

trans series, respectively, was discussed in terms of a structural isomorphism. In the *trans* compounds, the straight-chain arrangement of the molecules is such that the packing will be little affected by the position of the ring, provided it is near the center and in an odd-even position (e.g. Fig. 1, Brotherton & Jeffrey, 1957). In the *cis* molecules, a change in ring position from 11-12 to 9-10 will shift one half of the chain by about $a/4$ with respect to the other half, as shown in Fig. 3(b). The general orientation of the two halves will be unchanged, however, and this could account for the similarity in unit-cell dimensions and powder line side-spacings which have been observed.

A similar contrast in overall configuration between the *cis* and *trans* compounds, found in these C₁₉ cyclopropyl acids, might be expected in the *cis* and *trans* unsaturated fatty acids, with the double bond near the center of a chain of comparable length (e.g. oleic acid, C₁₈H₃₄O₂; *cis* and *trans* vaccenic acids, C₁₈H₃₄O₂; erucic acid, C₂₂H₄₂O₂; nervonic acid, C₂₄H₄₆O₂). The *trans* unsaturated acids, like the *trans* cyclopropyl compounds, can readily adopt a straight-chain shape which is very close to that of a normal saturated long chain acid (see Brotherton, Craven & Jeffrey, 1958). The *cis* unsaturated acids can adopt either the distorted straight-chain or the boomerang shape. Carter & Malkin (1947) discussed the stereochemical differences between *cis* and *trans* unsaturated acids and showed by means of powder photographs that the crystal structures of erucic and brassidic acids, *cis* and *trans* CH₃(CH₂)₇.CH:CH.(CH₂)₁₁COOH, respectively, are quite different. Rideal (1945) found that erucic acid on water formed a more 'open' monomolecular surface film than brassidic and, in relating this to the ease of permanganate oxidation in the surface film of the *cis* structure as compared with the *trans*, he postulated a bent *cis* and a straight

trans configurations rather similar to those described in this paper.

A similarity in the single crystal data for erucic and *cis* nervonic acids with that of the *cis* cyclopropyl fatty acids has been found by Craven & Jeffrey (1956b).

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A General Least-Squares Program for the Refinement of Anisotropic Thermal Parameters

BY WALTER M. MACINTYRE

Chemistry Department, University of Colorado, Boulder, Colorado, U.S.A.

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A program is described for the refinement of anisotropic thermal parameters and atomic coordinates on the IBM 704 computer. The program covers all space groups of the triclinic, monoclinic, orthorhombic and tetragonal systems. A set of general structure factor expressions has been derived, one expression covering all space groups in a single system. A modified diagonal approximation is used.

1. Introduction

The art of measuring X-ray intensities has improved greatly in the last few years, and the data published

in the reports of structure analyses are becoming increasingly exact. Concurrently, large high-speed electronic computers have been developed which are

taking over much of the tedious calculation formerly associated with X-ray analysis. Thus the crystallographer is now in a position to determine the individual anisotropic thermal parameters of atoms in molecules as a routine procedure provided he has measured the intensities with sufficient accuracy to warrant this treatment.

The program described here uses a least-squares procedure to refine atomic coordinates and individual anisotropic thermal parameters for any crystal in any space group. It has been written for use with the IBM 704 computer. Another program, for another computer, has been described (Sparks *et al.*, 1956), but this computer is not readily accessible to crystallographers. In addition the structure of the present program is rather different. Other programs have been written for other computers and are being used, but have not been described in detail (e.g., Busing & Levy, 1958; Jacobson *et al.*, 1958).

2. General features

The program has been written in two complementary parts, each of which is an independent program. The primary function of the short first program is to calculate the scattering factor for each element and each plane being considered. These are calculated by Vand's approximation (Vand *et al.*, 1957) in which the scattering factor of the atom at rest, f_0 , is given the empirical representation:

$$f_0 = A \exp(-a \sin^2 \theta) + B \exp(-b \sin^2 \theta) + C.$$

A , a , B , b , and C are constants, and θ is the Bragg angle for the plane in question. Dauben & Templeton's correction for dispersion effects (1955) may be included in the constant C . When all the scattering factors for a given plane have been calculated they are written, in binary, on a magnetic tape together with the Miller indices, the weighting factor and the observed structure factor. This tape is used as input to the second program.

If the subsequent refinement is interrupted it is unnecessary to use program I again. The binary tape output of that program may be used as often as necessary.

The second program, which carries out the refinement is designed to be as flexible as possible. It can be used simply to calculate structure factors. Atomic coordinates and thermal parameters may be refined separately or simultaneously. Provision is made for excluding the atomic coordinates and/or the thermal parameters of any atom from the refinement. As a convenience, the final atomic coordinates and thermal parameters are punched automatically on cards in case further refinement is necessary.

The quantity minimized in the least-squares procedure is $\sum \omega (|F_o|^2 - |F_c|^2)^2$. In addition to providing a convenient basis for assigning weights (Shoemaker

et al., 1950) this function is more sensitive to slight changes in the variables than the function

$$\sum \omega (|F_o| - |F_c|)^2.$$

Following Cochran (1951) the scale factor, d , is defined by the expression $\sum |F_o| = (1-d) \sum |F_c|$. After correction of d , the F_o values are divided by $(1-d)$.

