Acta Cryst. (1977). A33, 863-864

Use of Centric Projections in Direct Methods

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(*Received* 24 *January* 1977; *accepted* 11 *March* 1977)

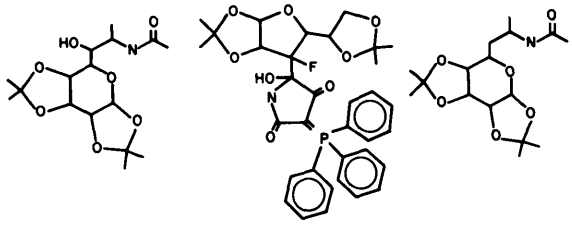
The selection of a starting set of phases in the determination of non-centrosymmetric structures by direct methods is facilitated by first obtaining a solution in a centric zone. The method is illustrated by the solution of three difficult sugar structures.

Introduction

During routine analyses of sugar structures in this laboratory several examples were found where conventional multisolution techniques failed to produce the correct solution. All these have now been solved by first examining a centric zone and by using the phases so established in the starting set of a three-dimensional analysis. This procedure is different from that described by Germain, Main & Woolfson (1971) in which Σ_1 phases of centric reflections are incorporated with appropriate weights in the starting sets and subsequently redetermined by tangent refinement. The program *SHELX*-76 (Sheldrick, 1976) which has been used in the present work completely ignores Σ_1 relations. Practical details of the method are now illustrated by a discussion of three structure determinations.

Examples

The structures of the hemihydrate of (I), the 1:1 acetone adduct of (II) and (III) could, for different reasons, not be solved by conventional direct methods.



(I) (II) (III)

(I) Space group $C2$, $a=18{\cdot}25$, $b=9{\cdot}47$, $c=11{\cdot}23$ Å, $\beta=102{\cdot}5°$, $Z=4$. Several starting sets of phases using the 200 reflexions with $E>1{\cdot}2$ gave similar E maps, characterized by a single dominant peak with several satellites, on the twofold axis. No recognizable fragments could be identified on any of the E maps.

(II) Space group $P2_1$, $a=15{\cdot}70$, $b=9{\cdot}18$, $c=13{\cdot}79$ Å, $\beta=115{\cdot}3°$, $Z=2$. Most starting sets gave E maps with many features in common and, although some ring systems were often thought to be recognized, the structure could not be developed from any of these by tangent refinement. Strong peaks corresponding to possible positions of the P atom consistent with the Patterson synthesis did not occur either. Fourier methods starting from possible P positions also failed.

(III) Space group $P2_12_12_1$, $a=24{\cdot}57$, $b=13{\cdot}80$, $c=5{\cdot}26$ Å, $Z=4$. A convergence map (Germain, Main & Woolfson, 1970) calculated for all reflexions with $E>1{\cdot}2$ in the complete data set showed 38 path breaks or weak links in the first 50 reflexions in the pathway. No less than 32 of these occurred for reflexions of the $hk0$ type. This is caused because in *SHELX*-76 those phases which are restricted to certain fixed values because of symmetry considerations are deliberately pushed up in the convergence map to allow the selection of a starting set involving fewer permutations. The selection of starting sets was complicated by this, and no interpretable E maps could be obtained.

Description of the procedure

In the first two cases the (010) projection is centrosymmetric and in principle the solution of the phase problem in this zone should be quite simple. No attempt was made to solve the structures in projection, but only to obtain sufficient phase information to use in the starting set of a three-dimensional analysis.

The very powerful and fast, centrosymmetric, direct-methods package of *SHELX*-76 was used to generate a number of E maps from the set of $h0l$ reflexions, without actually printing any of these. The four most promising E maps for (I) were calculated by allowing 2^{12} multisolution permutations. In order to include a reasonable number (55) of reflexions, the E limit was set at 0·75. The four maps corresponded to four possible sets of sign combinations for the origin and multisolution reflexions, as shown in Table 1, and it was argued that one of these should describe the structure correctly in (010) projection. All that remains is to establish y coordinates.

