eter β_1 was obtained by measuring the intensity as a function of tilt angle in the parallel position. The collimation parameters for the detector, α_2 and β_2, were obtained from the collimator geometry. The parameter η_{sh} was obtained from a rocking curve of the sample crystal in the parallel position, and η_{sv} was assumed equal to η_{sh}. The values of these parameters are shown in Table 1.

APPENDIX *B*

Coefficients of the intensity equation for diffuse scattering from a mosaic single crystal

The coefficient C_0 is given by

$$C_0=(2\pi)^{3/2}R_0'\left(N_{33}'+\frac{1}{D_{z'}^2}\right)^{-1/2}\left(N_{22}'+\frac{1}{D_{y'}^2}\right)^{-1/2}\times\left(N_{11}'-\frac{N_{12}'^2}{N_{22}'+\frac{1}{D_{y'}^2}}+\frac{1}{D_{x'}^2}\right)^{-1/2} \quad (B1)$$

and the matrix C_{kl} is given by

$$C_{11}=\frac{1}{D_{x'}^2}-\frac{1}{D_{x'}^4}\frac{1}{\left(\frac{1}{D_{x'}^2}+N_{11}'-\frac{N_{12}'^2}{N_{22}'+\frac{1}{D_{y'}^2}}\right)}$$

$$C_{12}=\frac{1}{D_{x'}^2}\frac{1}{D_{y'}^2}\frac{\left(\frac{N_{12}'}{N_{22}'+\frac{1}{D_{y'}^2}}\right)}{\left(\frac{1}{D_{x'}^2}+N_{11}'-\frac{N_{12}'}{N_{22}'+\frac{1}{D_{y'}^2}}\right)} \quad (B2)$$

$$C_{22}=\frac{1}{D_{y'}^2}-\frac{1}{D_{y'}^4}\frac{1}{\left(N_{22}'+\frac{1}{D_{y'}^2}\right)}\times\left[1+\frac{N_{12}'^2}{\left(N_{22}'+\frac{1}{D_{y'}^2}\right)\left(\frac{1}{D_{x'}^2}+N_{11}'-\frac{N_{12}'^2}{\left(N_{22}'+\frac{1}{D_{y'}^2}\right)}\right)}\right]$$

$$C_{33}=\frac{1}{D_{z'}^2}\frac{N_{33}'}{\left(N_{33}'+\frac{1}{D_{z'}^2}\right)}.$$

The N_{kl} are the transformed M_{kl} values, *i.e.*

$$\mathsf{N}'=\mathsf{T}\mathsf{M}'\mathsf{T}^{-1} \quad (B3)$$

where T is the transformation matrix.

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The Solution of Non-Centrosymmetric Crystal Structures by Symbolic Tangent Refinement

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(*Received* 18 *December* 1972; *accepted* 24 *January* 1973)

Starting from a restricted set of numerical and symbolic phase angles, the tangent formula is applied iteratively to determine numerical and symbolic phase indications for the other reflexions. Numerical values are then systematically substituted for the symbols to determine which combinations are most likely to yield the solution.

Introduction

While for centrosymmetric structures automatic computer programs using symbolic methods have been widely successful (Germain & Woolfson, 1968; Ahmed, 1970; Bednowitz, 1970; Dewar, 1970; Stewart, 1970), the symbolic approach for non-centrosymmetric structures has usually been restricted to use of the sum-of-angles formula in the early stages to determine likely numerical values of the symbols, after which further phasing is completed by numerical tangent refinement (Karle & Karle, 1966; Schenk, 1971; Dewar, 1970). Ideally this process leads to a single solution.

The program *SYMTAN* described here differs from

the above in that a complete cyclic weighted-tangent refinement is carried out using symbolic phases, after which numerical phases are substituted for the symbols to determine the combinations which give the best figures of merit. The speed of this trial-and-error substitution is such that hundreds of combinations can be tried in as many seconds on an IBM 360/50 computer. *SYMTAN* is therefore a multisolution method.

A second program *SYMTAN2* puts out phased E's corresponding to any desired combination so that an E map may be computed.

