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A Note on Practical Aspects of the Application of *DIRDIF*, a Procedure for Structure Elucidation When a Part of the Structure is Known

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Abstract

The *DIRDIF* procedure (*direct methods applied to difference structures*) has been tested on a variety of structures. It is shown that errors in the atomic positions of approximately 0.3 Å are acceptable, that the minimum size of the known molecular fragment is about 10% of the total scattering power, and that lack of knowledge about the unit-cell contents is not deleterious.

Introduction

When part of a structure is known, the *DIRDIF* method (Beurskens *et al.*, 1982) can be effectively used to solve the unknown part of the structure. Although the various *DIRDIF* procedures include unique features designed for solving enantiomorph and super-symmetry problems (see Prick, Beurskens & Gould, 1983, and references therein), the general *DIRDIF* method has proved to be a very efficient tool for routine crystal-structure analyses, particularly if the known part is only barely sufficient to solve the structure. The automatic computer program uses observed structure amplitudes and positions of the known atoms as input to a structure-factor calculation and scaling routine. This is followed by a weighted tangent refinement of the difference structure factors, to yield a greatly improved electron density map.

To explore the effects of errors or lack of information, we pose the following questions:

Q1. How small may the known part be so that *DIRDIF* is still helpful?

Q2. How much error can be tolerated in the positional coordinates of the known atoms?

Q3. What are the effects of 'incorrect atoms' in an otherwise correct molecular fragment?

Q4. What is the effect of unknown chemical composition?

We investigated these aspects using a few known crystal structures as test cases. The results are summarized in this note.

Calculations

All calculations were performed by the program *DIRDIF* using default executional parameters. A scaling procedure (Gould, Van den Hark & Beurskens, 1975) leads to the determination of the scale factor, SC , B_p , the (overall) isotropic temperature parameter of the known part (heavy atom or 'partial structure'), and B_r , the (overall) isotropic temperature parameter of the unknown part of the structure ('rest structure').

The contribution of the known part to the total scattering power is defined by the *a priori* scattering fraction:

$$p_z^2 = \sum_p Z_p^2 / \sum_l Z_l^2,$$

where Z is the atomic number, \sum_p denotes summation over the known atoms, and \sum_l denotes summation over all atoms in the unit cell.

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After the scaling procedure the scattering fraction is recalculated as

$$p_{\text{exp}}^2 = \frac{\sum_{\text{h}} |F_p|^2}{\sum_{\text{h}} |F_{\text{obs}}|^2},$$

where F_p is the partial structure factor, calculated with temperature parameter B_p , F_{obs} is on an absolute scale, and \sum_{h} denotes summation over all reflections.

Note that p_{exp}^2 depends on structural peculiarities as well as on the result of the scaling procedure.

Normalization of the difference structure factors,

$$\Delta F_1 = (|F_{\text{obs}}| - |F_p|) \exp(i\phi_p)$$

gives E_1 values. $|E_1|$ is the lowest possible estimate for $|E_p|$ (the $|E|$ value of the unknown part of the structure). E_1 is 'phased' by the known atoms. It is the purpose of the *DIRDIF* procedure to transform E_1 values into E_p values, by two or three cycles of weighted tangent refinement. The resulting E_p values

are converted into F_p values which are used as input to a Fourier synthesis and peak interpretation program.

The test structures are listed in Table 1; they are denoted by the code names MONOS, HEPTA and AU8P7.

MONOS is taken as an example of an organic molecule with one medium-heavy atom (sulphur). Structures of this type are usually solved by direct methods. We find it easier to obtain the sulphur position from a sharpened Patterson synthesis and to determine the remaining non-hydrogen atoms using *DIRDIF*. One interpretation of the Patterson synthesis of MONOS leads to a sulphur position with $x = 0.0$, which constitutes a centrosymmetric structure. This enantiomorph problem can be solved by *DIRDIF* (Prick, Beurskens & Gould, 1983). In this note, however, we report the *DIRDIF* results for slightly shifted positions of the input sulphur atom. For this compound, questions *Q2* and *Q4* (see above) are answered by the results collected in Tables 2 and 3. An error of 0.5 Å in the position of the sulphur atom is too much. An error of 0.4 Å leads to an incomplete structure; the highest peak in the Fourier synthesis gives an improved position of the sulphur atom. For comparison, Table 2 also includes the results obtained by a Sim's (1960) weighted Fourier synthesis. As can be seen from Table 3, satisfactory results occur for widely varying cell contents.

