BUERGER, M. J. (1944). *The Photography of the Reciprocal Lattice*. A.S.X.R.E.D. Monograph No. 1.
DELAUNAY, B. (1933). *Z. Kristallogr.* **84**, 109.
DONNAY, J. D. H. (1943). *Amer. Min.* **28**, 313, 470, 507. (See also *Amer. Min.* (1952). **37**, 1063.)
DONNAY, J. D. H. & NOWACKI, W. (1954). *Crystal Data*. Geological Society of America, Memoir No. 60.
International Tables for X-ray Crystallography, (1952), vol. 1, pp. 530–5. Birmingham: Kynoch Press.
ITO, T.-I. (1950). *X-ray Studies on Polymorphism*. Tokyo: Maruzen.
JONG, W. F. DE & BOUMAN, J. (1938). *Z. Kristallogr.* **98**, 456.

Acta Cryst. (1957). **10**, 116

An Efficient Process for Solving Crystal Structures by Sign Relationships

BY M. M. WOOLFSON

Physics Department, College of Science and Technology, Manchester 1, *England*

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It is shown that, by expressing sign relationships in a suitable tabular form, it is possible to deduce signs for other structure factors if the signs are known for the structure invariants (the structure factors of even indices whose signs do not vary with the choice of origin of the unit cell). The economy introduced by considering only the structure invariants as unknowns, and not all the structure factors, makes possible the determination of reasonably complex structures by hand calculation. The application of the method to the structure of azo-benzene 2-sulphenyl chloride is described.

1. Introduction

The role of direct methods, which make use of sign relationships for solving crystal structures, is becoming progressively more important in crystallography but it would be fair to say that, at the present time, they do not seriously challenge older methods in achievement. Almost all the structures which have been solved by direct methods would have yielded to some other method, but the converse is certainly not true. However, direct methods do have the important virtue that they may often be tried fairly quickly, and failure is not too costly in time.

The present paper describes an efficient, systematic process by which sign relationships may be applied to the solution of crystal structures. With the aid of electronic computers the process should be capable of application to structures outside the scope of other direct methods hitherto reported.

2. The basis of the method

The discussion of this section will, for simplicity, be restricted to two dimensions, although the method can be applied in three dimensions. The $hk0$ projection of salicylic acid (two-dimensional space group *pgg*) will be used as an example of the application of the method. The reflexions considered are those of large unitary structure factor which were used by Cochran & Douglas (1954).

The reflexions are divided into the following four groups:

(*a*) h even, k even;
(*b*) h odd, k odd;
(*c*) h odd, k even;
(*d*) h even, k odd .

The signs of the reflexions of group (*a*) are indicated by the symbols a_1, a_2, etc., those of group (*b*) by b_1, b_2, etc., and so on. For salicylic acid we shall first consider only groups (*a*) and (*c*), for which the symbols and their significance are listed below.

$a_1 = s(10, 4)$	$c_1 = s(3, 12)$
$a_2 = s\ (4, 6)$	$c_2 = s(3, 2)$
$a_3 = s\ (2, 12)$	$c_3 = s(1, 6)$
$a_4 = s\ (2, 10)$	$c_4 = s(7, 2)$
$a_5 = s\ (6, 2)$	$c_5 = s(3, 6)$
$a_6 = s\ (2, 4)$	$c_6 = s(5, 4)$
$a_7 = s\ (2, 6)$	$c_7 = s(9, 4)$
$a_8 = s\ (4, 0)$	
$a_9 = s\ (6, 0)$	

where $s(h, k)$ denotes the sign of the reflexion $hk0$. The signs of a_8 and a_9 are found from inequalities to be + and − respectively.

All the sign relationships are now sought which relate one member of group (*a*) with two of group (*c*) and it is found that the following products are probably positive:

$-a_1c_4c_5$	$-a_7c_4c_7$	$-a_5c_3c_6$
$a_1c_2c_4$	$a_7c_1c_3$	$-a_7c_4c_6$
$-a_2c_1c_3$	$a_8c_2c_4$	$-a_4c_5c_6$
$-a_3c_3c_5$	$a_6c_2c_3$	$a_5c_5c_7$
$a_5c_2c_7$	$-a_7c_2c_6$	$a_8c_6c_7$

The negative signs arise because, for the reflexions of group (*c*), $s(\bar{h}, k) = -s(h, k)$.

These relationships may be expressed in a tabular form as shown in Table 1.