The programs have been successfully tested on known structures, and have solved one unknown structure on which other methods had failed. These applications are described below.

The program *SYMTAN*

(*a*) *The tangent formula*

The program operates with a set of $\sum_2$ phase relations between a limited set (≤ 600) of non-equivalent reflexions of high $|E|$ which are generated by another program. They are derived from relations of the type

$$\varphi_{\mathbf{H}} \approx \varphi_{\mathbf{H}'} + \varphi_{\mathbf{H}-\mathbf{H}'} \tag{1}$$

where $\varphi_{\mathbf{H}}$ means 'the phase angle of reflexion **H**'. By making use of symmetry they are re-expressed in terms of the equivalent reflexions to which code numbers have been allotted, so on input to *SYMTAN* are actually of the form

$$\varphi_i \approx \pm\varphi_j \pm \varphi_k + \varphi_{ijk} \tag{2}$$

where i, j and k are the code numbers of three particular reflexions and φ_{ijk} is a numerical phase. The value of φ_{ijk} and the signs before φ_j and φ_k depend in each case upon the phase differences between the coded reflexions and their equivalent reflexions **H**, **H**′ and (**H**−**H**′) in the original relation (1). For simplicity the $\pm$ signs will be written as $+$ in the following. If no translational symmetry element (screw, glide or mirror) is present in the primitive cell all the numerical terms φ_{ikk} are zero.

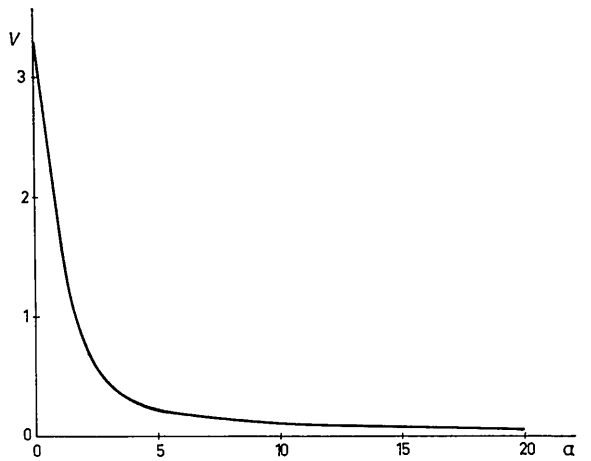

Fig. 1. Variance V in radian^2 as a function of α. (After Karle & Karle, 1966).

The quantity

$$M = 2\sigma_3\sigma_2^{-3/2}, \tag{3}$$

where

$$\sigma_n = \sum_{m=1}^{N} Z_m^n,$$

Z_m is the atomic number of the mth atom, and N is the number of atoms associated with each lattice point, is a constant for each structure which may be calculated at the outset in most cases. Multiplying each term by $M|E_i|$, the well known tangent formula (Karle & Hauptman, 1956) may be written in the above notation as

$$\tan\varphi_i = \frac{S_i}{C_i} \tag{4}$$

where

$$S_i = \sum_{j,k} \kappa_{ijk} \sin(\varphi_j + \varphi_k + \varphi_{ijk}), \tag{5a}$$

$$C_i = \sum_{j,k} \kappa_{ijk} \cos(\varphi_j + \varphi_k + \varphi_{ijk}), \tag{5b}$$

$$\kappa_{ijk} = M|E_iE_jE_k|. \tag{5c}$$

The summations are over all phase relations involving the phase φ_i. Karle & Karle (1966) have found an expression for the variance of the phases φ_i in terms of the quantity

$$\alpha_i = (S_i^2 + C_i^2)^{1/2}. \tag{6}$$

As shown in Fig. 1, the variance decreases as α increases. A table of numerical values for the V–α relationship is given by Germain, Main & Woolfson (1970).

