

One of us (Th. E. M. van den Hark) acknowledges support from the Dutch Foundation for Pure Research, ZWO/FOMRE.

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Application of Direct Methods on Difference Fourier Coefficients for the Solution of Partially Known Structures

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(Received 26 January 1976; accepted 1 April 1976)

A partially known structure, which may be a fragment of a molecule found by direct methods, can be solved completely by applying a weighted tangent refinement procedure on difference structure factors, similar to the authors' procedure for heavy-atom structures. Often the molecular fragment is found to be misplaced with respect to the symmetry elements: then, the space-group symmetry is reduced to $P1$, and the procedure is used to locate the symmetry elements.

Introduction

In previous papers (Gould, van den Hark & Beurskens, 1975; van den Hark, Prick & Beurskens, 1976) we have described a procedure (for centrosymmetric, and non-centrosymmetric structures respectively) for the solution of heavy-atom structures, where the positions of some heavy atoms are known. This procedure is called *DIRDIF*. Naturally, the procedure can also be used for equal-atom structures when a molecular fragment is known.

Application of direct methods for the solution of not too small structures often leads to an electron density map (or E map) from which a molecular fragment can be recognized. Patterson search techniques or tangent-formula recycling techniques may then be used to complete the solution of the structure. Often the molecular fragment is in the correct orientation but shifted with respect to the symmetry elements. The solution of the

structure can then be sought by translation functions, or by reducing the space-group symmetry to $P1$, where any position of the molecular fragment is correct by definition.

For these cases the *DIRDIF* procedure is a very convenient tool, which is illustrated by the following examples.

Examples

Heptahelicene, $C_{30}H_{18}$, (see Fig. 1) crystallizes in two modifications:

(I) Space group $P2_1$; $Z=4$; two independent molecules per unit cell (Beurskens, Beurskens & van den Hark, 1976). We had troubles in solving this structure, as could be expected. We managed to find one heptahelicene molecule, incorrectly placed, and we could solve the structure as described below.

(II) Space group $P2_1/c$; $Z=4$; one molecule per asymmetric unit (van den Hark & Beurskens, 1976). We had troubles in solving this structure, partly because of the relatively small number of reflexions that could be measured. One heptahelicene molecule was found, also incorrectly placed, and this was used as described below.

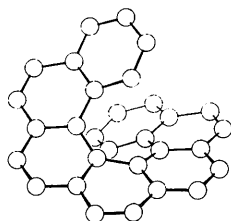


Fig. 1. Carbon skeleton of the heptahelicene molecule.

Description of the procedure

The symmetry is supposed to be $P1$, and the monoclinic reflexion data set is expanded using $|F_{obs}(h\bar{k}l)| =$

$|F_{\text{obs}}(hkl)|$. One molecule, found by application of direct methods, was used for the calculation of partial structure factors (F_H), and the computer program *DIRDIF.D* (van den Hark, Prick & Beurskens, 1976) was applied on the difference structure factors to find the most probable values of phases and amplitudes of the structure factors for the remaining three molecules. In contrast to the heavy-atom procedure, the overall temperature factors of the known molecule (B_H) and the remaining three molecules (B_L) were set equal.

The electron density map showed all four molecules, that is the input molecule as well as three new molecules. For structure I the twofold screw axis was easily found, the structure was shifted to bring the twofold screw axis to its proper position, and the coordinates of symmetry-dependent atoms were averaged. For structure II the centre of symmetry was easily found and shifted to the origin, and the symmetry-dependent atoms were averaged. The structures then refined rapidly in the proper space groups.

Some observations

The input molecule was also found on the electron density map; this is caused by small errors in scale factor and errors in atomic positions. The 'peaks' in a conventional difference Fourier map will be enhanced by the application of direct methods. From some trial runs it was learned that if more and more atoms are known, these atoms will disappear, and the remaining atoms will have higher peaks on the Fourier synthesis.

For structure II some numerical results are given in Tables 1 and 2. The input heptahelicene molecule (*A*) is found again equally as well as two symmetry-related molecules *B* and *C*, while the third molecule *D* had lower peaks on the average.

After the molecules had been shifted so as to bring the centre of symmetry to the origin, and after refinement of the structure, it was found that several input atoms had rather large deviations; the output peaks

for the same atoms are much better (see Table 2). The deviation for the averaged positions (from all four molecules) are also shown in this table.

Table 2. *Comparison of errors in the atomic positions of the heptahelicene molecule before and after the application of the procedure*

The tabulated deviations are calculated with respect to the refined atomic positions.

The deviations are given for seven atoms with the largest input error; the numbering of these atoms is as given in the report of the structure (van den Hark & Beurskens, 1976).

	Input molecule	Output <i>A</i>	Averaged positions of <i>A, B, C, D</i> *
C(29)	0.78 Å	0.11 Å	0.11 Å
C(18)	0.65	0.06	0.04
C(11)	0.40	0.08	0.04
C(15)	0.36	0.13	0.08
C(16)	0.35	0.04	0.10
C(14)	0.28	0.29	0.09
C(4)	0.27	0.12	0.07
Averaged	0.21	0.15	0.10

* See text.

There is an important difference between the tangent recycling procedure of Karle (1968) and the present procedure. In the former procedure the same reflexions and Σ_2 interactions (used in the initial phasing procedure that resulted in the recognition of a structural fragment) are used again for the refinement of phases. In contrast, quite different reflexions and Σ_2 interactions are used in our procedure. Weak reflexions, for example, may have a large contribution from the known structural fragment and may be important in our procedure.

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Table 1. *Distribution of peaks of the four heptahelicene molecules in the Fourier synthesis*

For each molecule the number of peaks that correspond with atoms is tabulated.

	Top 50 peaks	Top 100 peaks	Top 150 peaks
Input molecule <i>A</i>	14	20	26
Unknown molecules $\left\{ \begin{array}{l} B \\ C \\ D \end{array} \right.$	19	28	30
	14	26	29
	3	16	26
Missing atoms	70	30	9
Spurious peaks	0	10	39

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