|F_M(\mathbf{H})|$ values for reflections with $\sin\theta/\lambda > 0{\cdot}9$ Å^{-1} are too small in comparison with the $|F_{\text{I}}(\mathbf{H})|$ values. The relatively small values for (III) and (IV) are caused by omitting parts of reflections from the peak region. The omitted parts have, when going from the peak outwards, a systematic decrease in intensity which is small in comparison with the random errors in $Y(i)$. Especially for the high-order reflections this is liable to occur.

Comparison of systematic and random errors

In Fig. 2 systematic differences in F values due to changes in profile-analysis method, are compared with changes in F values due to random errors. The errors in $|F|$ as a function of $(\sin\theta/\lambda)^2$ are represented by

$$R = \sum |\Delta F(\mathbf{H})| / \sum |F(\mathbf{H})|, \tag{8}$$

where the summation is over the reflections in the interval considered. For the experimental points (▲) $|\Delta F(\mathbf{H})| = |F_{\text{I}}(\mathbf{H}) - F_{\text{III}}(\mathbf{H})|$. For the calculation of the random errors (□) we determined the number $N(t)\Delta t$

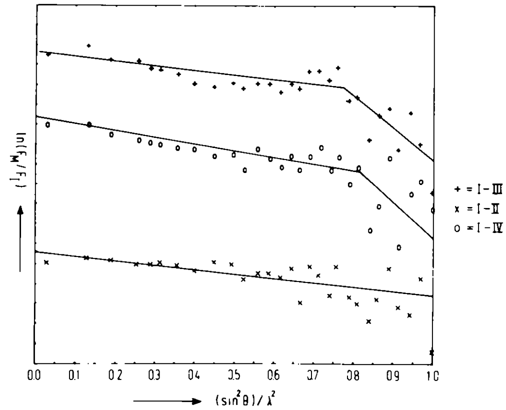

Fig. 1. Comparison of structure factors obtained by methods (I)–(IV) by means of Wilson-like plots. The figure is on a relative scale, $\ln[\langle|F_M(\mathbf{H})|\rangle / \langle|F_{\text{I}}(\mathbf{H})|\rangle]$ is given by $\ln(F_M/F_{\text{I}})$ at the vertical axis and is approximately 0 at $\sin\theta/\lambda = 0$.

of reflections having errors between $t\sigma_c$ and $(t + \Delta t)\sigma_c$ from the function

$$N(t)\,\Delta t = N(2\pi)^{-1/2}\exp(-t^2/2)\,\Delta t, \qquad (9)$$

where N is the total number of reflections. The reflections $N(t)\,\Delta t$ were randomly chosen from the data set and were given errors $|\Delta F(\mathbf{H})| = t\sigma_c[|F_{\rm I}(\mathbf{H})|]$, where $\sigma_c[|F_{\rm I}(\mathbf{H})|]$ is the e.s.d. of $|F_{\rm I}(\mathbf{H})|$ based on counting statistics. Fig. 2 shows that changes in $|F|$ due to a change in profile-analysis method are smaller than the errors expected on the basis of counting statistics. Nevertheless it cannot be excluded that profile-analysis errors have a significant effect on the scale factor and structural parameters because of their systematic nature.

Influence on scale, atomic positions and thermal parameters

Least-squares refinements were carried out for (I)–(IV) according to the following procedure. First low-order refinements ($\sin\theta/\lambda < 0{\cdot}65$ Å^{-1}) on $|F|$ were used to fix the parameters of the H atoms and of the (split) atoms of the disordered $[(CD_3)_2OH]$ group (Helmholdt & Vos, 1977) such that low-order difference maps were flat around these atoms. These parameters were kept fixed during the further refinement. The remaining parameters were determined in different ways.