(*b*) *Weighting*

Equations (5) and (6) giving α_i and hence the variance of φ_i are based on the supposition that the values of the contributing phases φ_j and φ_k in each phase relation are themselves without error. During refinement this is not the case. In *SYMTAN* the factors κ_{ijk} in equations (5) are modified in the following manner to allow for this. Although not rigorous this happens to be convenient for computing. The basis of the idea is that the κ_{ijk} may be used to associate a variance V_{ijk} with each phase relation, because if there is only one term in the sums of equations (5*a*) and (5*b*) then

$$\alpha_{ijk} = \kappa_{ijk} \tag{7}$$

and this value of α_{ijk} corresponds to some variance V_{ijk} using the V–α curve. Whenever the phase relation is used one can then allow for uncertainty in the contributing phases by adding their estimated variances $V_{\varphi j}$ and $V_{\varphi k}$ to that associated with the phase relation itself to obtain the modified variance

$$V'_{ijk} = V_{ijk} + V_{\varphi j} + V_{\varphi k}. \tag{8}$$

Let κ'_{ijk} be the value of α corresponding to V'_{jjk}. κ'_{ijk} will in general be less than κ_{ijk}.

SYMTAN then uses the tangent formula in the form

$$S_i = \sum_{j,k} \kappa'_{ijk} \sin(\varphi_j + \varphi_k + \varphi_{ijk}) \qquad 9a)$$

$$C_i = \sum_{j,k} \kappa'_{ijk} \cos(\varphi_j + \varphi_k + \varphi_{ijk}) \qquad (9b)$$

instead of the form (5) to which it reduces if there are no errors in the phases φ_j and φ_k. This makes it necessary to store the variance estimates for each phase.

The sum of the (modified) α's obtained from equation (6) is a useful measure of the self-consistency of a refinement.

Weighting of the above type is employed also in the author's numerical tangent refinement program *TANG* where it plays an essential part.

(*c*) *Symbols*

SYMTAN handles symbolic phases of the general form

$$\varphi_i = a_i + \sum_{l=1}^{6} a_{il} S_l \qquad (10)$$

where the S_l are the six symbols A, B, C, D, E, F; a_i is a numerical phase, and a_{il} are integers. The phases of the starting set are fixed throughout refinement but all derived phases are refined freely.

The application of the tangent formula to symbolic phases rests on the fact that the numerical parts of phases which have the same symbolic part can be combined separately by the tangent formula, and the symbolic part added to the resulting phase (Main, 1968). This may be shown as follows:

For some phase φ_i let there be p different phase indications

$$\varphi_{im} = \varphi_m + S \quad m = 1, 2, \ldots p \qquad (11)$$

which all have the same symbolic part S (*e.g.* $S = A + 2B$), but different numerical parts φ_m. The operation of the tangent formula on the numerical parts φ_m is represented graphically in Fig. 2 for the case where $p = 3$. The three phases φ_1, φ_2 and φ_3 combine to give a numerical phase angle φ_n and a resultant vector of magnitude α_i. But what of the symbolic parts, whose values are not known at this stage? Were the numerical values of the symbols in S added to each of the three phase angles, this would rotate each vector anti-clockwise through the angle S: the overall result would merely be to rotate the whole diagram anti-clockwise through the angle S without changing the length α_i of the resultant. This is equivalent to rotating the datum line OA clockwise through the angle S. It is clear that the result of combining the three phases is $\varphi_n + S$, where φ_n is the angle calculated from the numerical parts alone. Obviously the same result is true for any number of phases having the same symbolic part S, and moreover the value of α_i may always be calculated using the numerical parts alone.

(*d*) *Multiple symbolic-phase indications*

In view of the above, *SYMTAN* groups together all those indications for a given phase φ_i which have the same symbolic part and combines them by applying the tangent formula to the numerical parts and adding the symbolic part to the result. For each φ_i one is then in general left with several (combined) indications having different symbolic parts which cannot be further combined. *SYMTAN* makes provision for retaining up to six such indications for each reflexion φ_i, the idea being to retain the strongest indications as measured by the values of α. The maximum number to be retained (≤ 6) is an input parameter MAXIND. The idea of retaining multiple symbolic indications had been successfully employed in *GSAM*, the author's symbolic program for centrosymmetric structures. The basis of both programs is the notion that if phases corresponding to the correct solution are substituted in place of the symbols there will be general agreement among the multiple indications, so a figure of merit which measures the extent of agreement will point to the correct solution.