In order to conserve machine time, a modified diagonal approximation is used in the least squares procedure. The only cross terms included are those between the thermal parameters and the scale factor. Sayre had previously observed (1957) that when these cross terms were omitted the refinement went into oscillation, such that when the thermal parameters increased the scale factor (as usually defined) decreased, and vice versa. In the refinement of copper tropolone (Macintyre, 1957) using Sayre's *NY XR 1* program (1956) this oscillation resulted in the R -factor jumping back and forth between values of 0.16 and 0.22 in consecutive cycles. Convergence of the refinement was obtained only on damping the calculated corrections rather heavily. Using the same data and a damping factor of 0.5 no such oscillation was observed with the present program. In addition the structures of copper bromide and pteridine have been refined (Macintyre, 1958) without oscillation setting in.

Recently the diagonal approximation has been severely criticized (ACA Conference, 1958). The principal criticism is that the approximation is so crude that the refinement may well converge to a false minimum. In the present case, however, the approximation is probably valid since the structure should be rather well refined by other methods before this program is used. The probability of more than one minimum existing at very low R -values is slight.

Machine time is conserved in other ways, particularly in the evaluation of the differentials. For example, take the case of the space group $P\bar{1}$. Let φ_n be the contribution of the n th atom to $F_c(hkl)$. Then:

$$\begin{aligned} \varphi_n = & f_{0,n} \cos 2\pi(hx + ky + lz)_n \\ & \times \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + klb_{23} + hlb_{13})_n]. \end{aligned}$$

It is readily seen that: $(\partial \varphi / \partial b_{11})_n = -h^2 \varphi_n$.

Similar arguments may be applied to other space groups, and whenever time is saved by the procedure, the differentials are expressed as functions of φ_n . In the program φ_n has been calculated previously in the structure factor calculation. General details of the program are shown in Fig. 1.

3. Space group selection

A general least squares program should be able to handle any crystal in any space group. This was achieved in Sparks' program (1956) by treating each crystal as if it had crystallized in space group $P1$. For crystals with higher symmetry this approach is rather inefficient. In Sayre's *NY XR 1* program a