(*A*) High-order ($\sin\theta/\lambda > 0{\cdot}65$ Å^{-1}) least-squares refinement on $|F|$ with weighting scheme $w[|F(\mathbf{H})|] = 1/\sigma_c^2[|F(\mathbf{H})|]$. Carried out for all four sets of F values. Corresponding coordinates differ by 1·5 times the e.s.d. of about $0{\cdot}8 \times 10^{-4}$ Å, and corresponding thermal parameters lie within twice the e.s.d. of $1{\cdot}4 \times 10^{-5}$ Å^2. The variation in scale factors is larger. Whereas $K(\mathrm{I}) \simeq K(\mathrm{II})$ and $K(\mathrm{III}) \simeq K(\mathrm{IV})$, the scale factor $K(\mathrm{IV}) = 0{\cdot}988K(\mathrm{I})$, the difference being four times the e.s.d.

(*B*) High-order least-squares refinement on $|F|$ with weights $w[|F(\mathbf{H})|] = [\sigma_c^2(|F(\mathbf{H})|) + 0{\cdot}0005|F|^2]^{-1}$ making the variation in $\langle w\Delta^2\rangle$ as a function of $|F|$ as small as possible. Carried out for (I) only. The scale factor $K'(\mathrm{I}) = 0{\cdot}993K(\mathrm{I})$.

(*C*) Refinement (*B*) for (I) followed by determination of the scale factor from a full-angle refinement with all further parameters fixed. $K'(\mathrm{I};\,FA) = 0{\cdot}980K(\mathrm{I})$.

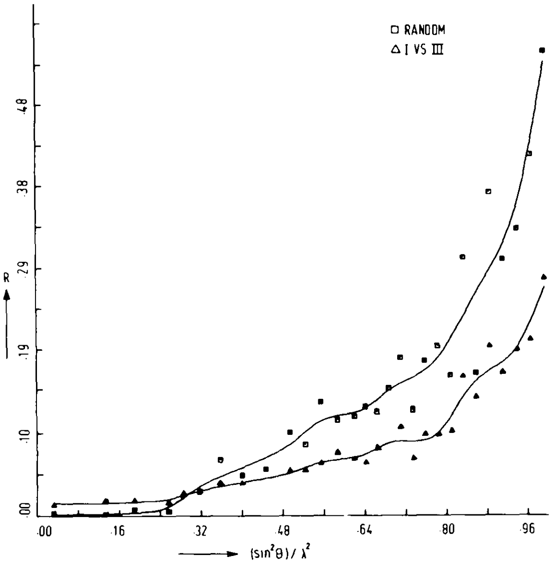

Fig. 2. Comparison of differences in $|F(\mathbf{H})|$ due to a change in profile analysis method (▲) with errors caused by random effects (□).

Changes in deformation density distributions

As the results for (I) and (II), as well as those for (III) and (IV), are similar, deformation maps are given only for (I) and (IV). The deformation density is defined as

$$D(\mathbf{r}) = K^{-1}\rho_0(\mathbf{r}) - \rho_c(\mathrm{atoms};\mathbf{r}) \qquad (10)$$

with $\rho_c(\mathrm{atoms};\mathbf{r})$ corresponding with the model of spherical non-bonded vibrating atoms. In all cases reflections with $\sin\theta/\lambda < 0{\cdot}65$ Å^{-1} were taken into account. The value for K and the atomic parameters were taken from the different refinements. Sections of $D(\mathbf{r})$ for the central part of the molecule at general position (Helmholdt & Vos, 1977) are given in Figs. 3, 4 and 5. It may be seen that in general, but especially at the atomic positions, the $D(\mathbf{r})$ values increase with decreasing value of the scale factor. Further, it is noticeable that between maps based on the same profile-analysis method (I) and different types of refinement (*A* and *C*), the differences are larger than for the same type of refinement (*A*) and different profile-analysis methods (I and IV). If account is taken of finite resolution, best agreement with Helmholdt's (1975) quantum theoretical calculations is obtained for $D(\mathbf{r})$ based on profile-analysis method (I) and refinement (*C*).