Whenever a reflexion having multiple symbolic-phase indications appears in a phase relation *SYMTAN* uses all these indications in turn, appropriately weighted. Thus if a phase relation involves two reflexions each having four indications, this gives rise to sixteen new indications for the third reflexion. If there are 20 phase relations contributing to the given phase and the parameter MAXIND equals 4, there could be as many as 20×16 individual indications. As shown above these can be grouped according to their symbolic parts, and those within each group reduced to a single indication using the tangent formula. All indications now have different symbolic parts, and of these the predetermined number MAXIND is retained.

The early cycles are fast but as the total number of multiple indications builds up the cycle time likewise increases. Typical CPU time on an IBM 360/50 for 10 cycles is 5 min (200 coded reflexions, 4000 redundant phase relations), using magnetic discs for much of the intermediate storage.

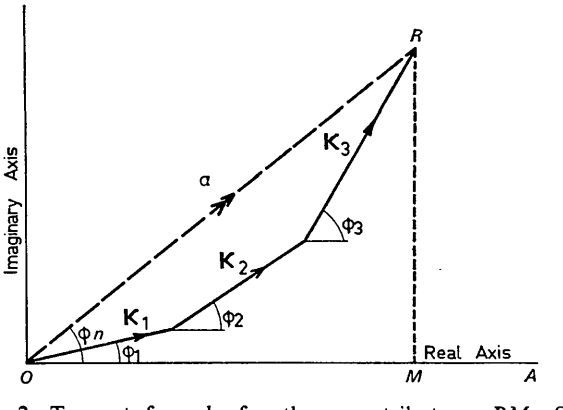

Fig. 2. Tangent formula for three contributors. $RM = S_i$, $OM = C_i$, $OR = \alpha_i$.

(*e*) *Refinement summary*

SYMTAN employs the tangent formula in the modified form (9) and phases of the form (10). When a phase relation such as (2) is encountered, where φ_j and φ_k are known (in symbolic or numerical form), the value of κ'_{ijk} is calculated using (8) and the V–α curve. The terms $\kappa'_{ijk} \sin \varphi_m$ and $\kappa'_{ijk} \cos \varphi_m$ (where φ_m is the numerical part of the phase indication) are accumulated in the stores associated with the appropriate symbolic part. Since there are in general multiple values for the two contributing phases, these steps must be repeated for all their combinations. *SYMTAN* then moves to the next phase relation involving φ_i. When all the phase relations for φ_i have been processed, the numerical parts associated with each different symbolic part are combined by applying the tangent formula (4), and the values of α calculated using (6). The MAXIND strongest indications are then stored for the next cycle, as *SYMTAN* employs segregated cycles.

The program then moves to the next reflexion and repeats all the above steps. At the end of the cycle all the α values are converted to variances and the new values of all the phases are read into the stores for the 'knowns'.

The whole of the above is repeated for the desired number of cycles.

(*f*) *Figures of merit*

On completing refinement, as many as six symbolic indications are available for each reflexion. *SYMTAN* makes provision for each symbol *A*, *B*, *C*, *D*, *E*, *F* to take on a succession of numerical values selected by the user. For example the symbol *A* might be given the 4 values 45, 135, 225 and 315° or the 8 values 22, 68, 112, 158, 202, 248, 292 and 338°, *B* the 2 values 0 and 180° *etc.*, according to whether they represent general or restricted phases. For each possible combination of these values numerical phase angles are evaluated for all phase indications. The various indications for each reflexion, now numerical, are combined using the tangent formula to give the overall phase indication and α is calculated. A figure of merit (f.o.m.) for each combination is obtained by summing the values of α for all reflexions. Unless there is good agreement between the various indications for each phase, the individual values of α and therefore their sum will be low. On an IBM 360/50 computer the calculation of the f.o.m. for one combination typically takes less than one second enabling the equivalent of tens or even hundreds of tangent refinements to be obtained very rapidly. If the first run fails to show a clear-cut winner *SYMTAN* allows the user to make any number of 'f.o.m. runs' with a different range of numerical values substituted for the symbols in each run (*e.g.* a finer gradation of values might be used).

