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 2π. 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.

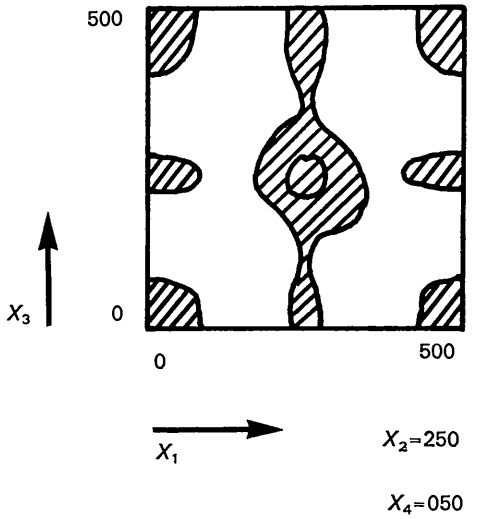

Fig. 2. Section through $x_2=250$, $x_4=50$ of the function $CI(x_1,x_2,x_3,x_4)$ of the sulphur steroid. The parameters are given in fractions multiplied by 1000. The regions with low CI values have been shaded.

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.

References

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
KARLE, I. L., KARLE, J. & ESTLIN, J. A. (1967). *Acta Cryst.* **23**, 494.
SCHENK, H. (1971). *Acta Cryst.* B**27**, 2037.
VEN, C. F. W. VAN DE & SCHENK, H. (1971). To be published.

Acta Cryst. (1971). B**27**, 2040

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

By H. SCHENK, *Laboratory for Crystallography, University of Amsterdam, Nieuwe Prinsengracht* 126, *Amsterdam, The Netherlands*

(*Received* 3 *May* 1971)

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.

Method

As discussed earlier (Schenk, 1971*b*) for structures with centrosymmetric projections

$$CI=\sum_m w_m|\sin\ (b_m+\sum_j a_{mj}\times x_j)|=\text{small}$$

is a good criterion for determining numerical values of x_j. A least-squares method can be used to refine these values, minimizing

$$CRI=\sum_m w_m|\sin\ (b_m+\sum_j a_{mj}x_j)|^2\ . \qquad (1)$$

The usual iterative procedure for non-linear equations can be followed.

Another more general criterion is

$$Q=\sum_l w_l\ (1-\cos\ \Delta\varphi_l)=\text{small}$$

(Schenk, 1971*a*), where $\Delta\varphi_l$ is a linear relation of the symbols x_j.

So in this case the x_j can be refined by minimizing

$$QRI=\sum_l w_l\ (1-\ \cos\ \Delta\varphi_l)^2\ . \qquad (2)$$

Gain of computer time will be scored if instead

$$QR2=\sum_l w_l|(\Delta\varphi_l^*)| \qquad (3)$$

is minimized, where $\Delta\varphi_l=\Delta\varphi_l^*\ (\text{mod}\ 2\pi)$ and $-\pi\leq\Delta\varphi_l^*<\pi$. Here the elements of the normal matrix are constant and have to be calculated only once. For this reason we use equation (3).

Applications

For structures with centrosymmetric projections the following four-step procedure is employed:

(1) *CI* search
(2) refinement of solutions of small *CI* value by the *CRI* procedure
(3) *QR*2 refinement of the lowest *CRI* solutions
(4) tangent-refinement of the lowest *QR*2 solutions.

An acceleration is obtained by inserting a *Q* search between steps 2 and 3, and limiting the *QR*2 refinement to the lowest *Q* solutions.

Structures without centrosymmetric projections could be attacked by a three-step procedure:

(1) *Q* search
(2) *QR*2 refinement of solutions of lowest *Q*
(3) tangent refinement of the lowest *QR*2 solutions.

Results and discussion

The method has been tested in the structure determinations of 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 about 100 solutions with the lowest *CI* values (Schenk, 1971*b*) have been refined minimizing *CRI*. They converge to the 8 solutions given in Table 1. The 4 best *CRI* solutions are used directly in a *QR*2 refinement, the results of which are given in Table 2. The 8 best solutions have been tested in the tangent refinement and four of them yield the correct phases.

Table 1. *Symbol parameters of the photolysis product, refined by the CRI procedure*

The sets parameters are given in order of increasing refinement criterion.

Criterion	Values of symbols		
CRI	x_1	x_2	x_3
141	250	250	250
142	0	0	250
153	0	250	0
154	250	250	0
161	0	0	0
162	0	250	250
188	250	0	0
190	250	0	250

Table 2. *Symbol parameters of the photolysis product, refined by the QR2 procedure*

The solutions are given in order of increasing refinement criteria. Only those solutions which correspond with low *CRI* values have been refined.