A three-dimensional convergence map was next calculated with the phases of the reflexions in Table 1 fixed, and a new starting set was selected on the basis of this. This starting set incorporated the reflexions of Table 1 with their phases fixed according to each of the combinations in turn. Each of these four starting sets was used in the normal way. The second set had the lowest reliability index and in fact the complete structure was reconstructed from the strongest peaks on the E map calculated with this starting set; $E>1{\cdot}2$. The

Table 1. *The 'best' phase combinations for* (I)

	408	804	10,0,1	$\bar{6}06$	800	$\bar{2}03$	806	404	$\bar{8}02$	$\bar{6}04$	401	603	404
1	+	−	+	−	−	−	+	+	−	−	+	+	−
2	−	−	+	+	+	−	+	+	+	−	+	−	+
3	+	−	+	−	−	−	+	+	−	+	+	+	−
4	+	+	+	−	−	−	+	−	+	+	+	+	−

Table 2. *Figures of merit obtained with the first five two-dimensional sets of* (II)

	CFOM	M_{abs}	SPT	R_α (3D)
1	3·803	1·248	−0·674	0·127
2	3·788	1·458	−0·670	0·122
3	3·449	0·744	−0·702	0·116
4	3·255	0·749	−0·641	0·109
5	3·196	1·297	−0·482	0·090

single peak, of average strength, which occurred on the twofold axis was found to correspond to the O atom of a molecule of water of crystallization.

The same procedure was used with structure II. Since *h*0*l* reflexions are more plentiful in this structure a two-dimensional E limit of 1·0 was tried initially, but none of the eight best sign combinations led to the correct solution. An E limit of 0·9 was also unsuccessful and only when it was lowered to 0·8 (88 signs) was the solution obtained, with $E(3D) > 1{\cdot}2$ used. The significance of this is not yet clear. It can be pointed out, however, that the E values computed for *h*0*l* reflexions in the absence of other reflexions are consistently lower than the E values obtained from three-dimensional data.

The complete structure was revealed in the three-dimensional E map based on two-dimensional set 5 which also had the lowest reliability index, R_α. Table 2 summarizes the two and three-dimensional figures of merit for the first five combinations. R_α is defined by Roberts, Pettersen, Sheldrick, Isaacs & Kennard (1973). The combined figure of merit for centrosymmetric problems combines an M_{abs} test (Germain, Main & Woolfson, 1971) with a seminvariant pair test (SPT) according to equation (12) of Giacovazzo (1974), as follows:

$$\text{CFOM} = (1 - \text{SPT})^2 + \begin{cases} (M_{abs})^2; & M_{abs} < 1 \\ 1 \quad\quad ; & M_{abs} > 1 \end{cases}.$$

The observed relation between R_α and SPT is probably significant. In all cases where this technique has now been used to solve a structure it was developed from one of the two-dimensional solutions with the highest SPT.

In structure III, which has three centric projections, it is evident that the (001) projection would yield the most valuable phase information. In order to have the symmetry element in projection at the origin, the symmetry operators were translated through $\frac{1}{4},0,0$ and the procedure outlined above was used; $E > 0{\cdot}8$, 91 signs. The two-dimensional set with third highest CFOM, but highest SPT led to the complete structure.

Discussion

Without any changes to the program (*SHELX*-76) structures with 70 non-hydrogen atoms are now being solved routinely by this method. The procedure is so well defined that any program using the multisolution method can probably be easily adapted to solve any structure with a centric projection without intervention, provided an efficient routine is available to handle the centrosymmetric two-dimensional part automatically.

As described here, the most serious defect is probably the recalculation of E values from two-dimensional data. This is easy to remedy and a little experimentation should reveal the appropriate two-dimensional/three-dimensional ratio of E limits. Furthermore, the centrosymmetric (two-dimensional) solutions should perhaps be assessed in terms of SPT rather than CFOM, for appropriateness as three-dimensional sets.

During use of this method with other structures an attempt was made to include an even higher number of fixed centric phases in the three-dimensional starting set, by considering more than 2^{12} permutations at the two-dimensional stage. In all cases this had an adverse effect on the resolution even when the signs which produce the correct solution are retained. The 4096 permutations appear to be a fortuitous optimum.

In retrospect, some of the two-dimensional E maps based on the correct sign combinations have been examined, but in no case was it possible to fully interpret them in terms of the known structures.

Stimulating correspondence with Dr G. M. Sheldrick is gratefully acknowledged.

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