Experience so far has shown that for structures having a translational symmetry element *SYMTAN* obtains the highest f.o.m. or one very near the top for the correct solution. Remarkable ability in picking the correct solution has been shown when all the symbols represent phases restricted by symmetry to a pair of values such as 0/180 or 90/270, as is possible in space group $P2_12_12_1$. On the other hand when the symbols all represent general phase angles there tends to be a continuum of figures of merit.

(*g*) *E maps*

Phased E's suitable for the calculation of an E map are computed by an auxiliary program *SYMTAN*2 for any selected combination of numerical values in place of symbols. It would seem from some tests detailed below that a few cycles of numerical tangent refinement of the phases from *SYMTAN*2 may be advantageous before calculating the E map.

Experimental results

*Solution of an unknown structure, methyl β-*D*-ribopyranoside* $C_6H_{12}O_5$

This was the first unknown structure to be solved by *SYMTAN* (James, 1973). It crystallizes in space group $P2_12_12_1$. Surprisingly for such a small molecule it did not yield to conventional numerical tangent-refinement trials, possibly because many of the atoms lie close to the planes $x/a=0$, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$.

The structure was solved immediately with *SYMTAN* using an E map computed from the set of phases having the highest figure of merit. The six highest peaks were all at atomic positions, followed by two spurious, one genuine, one spurious and then two genuine peaks. The remaining two non-hydrogen atoms had very small peaks. The initial structure-factor calculation using all eleven atoms gave the residual 0·43.

In this solution the program used 3802 phase relations (redundant listing) generated from 289 reflexions having $|E| \geq 1{\cdot}0$. The *SYMTAN* refinement started with four origin- and enantiomorph-fixing phases and six symbolic phases (Table 1). All ten reflexions each had one zero index and were therefore restricted (in this space group) to either 0/180° or 90/270°. Symbolic phases for most of the 289 reflexions were developed using 10 cycles of symbolic tangent refinement, retaining up to 4 different symbolic indications for each reflexion each cycle (*i.e.* the parameter MAXIND=4). Then figures of merit were automatically generated for the 64 possible combinations with numerical values substituted for the 6 symbols. Of these half proved to be redundant as the symbol *C* had been eliminated from the refinement – an unusual event for *SYMTAN* – and the figures of merit with *C* equal to either 90 or 270° were therefore identical for each combination of the other 5 symbols. Table 2 lists the solutions corresponding to the first few f.o.m.'s in decreasing order, showing the correct solution to be well defined. The E map mentioned above was computed from the phases put out by *SYMTAN*2 for the solution with the highest f.o.m.

Table 1. *Starting phases for unknown structure*

h	*k*	*l*	Phase	
4	11	0	0	
5	9	0	90	
0	11	4	90	
0	4	5	0	
4	10	0	*A*	0 or 180°
4	0	0	*B*	0 or 180°
0	21	3	*C*	90 or 270°
0	13	3	*D*	90 or 270°
0	17	2	*E*	90 or 270°
0	15	1	*F*	90 or 270°

Table 2. *Solutions with* 16 *highest figures of merit*

Values of symbols						Figure
A	*B*	*C*	*D*	*E*	*F*	of merit
180	0	270	90	90	270	13541
180	0	90	90	90	270	13541
0	180	270	90	90	270	13360
0	180	90	90	90	270	13360
180	0	270	90	90	90	12909
180	0	90	90	90	90	12909
0	180	270	90	90	90	12725
0	180	90	90	90	90	12725
180	0	270	270	270	270	12496
180	0	90	270	270	270	12496
0	180	270	270	270	270	12305
0	180	90	270	270	270	12305
180	0	270	270	270	90	11907
180	0	90	270	270	90	11907
0	180	270	270	270	90	11719
0	180	90	270	270	90	11719

Experiments on a known structure: the photolysis product $C_{12}H_{13}NO_4$ *(cited below)*

Experiments have been carried out using *SYMTAN* with published data for this photolysis product first solved by Karle, Karle & Estlin (1967). This was chosen partly because, as the original authors found, it can prove difficult to solve, and also because it has been used for testing other programs (Schenk, 1971; Gassman & Zechmeister, 1972). However it is not ideal as the data were measured visually.