Table 1

	c_1	c_2	c_3	c_4	c_5	c_6	c_7
c_1			$-a_2$ a_7				
c_2			a_6	a_1 a_8		$-a_7$	a_5
c_3	$-a_2$ a_7	a_6			$-a_3$	$-a_5$	
c_4		a_1 a_8			$(-a_1)$	$-a_7$	$-a_7$
c_5			$-a_3$	$(-a_1)$		$-a_4$	a_5
c_6		$-a_7$	$-a_5$	$-a_7$	$-a_4$	·	a_8
c_7		a_5		$-a_7$	a_5	a_8	

Thus the first product of the list, $-a_1c_4c_5$, is represented by $-a_1$ in the squares c_4c_5 and c_5c_4. These are enclosed in brackets in the table.

We now assume that the signs of the reflexions of group (*a*) are known. The correct signs for this group are:

a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9
+	−	−	+	−	−	+	+	−

When these signs are substituted for the appropriate symbols we obtain Table 2.

Table 2

	c_1	c_2	c_3	c_4	c_5	c_6	c_7
c_1			+ +				
c_2			−	+ +		−	−
c_3	+ +	−			+	+	
c_4		+ +			−	−	−
c_5			+	−		−	−
c_6		−	+	−	−		+
c_7		−		−	−	+	

It can be seen that the rows c_3 and c_4 include the following information:

$c_2c_3 \approx -$, $c_2c_4 \approx +$ with double weight,
$c_5c_3 \approx +$, $c_5c_4 \approx -$,
$c_6c_3 \approx +$, $c_6c_4 \approx -$,

where the symbol $\approx$ indicates 'probably equals'. From these relationsips it is clear that $c_3 \approx -c_4$ with a very high degree of probability. If the sign of c_3 is arbitrarily fixed as +, then c_4 is −. The lines c_3 and c_4 may be combined to give the revised Table 3.

Table 3

	c_1	c_2	c_3	c_4	c_5	c_6	c_7
c_1			+ +				
c_2			−	+ +		−	−
c_3-c_4	+ +	− − −			+ +	+ +	+
c_5			+	−		−	−
c_6		−	+	−	−		+
c_7		−		−	−	+	

It is now evident from an examination of the rows c_3-c_4, c_2, c_6 and c_7 that $c_2 \approx -$ and $c_6 \approx c_7 \approx +$. Revising the table once again we have Table 4.

Table 4

	c_1	c_2	c_3	c_4	c_5	c_6	c_7
c_1			+ +				
c_5			+	−		−	−
$c_3-c_4-c_2+c_6+c_7$	+ +	− − − − −	+ +	− − − − −	+ + − −	+ + + + +	+ + + + +

For the remaining signs $c_1 \approx +$ and c_5 is indeterminate. The set of signs thus derived for group (*c*) is

c_1	c_2	c_3	c_4	c_5	c_6	c_7
+	−	+	−	?	+	+

and the six signs determined are the correct signs. This set of signs is such that as many as possible of the sign relationships under consideration are satisfied.

It can be seen that a knowledge of the signs of the

members of group (*a*), the structure invariants (those structure factors whose signs do not vary with the choice of origin), enables signs to be deduced for members of other groups. The way in which this technique is used in a structure determination will now be explained.

3. The process of structure determination

The complete process of structure determination will be described for the *hk*0 projection of salicylic acid. First the sign relationships are found which interrelate the members of group (*a*). These are

$$a_1a_2a_5 \approx +\,,$$
$$a_2a_7a_9 \approx +\,,$$
$$a_2a_5a_6 \approx +\,,$$
$$a_2a_4a_6 \approx +\,,$$
$$a_2a_3a_7 \approx +\,.$$

The number of these relationships satisfied is found for each of the 128 (2^7) possible sets of signs for a_1–a_7, the unknown members of group (*a*). It can be deduced that at least four of these relationships should be satisfied (Cochran & Woolfson, 1955) and 22 of the 128 sets of signs for the members of group (*a*) are found to meet this requirement. For each of these 22 sets the technique of the previous section is used to find signs for the members of groups (*b*), (*c*) and (*d*). In § 2 the signs of group (*c*) have already been found for the correct solution. Groups (*b*) and (*d*) are rather small and are

$$b_1 = s(3, 5), \quad d_1 = s(2, 1)\,,$$
$$b_2 = s(5, 5), \quad d_2 = s(4, 11)\,.$$

The only sign relationship relating groups (*a*) and (*b*) is

$$a_4b_1b_2 \approx +\,.$$

The correct sign for a_4 is + so that the available information gives $b_1 \approx b_2 = +$, say.