Table 1. *Crystal data of test structures*

Compound Reference	MONOS (a)	HEPTA (b)	AU8P7 (c)
Chemical formula	C ₁₅ H ₁₆ N ₂ O ₂ S	C ₃₀ H ₁₈	[Au ₈ (PPh ₃) ₇](NO ₃) ₂
<i>N</i> (asym.u.)	20	60	149
<i>Z</i>	4	4	4
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.166(4)	14.022(4)	25.444(6)
<i>b</i> (Å)	11.405(3)	15.094(4)	17.332(6)
<i>c</i> (Å)	15.936(4)	9.221(3)	28.795(6)
α (°)	90	90	90
β (°)	90	93.20 (2)	97.66 (3)
γ (°)	90	90	90
<i>N</i> (refl.)†	3368	3565	2829
Final <i>R</i>	0.046	0.065	0.056

References: (a) Noordik, Beurskens, Ottenheim, Herscheid & Tjhuis (1978); (b) Beurskens, Beurskens & Van den Hark (1976); (c) Van der Velden, Bour, Bosman & Noordik (1981).

* *N* (asym.u.) = Number of non-hydrogen atoms in the asymmetric unit.

† *N* (refl.) = number of independent reflections.

Table 3. *Test runs for MONOS: varying cell content*

Error in the total scattering power	B_p	p_z^2	p_{exp}^2	N_{24}^*
+50%	3.74	0.16	0.25	19
+25%	4.19	0.20	0.27	19
0%	4.81	0.25	0.29	19
-25%	5.77	0.33	0.34	19

* N_{24} : see Table 2.

Table 2. *Test runs for MONOS: error in the position of the input S atom*

Input deviation†	Statistics					Results from <i>DIRDIF</i> Fourier synthesis		Results from conventional Fourier synthesis	
	B_p	B_r	<i>SC</i>	p_{exp}^2	$R\ddagger$	N_{24}^*	Deviation† (Å)	N_{24}	Deviation†
0.00	4.81	4.17	0.411	0.29	0.565	19	0.02	13	0.01
0.10	5.12	4.10	0.409	0.28	0.567	18	0.03	13	0.06
0.20	6.33	3.75	0.406	0.24	0.615	17	0.04	10	0.15
0.30	7.65	3.63	0.400	0.20	0.660	16	0.04	9	0.27
0.40	8.12	3.61	0.395	0.20	0.674	7	0.26	7	0.38
0.50	7.26	3.59	0.409	0.21	0.652	1	0.61	3	0.51

The scattering fraction $p_z^2 = 0.25$.

* N_{24} = number of peaks representing atomic positions out of the highest 24 peaks (maximum: 20).

† Deviation (Å) of input or output sulphur position with respect to the refined position.

‡ *R* is the conventional residual (using *SC* and B_p).

HEPTA is taken as an example of an equal-atom structure. The two independent molecules consist of fused hexagons. Such structures often lead to *E* maps in which hexagonal patterns are found ('chicken wire'). Here, we report the *DIRDIF* results for fragments of different size and quality, at approximately correct position and orientation. (For the application of *DIRDIF* translation functions to misplaced fragments, see Doesburg & Beurskens, 1983). For the fragments, which are defined in Table 4, the answers to the questions *Q1*, *Q2* and *Q3* are given in Tables 5, 6 and 7, respectively. The results for different fragments show large variations, related to the nature of the fragments. For instance, the fragment *F6a* constitutes a hexagon, which is not a unique feature in this structure, while *F6c* constitutes a connected chain of six carbon atoms belonging to different hexagons. As can be seen in Table 5, all fragments but *F6a* give satisfactory results. The answer to *Q2* depends on the size of the fragment:

