

An application of DIRDIF to troublesome heavy-atom structures

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Abstract

When a heavy-atom structure determination presents difficulties, the structure may be solved by expanding the data to triclinic symmetry, putting one heavy atom at the origin, and using the program DIRDIF (*direct methods applied to difference structure factors*) to locate the remaining heavy atoms.

Introduction

Nowadays most heavy-atom structures are solved in routine fashion by either direct methods or Patterson methods. In contrast to direct-methods program, most Patterson programs are *not* automated. The majority of heavy-atom structures, solved by Patterson techniques, are solved by first obtaining one or more atomic positions by inspection of the Patterson map, and then finding the remaining atoms by successive Fourier syntheses. As this approach is rather slow, most crystal-structure-solving crystallographers prefer to solve medium- to heavy-atom structures (e.g., sulfur- or copper-containing small molecules) by direct methods.

In our experience the Patterson approach can be faster and less expensive if the heavy atom is located by an automatic Patterson interpretation program, and the location of the remaining atoms then done by the program DIRDIF (Beurskens *et al.*, 1982).

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In relatively few cases problems are encountered in the location of the heavy atoms. Four examples are given in this paper. The reasons for the failure to locate the heavy atoms were:

- i) incorrect assumptions about the space-group symmetry,
- ii) incorrect information about the composition of the compound,
- iii) erroneous interpretation of the Patterson synthesis.

For such cases we present a surprisingly simple procedure.

Experimental

DIRDIF in P1

The elucidation of the structure is accomplished by the following steps. We assume that a unique set of reflections is available, and that Friedel-related reflections, if measured, have been averaged.

a. For space group $P\bar{1}$ the symmetry is discarded. For other space groups the reflection data are expanded to one half-sphere by applying the Laue symmetry relations to the unique set of reflections. (Friedel-related reflections are not generated.) Thereafter the symmetry elements are discarded; the original and generated reflections are considered to be symmetry independent, and we now have a "symmetry reduced" space group which is either $P1$ or a centered equivalent for nonprimitive space groups.

b. The origin is taken as the position of one heavy atom. This is permissible no matter what the space group or the composition of the crystal. The program *DIRDIF* is used to calculate phases for a Fourier synthesis. The heavy atom at the origin leads to calculated phases equal to 0, which constitutes an enantiomorph problem. The enantiomorph, however, is fixed by *DIRDIF*; see Prick *et al.* (1983). The Fourier program is followed by a peak search and interpretation routine.

c. Since the phasing power of the one input atom is usually not sufficient to reveal the complete structure in one pass through *DIRDIF*, it is necessary to select a few of the highest peaks from the *DIRDIF*-Fourier map. No symmetry should be imposed on the selected peaks. One may even leave out one or two peaks to force the model to be less symmetric than the original Laue symmetry.

d. The selected atoms (including the atom at the origin) are input to a second run of *DIRDIF*, again in the symmetry-reduced space group. This may result in the solution of the complete structure; if not, then a large number of peaks may be identifiable. In some difficult cases one or two additional *DIRDIF* cycles may be necessary to recognize the structure.

e. When a significant portion of the atoms is located in the symmetry-reduced space group, the symmetry relations between equivalent molecules can be recognized and identified. The structure is then shifted to get the symmetry elements to their proper positions, and the positions of symmetry-equivalent atoms are averaged to get a best position. The original $|F_o|$ data are now used with the proper symmetry in either another DIRDIF run or for the calculation of a Sim (1960) weighted Fourier synthesis to locate the remaining atoms.

The overall result of these five steps is the determination of the correct structure and the correct space group. Because the structure is actually solved in the symmetry-reduced space group, the outcome is not influenced by any errors in the original assumption about symmetry and/or composition.

Examples

Four structures, denoted NISOMS, SPAN2, NAB5, and KHMAL, were recently solved by the procedure described in this note; details about these structures are given in Table 1. These papers appear in this and following issues.

Discussion

The success of the present method is largely due to the enantiomorph-discriminating power of DIRDIF. All calculations needed for this method can be performed in an automatic fashion. The user, however, selects the peaks to be used as input to the next cycle.

Table 1. Structures solved by the present method

	Code ^a			
	NISOMS	SPAN2	NAB5	KHMAL
Composition	C ₁₆ H ₂₀ N ₅ Se ₂ NiS ₂	C ₃₆ H ₃₀ Cl ₂ NiP ₂	C ₁₀ H ₆ Br ₂	C ₁₂ H ₁₆ O ₁₅ K ₂
Space group	P $\bar{1}$	P2/c	C2/c	P2 ₁ 2 ₁ 2 ₁
Cell: <i>a</i> (Å)	7.515(2)	11.712(2)	14.576(5)	7.719(5)
<i>b</i>	8.717(2)	8.258(1)	4.0490(8)	7.916(5)
<i>c</i>	12.870(2)	17.370(2)	15.046(6)	29.863(20)
α (deg)	86.84(2)	90.	90.	90.
β	76.40(2)	106.55(2)	92.18(3)	90.
γ	76.27(2)	90.	90.	90.
Z	1	2	4	4

^aNISOMS: Bruins Slot *et al.* (1984a). SPAN2: Bruins Slot *et al.* (1984b). NAB5: Haltiwanger *et al.* (1984). KHMAL: Van Havere *et al.* (1984).

The recognition and location of the symmetry elements still requires some crystallographic knowledge. We will automate this using autoconvolution techniques: only minor modifications in the program TRADIR (translation functions in DIRDIF-Fourier space; Doesburg and Beurskens, 1983) are required for the location of symmetry elements in any Fourier map.

The computing time involved for each cycle is comparable to the time needed for a standard DIRDIF run. One may speed up the first one or two runs by imposing a severe $\sin \theta/\lambda$ limitation (0.3 or 0.4 \AA^{-1}); a small number of heavy atoms are easily found with low-resolution data.

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