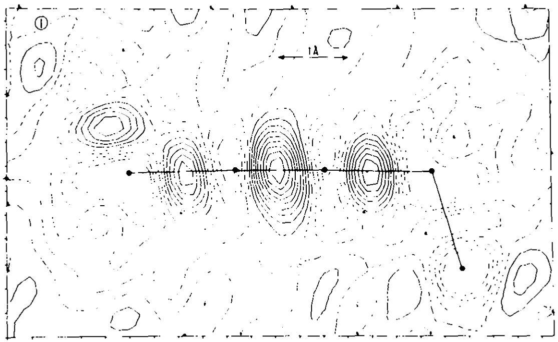

Fig. 3. Deformation density distribution in the plane through the atoms $\mathrm{C{-}C{\equiv}C{-}C}\underset{\mathrm{O}}{\diagdown}$. Amplitudes $[K^{-1}(\mathrm{I})F_o(\mathbf{H}) - F_c(\mathbf{H})]$ for method (I) and refinement (*A*). Contours in this and following figures at intervals of 0·05 e Å^{-3}. Full lines are positive, short dashed lines zero and long dashed lines negative contours.

Conclusions

The above information leads to the following conclusions:

(*a*) Differences in profile-analysis method may change the coordinates and thermal parameters by $1{\cdot}5\sigma$ and $2{\cdot}0\sigma$ respectively.

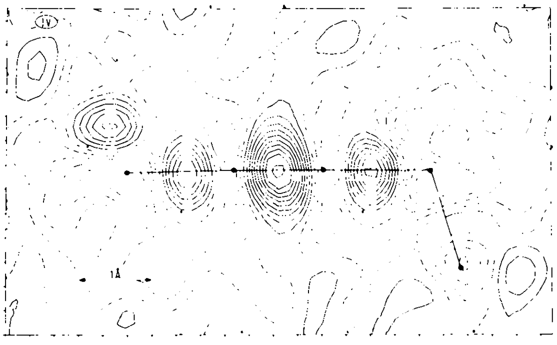

Fig. 4. Deformation density distribution with amplitudes $[K^{-1}(\mathrm{IV})F_o(\mathbf{H}) - F_c(\mathbf{H})]$ for method (IV) and refinement (*A*). $K(\mathrm{IV}) = 0{\cdot}988K(\mathrm{I})$.

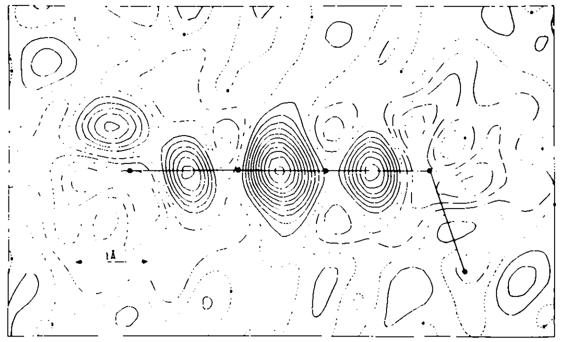

Fig. 5. Deformation density distribution with amplitudes $\{[K'(\mathrm{I}; FA)]^{-1} F_o(\mathbf{H}) - F_c(\mathbf{H})\}$ for method (I) and refinement (*C*). $K'(\mathrm{I}; FA) = 0{\cdot}980K(\mathrm{I})$.

(*b*) The deformation densities are influenced strongly by the value of the scale factor.

(*c*) Choice of a correct refinement procedure is more important than the type of profile-analysis method used. Care should be taken in the determination of the weighting scheme (preferably by repeated measurements of the same reflection). As high-order data are liable to be in error due to, for instance, thermal diffuse scattering (Kroon & Vos, 1979) or incorrect choice of profile-analysis method (present paper), full-angle data must be used for the determination of the scale (and the overall thermal motion).

(*d*) Profile-analysis method (I), where the reflection width is based on a physical criterion is to be preferred.

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