The following experiments demonstrate the performance of *SYMTAN* under a variety of conditions. The demands on such a program are firstly that it should be able to reliably distinguish which of the multiple solutions is the best, and secondly that the phases belonging to the best solution produce an *E* map in which the atoms are easily recognizable. Regarding the latter, unless the *n* atoms are identified with the *n* strongest peaks, *E*-map interpretation is highly subjective. In the following experiments the course has therefore been adopted of simply recording the *E* map peaks in order of decreasing height and identifying those which are close to known atomic positions and those which are spurious. In this way meaningful objective comparisons are possible.

Experiment (i)

An important feature of this particular structure which goes a long way towards explaining the prevalence of only partial solutions is the unfortunate distribution of the reflexions with high $|E|$. Taking the 200 reflexions with $|E| > 1{\cdot}25$ and computing an *E* map using the published phase angles, a rather poor *E* map results in which there is a large spread in the heights of the atomic maxima [column (i) of Table 3]. However the 17 highest peaks do (just) represent all 17 non-hydrogen atoms. Clearly if these reflexions cannot give a good *E* map when correctly phased, they are unlikely to do as well when phased by a program such as *SYMTAN*.

Table 3. *Relative heights of peaks in E maps for experiments on photolysis product*

See text for details. Spurious peaks are represented by an asterisk. Atom names are those in the original paper by Karle Karle & Estlin (1967). Each column is terminated when continuation seems pointless.

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
100	C11	O3	O3	O3	O3	O3	C11
	O2						O3
	O3						
90	N4	C11					
					C11	C11	
80	C6	O2					
	C10						
	C7	N4					
70	O4						
	C5						O2O4
		O4		C11			C12
	O1				O2	O2	
60	C8			N4O4			
	C9						O1
	C13	C6	C11	O2			C5C13
	C12				O4	O4	
	C3	C7	N4				N4
50		O1C5	O2	C5			
		C12C13			N4	N4	*
		C8	O4C5				**
			*	C12C13 *			C1 **
40	C1	C10					***
	C2	C3		**	*	*	C6 *
	*				C7	C7O1	
	*	C9		O1	C13O1		C8 ***
	*	C1 **	C6C13	C6 ****	C1C6 *	C1C6 *	C2C3 *
30	....		C12C7*	***	***	C13 *	***
		* C2	O1 **	***	C8C12C5	**	
		***	*****	C3	**C2C9	C8C5C12 *	C10
		***	C8	.....	C10 ****	C2C9C10	C7
		....	.....		***** C3	**********	C9
20					.....	C3	.....
						.....	
10							

Experiment (ii)

This demonstrates the further deterioration in the quality of thc *E* map when phased by a program which employs the tangent formula. The 200 reflexions with $|E| > 1{\cdot}25$ were used as input to the author's weighted numerical tangent-refinement program *TANG*. All reflexions were initially assigned phases equal to their published values. The refinement used 3879 phase relations having a triple $|E|$ product $> 4{\cdot}0$ derived from the 200 reflexions. During 10 cycles of 'refinement' the root-mean-square deviation of the phases from the

published values rose from 0 to 40°. In an E map computed with the 'refined' phases there was a greater range of atomic peak heights, and two spurious peaks were slightly higher than the peak corresponding to the 17th atom [column (ii) in Table 3].

Thus even under ideal conditions the tangent refinement method did not give a good E map for the photolysis product. *SYMTAN* which is also based on the tangent formula cannot hope to do better than this using the same set of phase relations.