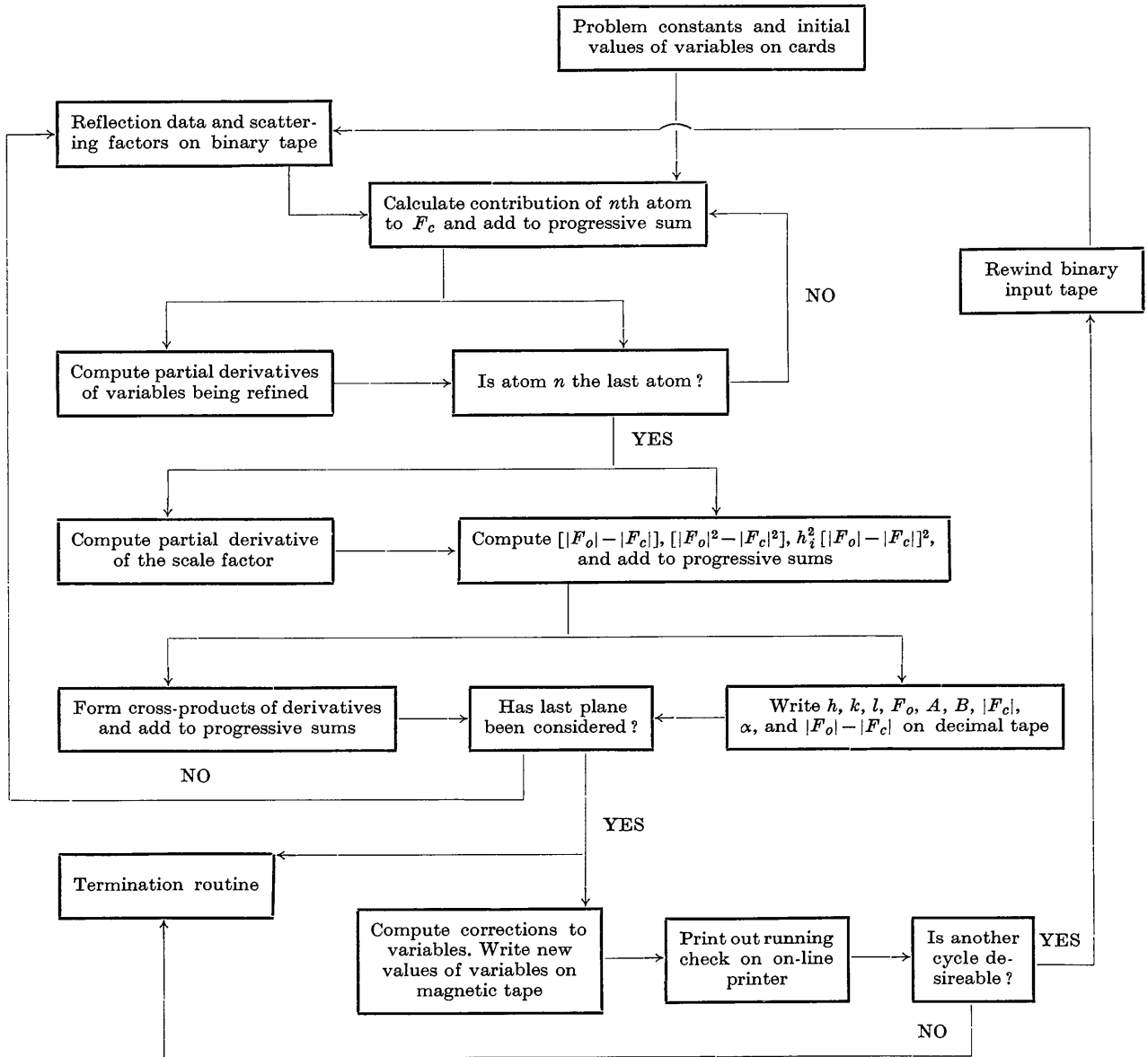


Fig. 1. Flow diagram for the refinement program. The scattering factors are calculated in a short preliminary program and put on binary tape together with the reflection data.

separate sub-routine was written for each space group. In terms of machine time this is the most efficient way to approach the problem since full use can be made of the specific forms of the structure factor expressions as listed in *International Tables*. However, it is questionable whether the time spent on coding 230 different sub-routines is worthwhile.

A compromise between these two extremes was adopted in the program described here. It is somewhat similar to that given by Ahmed (1958). For each crystal system it is possible to derive a general structure factor expression covering all space groups within the system. For example, in the monoclinic system the

real and imaginary parts of the geometrical structure factor may be expressed as follows:

$$A = 2L \cos 2\pi(hx + lz + Mk + Nl) \times \cos 2\pi[ky - (Mk + Nl)]$$

$$B = 2L \cos 2\pi(hx + lz + Mk + Nl + R_1) \times \cos 2\pi[ky - (Mk + Nl) + R_2].$$

These expressions are reduced to the specific expressions for the space group in question by introducing into the computer the appropriate values of the constants L , M , N , R_1 and R_2 . The values of these constants are obtained by inspection from the

specific expressions for the space group. For example in Pc :

$$A = 2 \cos 2\pi(hx + lz + \frac{1}{4}l) \cos 2\pi(ky - \frac{1}{4}l)$$

$$B = 2 \sin 2\pi(hx + lz + \frac{1}{4}l) \cos 2\pi(ky - \frac{1}{4}l)$$

Then,

$$L = 1, M = 0, N = 0.25, R_1 = -0.25, R_2 = 0.$$

The quantities $(Mk + Nl)$, $(Mk + Nl + R_1)$ and $(Mk + Nl + R_2)$ are computed only once for each plane. After this has been done the calculation of the structure factor takes no longer than it would if the specific space group expression were used. In particular where the number of atoms in the asymmetric unit is large, (ca. 20), the time spent on calculating structure factors by the general expression is about the same as would be spent if the specific space group expression were used.

So far, general structure factor expressions have been derived for the triclinic, monoclinic, orthorhombic and tetragonal systems, and the corresponding sub-routines written into the program.

The symmetry transformations of the thermal parameters (Trueblood, 1956) fit into this program rather well since, except for the hexagonal system, the transformations are the same for all space groups in a given crystal system.

4. Convergence

When a least-squares refinement of many cycles is being carried out on a fast computer it is difficult to determine when the structure has converged to a true minimum. Ideally only one cycle of refinement at a time should be carried out and the results examined at leisure. In planning subsequent cycles due attention can then be paid to all pertinent data. For example the reliability index may be misleading (Donohue & Trueblood, 1956). A decision as to whether or not to continue the refinement is seldom based on the value of the R -factor alone. R -prime, defined as

$$\Sigma(|F_o|^2 - |F_c|^2)$$

and the magnitudes of the corrections indicated by the completed cycle, are useful criteria which help decide the course of further refinement.

At the end of each cycle of refinement the computer prints out on the attached printer the values of R and R -prime (from the previous cycles), the average corrections to the thermal parameters and atomic coordinates, and the magnitude of the correction to the scale factor (from the current cycle). It then stops.

In a few seconds the operator can judge the progress of the refinement, decide which of the alternative routes the next cycle of refinement should follow, and restart the computer.

5. Timing

One cycle of refinement of pteridine was timed very carefully. The data of Hamor & Robertson (1956) were used. Pteridine is orthorhombic, space group $Pna2_1$, with 14 atoms in the asymmetric unit (excluding hydrogen atoms). This involves the refinement of $9 \times 14 = 126$ atomic parameters; including the scale factor, the total number of variables equals 127. 133 planes were included in the refinement. This cycle was completed in 157 sec. Thus in the orthorhombic system the time required for refinement may be calculated as 0.0093 sec., per parameter per plane. The tetragonal routine requires slightly more time; the monoclinic and triclinic routines slightly less time.

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