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## Automation of the non-centrosymmetric symbolic addition. II. Use of centric reflexions for symbol determination.

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In non-centrosymmetric symbolic addition, applied to structures with centric projections, a systematic use of the phase indications of the centric reflexions accelerates the determination of numerical values for the symbols and avoids solutions which are unacceptable in projection.

### Introduction

In the automation of non-centrosymmetric symbolic addition the systematic use of reflexions, the phases of which are restricted by symmetry operations can be very helpful in the determination of the values of the unknown symbolic phases. The most common symmetry element is a centre of symmetry in projections. In this paper a method for determining the values of unknown symbols from the phase indications of centric reflexions is presented.

### Method

A basic set of symbolic phases $\varphi_H = a_H + \sum_i a_{Hi}x_i$, where $a_H$ is a constant, $a_{Hi}$ are integers and $x_i$ are the unknown symbols, is obtained by the symbolic addition procedure (Karle & Karle, 1966) using a high-acceptance criterion. Then for all centric reflexions the symbolic phase indications are calculated. These indications have values restricted to $s$ and $s+\pi$, where $s$ in monoclinic and orthorhombic space groups equals either 0 or $\frac{1}{2}\pi$, depending on the space group and the choice of origin. Then for each phase indication it follows that:

$$\varphi_{H'} + \varphi_{H-H'} - s = 0 (\mathrm{mod}\ \pi) \qquad (1)$$

in which $H$ is a centric reflexion and $H'$ and $H-H'$ belong to the basic set of symbolic phases. With these relations the following figure of merit can be constructed:

$$CI = \sum_H \sum_{H'} K_{H'H-H'} |\sin(\varphi_{H'} + \varphi_{H-H'} - s)| = \text{minimum} \qquad (2)$$

which can be rewritten to

$$CI = \sum_l k_l |\sin(b_l + \sum_j a_{lj}x_j)| \qquad (3)$$

where

$$\varphi_{H'} + \varphi_{H-H'} - s = a_{H'} + \sum_j a_{H'j}x_j + a_{H-H'} + \sum_j a_{H-H'j}x_j - s = b_l + \sum_j a_{lj}x_j$$

and $K_{H'\,H-H'} = k_l$.

In (3) many terms $(b_l + \sum_j a_{lj}x_j)$ are identical. By summing their $k_l$'s the number of terms in (3) can be reduced:

$$CI = \sum_m w_m |\sin(b_m + \sum_j a_{mj}x_j)| . \qquad (4)$$

Usually $CI$ is dominated by a number of large $w_m$'s so that the very small $w_m$ may be neglected.

From $b_m + \sum_j a_{mj}x_j = p \pmod{\pi}$ it follows that:

$$CI(x_1 \cdots x_n) = CI(x_1 + \pi \cdots x_n) = CI(x_1 + \pi \cdots x_n + \pi) .$$

Thus it is impossible to differentiate between $x_i = q$ and $x_i = q + \pi$. These ambiguities can be solved for instance by calculating the $Q$ value, which is based on all reflexions (Schenk, 1971), for each of these possibilities.

Two other figures of merit suggest themselves for screening the trial sets $x_i$ in centrosymmetric projections:

$$CII = \sum_m w_m \{1 - \cos 2(b_m + \sum_j a_{mj}x_j)\} \qquad (5)$$

and

$$CIII = \sum_m w_m |(b_m + \sum_j a_{mj}x_j)_{\mathrm{restr}}| . \qquad (6)$$

In (6) the restriction is $-\frac{1}{2}\pi \le (b_m + \sum_j a_{mj}x_j)_{\mathrm{restr}} < \frac{1}{2}\pi$.

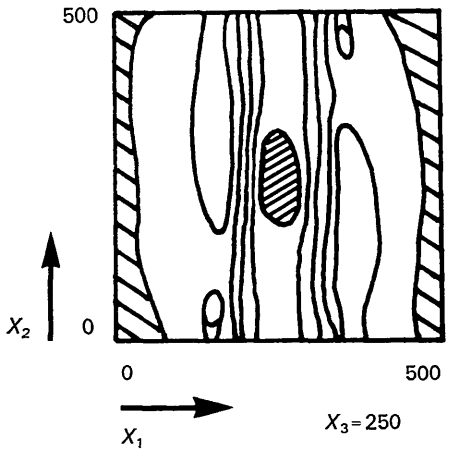


Fig. 1. Section through $x_3 = 250$ of the function $CI(x_1, x_2, x_3)$ of the photolysis product. The parameters are given in fractions multiplied by 1000. The regions with low $CI$ values have been shaded, regions with very low $CI$ values have been heavily shaded.