Experiment (iii)

Several *SYMTAN* tests were carried out treating the photolysis product as unsolved, but checking the results against the known structure. In the first of these, eight reflexions were chosen, using the normal kinds of criteria, as the starting point for the symbolic refinement procedure. These comprised 4 origin- and enantiomorph-fixing reflexions together with 4 symbolic phases (Table 4). Published values for the phases were assigned to the first four to facilitate comparison with the published structure, and suitable symbolic values for the rest, where each of the symbols A, B, C, D was restricted to the two values 0 or 180°. *SYMTAN* was then employed for 10 cycles of refinement leading to symbolic/numerical phases for 191 reflexions. For this trial the above-mentioned set of 3879 phase relations was used, and the parameter MAXIND was set at 4 thereby allowing up to 4 different symbolic indications to be retained for each reflexion each cycle. *SYMTAN* then automatically obtained figures of merit for the 16 possible combinations of values for the symbols A, B, C and D. The correct solution had a figure of merit 3·3% higher than the next highest figure.

Table 4. *Starting reflexions for photolysis-product experiments* (iii)–(vi)

h	k	l	Phase
0	1	15	270
0	3	14	90
1	0	13	270
4	0	7	90
5	4	0	$90+A$
1	6	0	$90+B$
8	0	7	$90+C$
4	0	4	D

An E map was computed from the 178 reflexions phased directly by *SYMTAN*2 whose estimated variance V was less than 1·0 radian^2. The peaks are shown in column (iii) of Table 3 in order of decreasing height. Comparison with the published structure showed, in order, 6 genuine, 1 spurious, 4 genuine, 1 spurious and then 1 genuine peak. The remaining 5 atomic peaks were submerged in the background: although they might be recognized from chemical considerations they are best considered as not defined for the present purposes. In this trial *SYMTAN* therefore found 10 or 11 atoms out of 17, which would be sufficient for ultimate solution. It is to be noted that the relative positions of the peaks belonging to specific atoms in columns (i), (ii) and (iii) are very similar, and that the atoms which were not found by *SYMTAN* are those which were weak even using the published phases for these reflexions.

Experiment (iv)

This experiment was designed to observe the effect on the E map of using only reflexions whose phases seemed to be strongly determined by *SYMTAN* – a crude form of weighting. Using only the 113 reflexions from *SYMTAN*2 for which $V<0{\cdot}2$ radians^2, the peaks shown in column (iv) of Table 3 were obtained, *viz.* 8 genuine, 3 spurious, and then 2 genuine peaks. This is a slightly inferior result to that in (iii) which included V as high as 1·0 radian^2.

Experiment (v)

The effect on the E map of subjecting the phases output by *SYMTAN*2 in experiment (iii) to 10 cycles of numerical tangent refinement is shown in column (v). The E map included 194 reflexions with V less than 1·0 radian^2. This gave a significant improvement, as 10 atoms were found with only 1 spurious peak interspersed, while 16 atoms were found with 7 interspersed peaks.

Additional numerical tangent refinement therefore seems advisable, at least where all the symbols are restricted to a pair of values: this has been confirmed in other similar cases.

Experiment (vi)

This aimed to determine the best value of MAXIND. A complete refinement was performed as in (iii) with the same starting reflexions and the same set of phase relations, but with MAXIND reduced from 4 to 2. The refinement took about half as long ($3\frac{1}{2}$ min) as with MAXIND set at 4. The correct solution was indicated by a margin of 3·3% in the figure of merit. The phases output by *SYMTAN*2 were subjected to 10 cycles of numerical tangent refinement ($\frac{3}{4}$ min) and the E map was computed from 194 reflexions having $V<1{\cdot}0$. The result, in column (vi), is seen to be at least as good as the corresponding experiment (v) with MAXIND=4, showing that for this case at least there is no harm in saving computing time by setting MAXIND=2.

Another *SYMTAN* refinement not listed in Table 3 had MAXIND=3, and the correct solution was indicated this time by a 3·9% margin in the figure-of-merit list. The raw phases determined by *SYMTAN*2 for this solution gave an E map comparable with the corresponding one for MAXIND=4.