Table 4. Description of fragments of HEPTA

Code	Carbon atoms entered*											p_z^2	
<i>F6a</i>	5	6	27	28	29	30						0.10	
<i>F6b</i>	7	8	25	26	27	28						0.10	
<i>F6c</i>	19	21	23	25	27	29						0.10	
<i>F8a</i>	8	11	21	23	24	25	26	27				0.13	
<i>F8b</i>	7	8	23	25	26	27	28	29				0.13	
<i>F8c</i>	1	18	19	21	23	25	27	29				0.13	
<i>F8d</i>	7	8	9	23	25	26	27	28				0.13	
<i>F10a</i>	8	9	10	11	21	23	24	25	26	27			0.16
<i>F10b</i>	7	8	9	10	23	24	25	26	27	28			0.16
<i>F12a</i>	8	9	10	11	12	21	22	23	24	25	26	27	0.20
<i>F12b</i>	7	8	9	10	11	21	23	24	25	26	27	28	0.20

* Numbering as in Beurskens, Beurskens & Van der Hark (1976):

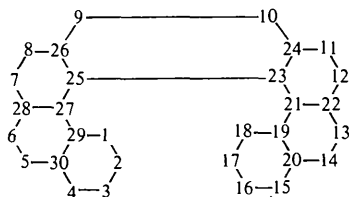


Table 5. Test runs for HEPTA: correct input fragment

Code	p_{exp}^2	N_{30}^*	N_{75}^\dagger
<i>F6a</i>	0.24	16	27
<i>F6b</i>	0.20	24	40
<i>F6c</i>	0.12	30	60
<i>F8a</i>	0.17	27	49
<i>F8b</i>	0.25	29	52
<i>F8c</i>	0.19	30	60
<i>F10a</i>	0.21	29	55
<i>F12a</i>	0.24	30	60

* N_{30} = number of peaks representing atomic positions out of highest 30 peaks.

† N_{75} = number of peaks representing atomic positions out of highest 75 peaks (maximum: 60).

Table 6 shows that the atomic positions of a 12-atom fragment may have standard deviations up to 0.4 Å, while the smaller fragments only give satisfactory results with more accurate positions. The six-atom fragment *F6b* with a standard deviation of 0.20 Å (which implies larger deviations for two or three atoms) is only marginally sufficient for the elucidation of the structure. In Tables 5 and 6 it is shown that for small or poor fragments, which do not lead to the determination of the complete structure, the first thirty peaks include a relatively large number of correct atomic positions. Table 7 gives the results for some fragments to which 1, 2 or 3 'wrong atoms' were added at

Table 6. Test runs for HEPTA: input fragments with error

Input fragment	Code	S.d.*	Statistics		Results from <i>DIRDIF</i> Fourier synthesis		Resulting average deviation†
			B_p	p_{exp}^2	N_{30}^\ddagger	N_{75}^\ddagger	
<i>F6b</i>		0.00	1.10	0.20	24	40	§
		0.20	1.35	0.14	18	25	0.16
		0.40	2.33	0.10	5	9	0.37
		0.60	7.22	0.04	14	22	0.31
<i>F8b</i>		0.00	1.45	0.25	29	52	§
		0.20	2.40	0.13	26	34	§
		0.40	3.66	0.10	15	23	0.27
		0.60	4.40	0.11	1	3	0.60
<i>F10a</i>		0.00	2.09	0.21	29	59	§
		0.20	2.60	0.16	30	57	§
		0.40	5.35	0.09	17	28	0.22
		0.60	6.81	0.07	12	16	0.39
<i>F12a</i>		0.00	2.39	0.24	30	60	§
		0.20	2.75	0.19	30	60	§
		0.40	3.47	0.16	26	45	0.26
		0.60	7.25	0.08	6	12	0.46

* Standard deviation (Å) of the at-random-shifted input atoms (in Å), relative to their refined positions.

† Average deviation (Å) of the new positions of the input atoms.

‡ N_{30} , N_{75} : see Table 5.

§ Average deviation less than 0.1 Å primarily due to interpolation errors.