### Program

A computer program, written in Algol 60 for the X8 Electrologica Computer (2·5 microsecond), calculates all $b_m + \sum_j a_{mj}x_j$ and their weights $w_m$. Then $CI$ is calculated as a function of numerical values of the symbols $x_j$. For a structure with 96 non-hydrogen atoms in the unit cell ($P2_12_12_1$) this computation consumed only 2 minutes, where the 4 symbols $x_j$ were allowed to have the values $0{\cdot}1\pi$, $0{\cdot}3\pi$, $0{\cdot}5\pi$, $0{\cdot}7\pi$, $0{\cdot}9\pi$.

The grid may be chosen wider so that it is expected that up to 8–10 symbols can be analysed in an appreciably short time.

### Discussion and results

In the symbolic addition of non-centrosymmetric structures with centric projections the use of the $CI$ search followed by a $Q$ search has two advantages above the use of the $Q$ search only:

(1) The procedure is less time consuming. The range of the symbols is from 0 to $2\pi$. If an interval of say $\frac{1}{4}\pi$ is used, then for the $Q$ search 4 values ($\pi/4$, $3\pi/4$, $5\pi/4$, $7\pi/4$) have to be tested, whereas for the $CI$ search 2 values have to be considered ($\pi/4$, $3\pi/4$). In the case of $n$ symbols $Q$ has to be calculated for $4^n$ sets of numerical values for the symbols. For $CI$ this number is $2^n$; $m$ sets with small $CI$ ($m \ll 2^n$) have to be tested in the $Q$ search. So in all $(m+1)2^n$ sets have to be screened either with $CI$ or $Q$. Since one $Q$ calculation is comparable in computer time to one $CI$ calculation, using first $CI$ search and then $Q$ search is considerably faster than using $Q$ search only.

(2) Solutions with a small $Q$ value sometimes have a high $CI$ value. Thus although the internal consistency of the phase indications can be very good, the corresponding centrosymmetric projections may make no physical sense.

The method has been tested in two structure determinations, the photolysis product of Karle, Karle & Estlin (1967) and a sulphur steroid (van de Ven & Schenk, 1971), both of space group $P2_12_12_1$.

In the photolysis product 3 symbols were chosen in order to build up a starting set of 42 symbolic phases, which shows no inconsistencies. In Fig. 1 the section $x_3=250$ through the function $CI(x_1,x_2,x_3)$ has been drawn, in which the coordinates are given in fractions multiplied by 1000. In the complete function minima were found for $x_1$, $x_2$ and $x_3$ equal to 0 or 250. As pointed out above $x_1$, $x_2$ and $x_3$ then may have the values 0.500,250 and 750. For the 64 combinations the $Q$ values were calculated. By tangent refinement 4 of the 8 combinations of lowest $Q$ converged to the correct solution or to its enanthiomorph.

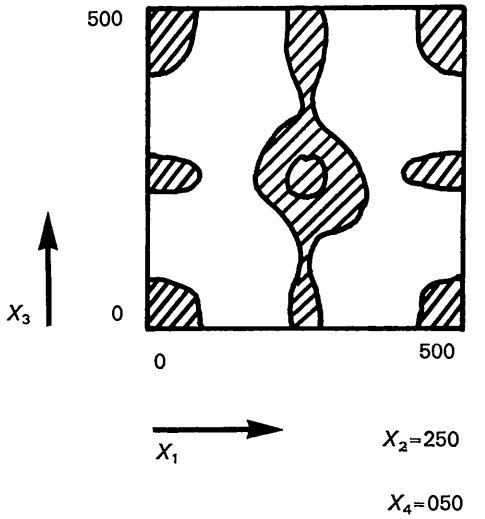


Fig. 2. Section through $x_2=250$, $x_4=50$ of the function $CI(x_1,x_2,x_3,x_4)$ of the sulphur steroid. The parameters are given in fractions multiplied by 1000. The regions with low $CI$ values have been shaded.

In the second structure 4 symbols were required for the determination of 50 symbolic phases. In Fig. 2 the section $x_2=250$, $x_4=50$ of the function $CI(x_1,x_2,x_3,x_4)$ is given which contains the lowest $CI$ values, occurring at $x_1=0$ or 250, $x_2=250$, $x_3=0$ or 250 and $x_4=50$. Some additional low $CI$ values have the same $x_1$, $x_2$ and $x_3$ coordinates and $x_4=250$. The solution $x_1=x_3=0, x_2=750$ and $x_4=50$ with the lowest $Q$ value refines by the tangent procedure to the correct solution.

Up till now only $CI$ has been employed. A comparison of the strength of $CI$, $CII$ and $CIII$ is planned.

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## Automation of the non-centrosymmetric symbolic addition. III. Iterative-least-squares procedures for refining numerical values of the symbols.

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Iterative procedures are described for refining rough numerical values of the symbols, used in the non-centrosymmetric symbolic addition.

### Introduction

In the preceding papers I and II (Schenk, 1971*a*,*b*) it has been shown that in non-centrosymmetric symbolic addition a fast symbol analysis can be carried out, resulting in sets of rough values for the symbols. In order to limit the number of solutions to be tested in the tangent refinement a least-squares procedure is proposed to refine these rough numerical values.