Yet another trial was made in which MAXIND was reduced to 1. This was not successful, as after 29 cycles of *SYMTAN* refinement the correct solution was number 3 on the figure-of-merit list, 8% below the highest. This supports the *SYMTAN* concept of retaining multiple symbolic indications for use in the next cycle.

The conclusion to be reached is that the value of MAXIND is not critical provided it is not unity. There is little to choose between the values 2, 3 and 4 in regard to choosing the correct solution and phasing the reflexions.

Experiment (vii)

Since other workers (Gassman & Zechmeister, 1972) have successfully employed fewer than 200 reflexions, *SYMTAN* was applied using 139 reflexions with $E>1{\cdot}40$ from which 2031 phase relations having the triple $|E|$ product greater than 4·0 had been obtained. Using the same 8 starting phases as in (iii) and MAXIND=4, *SYMTAN* this time chose the correct solution by a margin of only 1·25% in the figure of merit. The phases output by *SYMTAN*2 were subjected to numerical tangent refinement and the 82 reflexions with $V<0{\cdot}2$ radian^2 were used to compute an E map. The peaks are shown in column (vii) of Table 3. The 9 highest peaks are at atomic locations, a result comparable with the corresponding trial (iv) with 200 reflexions. There does not seem to be much to choose between 139 and 200 reflexions in this trial.

It is interesting to note however that a refinement identical with the preceding but having MAXIND=1 instead of 4 gave the correct solution by a margin of 2·2%. Comparing this with the corresponding trial (vi) for 200 reflexions (which failed altogether), perhaps there is something to be said in favour of the lower number of reflexions.

No attempt was made to determine the optimum number for this structure: one suspects it may depend upon chance factors, *e.g.* whether a reduction in the number of reflexions happens to exclude a particularly inaccurate phase relation from the first few cycles. In the case of the photolysis product exactly this does happen, for using 200 reflexions with $E>1{\cdot}25$ the magnitudes of the errors (as calculated from the published phases) in the 9 phase relations used in the first cycle of either *SYMTAN* or *TANG* are respectively 0, 0, 0, 18, 8, 22, 61, 46 and 0°, whereas when using the 139 reflexions with $E>1{\cdot}40$ the last four of these are eliminated thereby avoiding some of the largest errors.

Experiment (viii)

This experiment compares the symbolic-tangent approach with the numerical tangent trial-and-error approach. Sixteen complete numerical tangent refinements were performed with the program *TANG* using as a starting point the same 8 reflexions (Table 4) and employing the same set of phase relations involving 200 reflexions as in experiments (ii) to (vi). The first four starters were given the same numerical phases in all 16 trials. The other four phases each in turn took their two possible values so as to give the 16 possible combinations. After 10 cycles in each case the figures of merit put out by *TANG* were compared with the figures of merit put out by *SYMTAN* in the three comparable trials with MAXIND=2, 3 and 4.

It was found that whereas the order-of-merit lists for the three *SYMTAN* trials agreed very closely for the sixteen combinations, there was a poor correlation between these lists and any of the figures of merit put out by *TANG*. Only the computing of E maps for all these would really determine which was the 'true' order of merit, if indeed such a concept exists. However the various figures of merit for *TANG* were found not to agree among themselves. Thus while the correct solution was correctly identified by the highest mean value of α (by a margin of 4%), it was placed equal to two other solutions by its estimated standard deviation, and placed third (equal with 5 others) by the E residual. The two solutions ranked last by *SYMTAN* were ranked second and third by *TANG* as judged by the mean value of α.

The differences are surprising since both *TANG* and *SYMTAN* work through the phase relations in exactly the same fashion. The only difference is that *SYMTAN* discards some of the indications in the later cycles whereas *TANG* retains virtually all of them.

Conclusion

SYMTAN has demonstrated the feasibility of carrying out a full tangent refinement using symbolic phases and has shown the advantages of retaining multiple symbolic phase indications in conjunction with some form of weighting.

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