Table 7. Test runs for HEPTA: effect of incorrect atoms: peak numbers of 'wrong atoms'

Input fragment	N^*	$N + F8d$		$N + F10b$		$N + F12b$	
		(a)†	(b)‡	(a)	(b)	(a)	(b)
1	13	6§	21	57	42	40	
1	§ 7	26	15	26	30	24	
1	18	15	17	19	24	30	
2	16, 17	19	18, 30	35	22, 41	44	
2	17, 23	29	21, 23	20	25, 52	22	
2	§ 5, 18	19	12, 20	21	§ 10, 24	32	
3	§ 8, 17, 27	20	11, 21, 37	19	14, 31, 52	30	

* N = number of incorrect peaks.

† (a) Peak numbers for 'wrong atoms' (peaks are numbered in order of decreasing peak heights).

‡ (b) Peak number of the highest new erroneous peak.

§ Unsatisfactory result because a 'wrong atom' or an erroneous peak does not occur below all correct input atoms.

Table 8. Test runs for AU8P7: error in the position of input atoms

The known fragment consists of three Au atoms.

Deviation*	p_{exp}^2	B_p	R	N_8^\ddagger
0.1	0.36	<0‡	0.554	8
0.2	0.36	<0‡	0.559	8
0.4	0.35	<0‡	0.572	8
0.6	0.34	<0‡	0.584	8
>1.0	0.28	12.41§	0.672	8
>1.0†	0.35	21.75§	0.643	—

* Error (Å) in the position of one Au atom. (Two other atoms at correct positions.)

† For this entry all three Au atoms of the input fragment have an error >1.0 Å.

‡ Temperature factor B_p was reset to 0.

§ Temperature factors B_p and B_r were reset to default values.

¶ N_8 : number of gold atoms located in the DIRDIF Fourier synthesis (maximum: 8).

Table 9. Test runs of AU8P7: varying cell content

The known fragment consists of one Au atom at correct position.

Error in total scattering power	B_p	N_8^\ddagger
0%	≤0*	8
−50%	<0†	8
−75%	<0†	8

* Temperature factors B_p and B_r were reset to default values.

† Temperature factor B_p was reset to 0.

‡ N_8 : number of gold atoms located in the DIRDIF Fourier synthesis (maximum: 8).

incorrect though chemically reasonable positions, extending the hexagonal pattern. There is a strong tendency for the 'wrong atoms' not to appear within the list of the highest peaks.

Au8P7 is taken as an example of a troublesome heavy-atom structure. In this type of gold cluster compound the composition and the skeleton geometry are often not known. We have solved several cluster compounds by finding a few gold atoms from partial interpretation of a Patterson synthesis, and locating the remaining heavy atoms using DIRDIF. The questions Q2, Q3 and Q4 are answered in Tables 8 and 9. A known fragment consisting of three Au atoms revealed in all cases the positions of the remaining Au atoms, except when all positions were wrong. An error in the cell contents up to 75% has little effect on the DIRDIF results, as Table 9 shows: all Au atoms were located.

Discussion of the results

From these experiments, it may be concluded that errors in the atomic positions of approximately 0.3 Å are acceptable (Tables 2, 6 and 8), that 'wrong atoms'

in the peak list are de-emphasized (Table 7), that the minimum size of the known fragment is about 10% of the total scattering power (Tables 5 and 6), and that errors in the cell contents have little effect (Tables 3 and 9).

These results cannot be generalized quantitatively, since structures of different complexities and with different structural peculiarities may behave differently in a given situation. However, they are consistent with our many practical applications of DIRDIF to the solution of unknown structures.

When DIRDIF fails to reveal the structure, valuable information about the nature of the problem is given by various statistical quantities, some of which are collected in the tables.

Tables 2 and 6 show that a bad partial structure (large errors in the positions of the input atoms) leads to large values of B_p . (An incorrect input model is 'blown up' by the scaling procedure.) B_r is not that much affected by the model. (For a small fragment B_r is largely determined by the overall temperature parameter.)

The effect of varying cell contents is minimized by the scaling procedure. The resulting temperature factor B_p is a function of the assumed relative scattering power of the input fragment. (Table 3).