*QR*2	x_1	x_2	x_3	Convergence in tangent refinement
2273	749	752	856	corr
2273	251	748	644	incorr
2285	749	751	139	corr
2285	251	749	361	incorr
2289	250	747	143	incorr
2289	750	753	357	corr
2301	750	752	639	corr
2301	250	748	861	incorr
4130	0	254	−67	–
4130	0	754	433	–
4874	1	754	266	–
7143	500	244	−60	–
7143	501	744	440	–
7883	501	743	233	–

The refined *CRI* solutions of the sulphur steroid are given in Table 3. A *QR*2 refinement was carried out with the two best solutions, the results being given in Table 4. By tangent refinement the two solutions with lowest *QR*2 both converge to the correct solution, but the first one needed a few more refinement cycles.

Table 3. *Symbol parameters of the sulphur steroid, refined by the CRI procedure, given in order of increasing refinement criterion*

CRI	x_1	x_2	x_3	x_4
79	2	250	2	251
87	2	250	2	38
95	250	250	250	250
97	250	250	250	30
128	251	249	11	8
130	0	250	250	9
136	251	248	16	252
+ higher values				

In the case of the sulphur steroid the computer time involved in the four steps was approximately 1 min (*CI* search) + 3 min (*CRI* refinement) + 2 min (*QR*2 refinement)

+4 min (tangent refinement). The computation of the *E*-Fourier map consumed 8 min. All computations have been carried out on a X8-Electrologica computer (2·5 microsecond) by means of Algol 60 programs.

Table 4. *Symbol parameters of sulphur steroid, refined by the QR2 procedure*

The solutions are given in order of increasing refinement criteria. Only the 2 solutions with the best *CRI* criteria have been refined.

QR2	x_1	x_2	x_3	x_4	Convergence in tangent refinement
8797	942	747	15	428	corr
9965	973	746	11	103	corr
11272	220	745	705	407	incorr
11500	792	752	202	132	incorr

Table 4 (*cont.*)

QR2	x_1	x_2	x_3	x_4	Convergence in tangent refinement
16053	876	250	101	638	–
16350	395	246	569	828	–
17272	749	750	302	342	–
17991	420	245	565	656	–
>20000	all other solutions				

References

KARLE, I. L., KARLE, J. & ESTLIN, J. A. (1967). *Acta Cryst.* **23**, 494.
SCHENK, H. (1971*a*). *Acta Cryst.* B**27**, 2037.
SCHENK, H. (1971*b*). *Acta Cryst.* B**27**, 2039.
VEN, C. F. W. VAN DE & SCHENK, H. (1971). To be published.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J. N. King, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England).

Professor N. V. Belov

The November 1971 issue of *Acta Crystallographica*, Section A will contain a photograph of Professor Belov as frontispiece and a review of his scientific and social activities, to commemorate Professor Belov's eightieth birthday, 15 December 1971.

Workshop on the Use of Structure Invariants in Phase Determination. Buffalo, 10-30 July 1972

The Medical Foundation of Buffalo and the Faculty of Natural Sciences and Mathematics of the State University of New York at Buffalo are jointly sponsoring a three week workshop on the use of structure invariants in phase determination to be held at the Medical Foundation of Buffalo, 10–30 July 1972.

During the first two weeks there will be two lectures daily concerned with the theoretical basis of the direct methods of phase determination and other background material. The lectures will be given by members of the Laboratory staff and a number of invited speakers. The remainder of the time will be devoted to instruction in the implementation of the theoretical results and the application of these methods to the structure determination of crystals of interest to the students. Participants are strongly urged to supply the required experimental data. The total number of participants will be limited to thirty. Further information and registration forms may be obtained from Dr Herbert Hauptman, Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, U.S.A. The closing date for registration is 1 March 1972.

International Union of Crystallography

Ninth General Assembly and International Congress of Crystallography

The *First Circular* for this meeting was despatched during September by air-mail to those persons who completed and returned a Pre-Registration Card. Requests for further copies of the *First Circular* should be sent to Professor Y. Saito, General Secretary, Organizing Committee Crystallography, Science Council of Japan, 22–34 Roppongi 7-chome, Minato-ku, Tokyo 106, Japan, or to Dr J. N. King, Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The American Crystallographic Association is organizing a charter flight from the U.S.A. to Japan. European members of the A.C.A. might also seriously consider this method of travel to Japan. Further information may be be obtained from ACA Charter Flight, c/o Dr B. C. Wang, Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A. The European Crystallographic Committee is not organizing a charter flight from Europe but is considering several proposals for group flights from various cities in Europe.