The *a priori* calculated scattering power of the known fragment, p_z^2 , depends on the number and the type of atoms only; the experimental scattering fraction, p_{exp}^2 , depends on the quality of the model, on structural peculiarities, and also on the result of the scaling procedure. Therefore, B_p and p_{exp}^2 are strongly correlated. Nevertheless, we find it useful to observe the results for p_{exp}^2 : its value decreases if the model is bad.

Other statistical quantities, such as the expectation value of $|E_r|$, have been discussed previously (Beurskens, Prick, Doesburg & Gould, 1979).

Tables 5 and 6 show that in cases in which the known fragment is only barely sufficient to solve the structure (very small fragment and/or large errors in the atomic positions), the input model is obtained from the DIRDIF Fourier synthesis with improved positions, and that some new atomic positions may be selected from the list of the largest peaks. Also, Table 7 shows that possible 'wrong atoms' will sink to the bottom of the peak list. One may therefore use selected output positions as input to another DIRDIF run, while considering the following:

– If a well defined structure is found in the DIRDIF Fourier map, and only a few atoms are missing, a conventional Fourier synthesis may be used to locate the missing atoms. (At this stage the difference structure factors are largely determined by errors in the model and errors in the observed intensities; tangent refinement now is not advisable; the program DIRDIF automatically bypasses the refinement, and produces a conventional Fourier synthesis).

– If the complete structure is recognized, but of poor quality, a conventional Fourier synthesis may be used to obtain refined parameters.

– If only a fragment is recognized (say less than 60% of the total scattering power), this fragment may be used as input to *DIRDIF*.

– If the structure is not recognized, one should pay attention to the printed statistical quantities, and examine the input model. Large B_p and small p_{exp}^2 indicate a bad model. Too large or too small B_p values or an $|E_p|^2$ average which deviates too much from unity are often related to scaling problems: in this case the user may supply reasonable values for B_p and B_r and rerun *DIRDIF* with a severe $\sin \theta/\lambda$ cut-off. The following rerun options may be considered:

* If the model consists of one or more heavy atoms, which appear to be shifted by more than 0.1 Å, the new positions may be used as input.

* For a light-atom fragment the same option can be applied and one may also reject the atoms that return low in the peak list, and include some higher peaks.

* If the input fragment completely returns in the *DIRDIF* Fourier, with atomic shifts less than 0.1 Å, we suggest adding a number of high peaks to the known fragment: this number may be 10, 20% of the total number of non-hydrogen atoms, or 50% of the number of atoms of the input model, depending on the problem at hand.

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General Lattice Factor of the Ideal Paracrystal

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Abstract

The lattice factor of a paracrystalline lattice with oblique axes and with general orientation of the fluctuation tensor ellipsoid is calculated. Directly applicable formulas for the special case of a monoclinic (macro) lattice, which is of interest in connexion with the small-angle scattering of oriented semicrystalline polymers, are given.

1. Introduction

The ideal paracrystal is a model of a statistical distorted crystal lattice or macro lattice (Hosemann &

Bagchi, 1962). The distortions are described by the cell-edge statistics $H_k(\mathbf{x})$ ($k = 1, 2, 3$) and the mean cell-edge vectors are

$$\mathbf{a}_k = \int \mathbf{x} H_k(\mathbf{x}) d^3 \mathbf{x}. \quad (1)$$

For statistics $H_k(\mathbf{x})$ having a center of symmetry, the statistical amplitude $F_k(\mathbf{b})$, the Fourier transform, $\mathcal{F}\{H_k(\mathbf{x})\}$, can be expressed in the form

$$F_k(\mathbf{b}) = |F_k(\mathbf{b})| \exp[-2\pi i \mathbf{b} \cdot \mathbf{a}_k], \quad (2)$$

where, for statistics $H_k(\mathbf{x})$ Gaussian (otherwise as an approximation),

$$|F_k(\mathbf{b})| = \exp[-2\pi^2 \mathbf{b} \cdot \mathbf{T}(k) \cdot \mathbf{b}]. \quad (3)$$