The sign relationships relating groups (*a*) and (*d*) are

$$-a_3d_1d_2 \approx +, \quad a_4d_1d_2 \approx +\,,$$

and these both indicate that $d_1d_2 \approx +$. We may take $d_1 \approx d_2 = +$.

It should be noticed that reversing the signs of all the members of one of the groups (*b*), (*c*) or (*d*) is equivalent to a change of origin of the unit cell. However, since there are but four choices of origin for the unit cell (in projection) the signs for only two of the groups may be taken in arbitrary fashion, either as they are determined or completely reversed, while the signs for the remaining group are not free of restraint. To fix the non-arbitrary group, sign relationships of the type $b_rc_sd_t$ are used. For the salicylic acid example the ones taken are

$$b_1c_3d_2 \approx +, \; -b_1c_3d_1 \approx +, \; -b_1c_6d_1 \approx +, \; -b_2c_3d_2 \approx +\,.$$

If the signs for the members of groups (*b*), (*c*) and (*d*) are taken as they have been determined, then only one of these sign relationships is satisfied. If the signs for any one group are all reversed, then three of these four sign relationships are satisfied. Reversing the signs for group (*b*) gives the correct signs for all the reflexions (except c_5) with the same choice of origin as used by Cochran & Douglas.

Unfortunately there are 22 sets of signs for group (*a*), including the correct one, for which this process must be carried out. For some of these sets, however, it is difficult to develop signs from the tables for many members of other groups; in other cases the signs for the various groups do not interrelate very well. A few of the 22 sets could be rejected on these grounds and eventually 15 plausible solutions are left. For many of these, including the correct solution, not all the signs are determined; either choice of sign for some reflexions is equally good, or bad, for fitting in with the remainder of the group table. The significance of this ambiguity is discussed in § 5.

To decide which of the 15 plausible solutions is the correct one, the most straightforward course is to calculate the electron-density maps corresponding to each of them. This is tedious by hand calculation but it has been found possible to produce the maps on an electronic computer at the rate of one every two minutes with the output arranged on a rectangular mesh which can be contoured directly. This makes feasible the examination of anything up to about 100 possible solutions.

4. The structure of azo-benzene 2-sulphenyl chloride

Azo-benzene 2-sulphenyl chloride, $C_{12}H_9N_2SCl$, has space group *Pna*2, with a=7·59, b=20·3, c=7·58 Å. A solution was sought for the *hk*0 projection which has the two-dimensional space group *pgg*. The reflexions used, listed in their four groups together with the modulus of the unitary structure factor (in square brackets), were:

a_1 = $s(4, 12)$	[0·22]	b_1 = $s(3, 7)$	[0·36]
a_2 = $s(6, 6)$	[0·29]	b_2 = $s(3, 9)$	[0·32]
a_3 = $s(4, 6)$	[0·23]	b_3 = $s(3, 15)$	[0·29]
a_4 = $s(2, 2)$	[0·24]	b_4 = $s(3, 23)$	[0·28]
a_5 = $s(2, 14)$	[0·23]	b_5 = $s(5, 7)$	[0·26]
a_6 = $s(0, 18)$	[0·22]	b_6 = $s(7, 1)$	[0·22]
a_7 = $s(0, 24)$	[0·33]	b_7 = $s(7, 3)$	[0·22]
a_8 = $s(0, 14)$	[0·23]	b_8 = $s(1, 7)$	[0·22]
a_9 = $s(0, 16)$	[0·39]		
a_{10} = $s(2, 0)$	[0·40]	c_1 = $s(1, 8)$	[0·31]
a_{11} = $s(6, 0)$	[0·23]	c_2 = $s(1, 10)$	[0·24]
		c_3 = $s(1, 20)$	[0·23]
d_1 = $s(2, 15)$	[0·30]	c_4 = $s(1, 22)$	[0·35]
d_2 = $s(2, 17)$	[0·25]	c_5 = $s(1, 24)$	[0·25]
d_3 = $s(4, 15)$	[0·27]	c_6 = $s(5, 2)$	[0·23]
		c_7 = $s(1, 2)$	[0·22]

Probable signs for the axial reflexions a_8, a_9, a_{10} and a_{11} were deduced from sign relationships of the type

$$s(2h, 0, 0) \approx s(hk0)s(\bar{h}k0) ,$$

(Woolfson, 1954), and these signs were +, −, −, + respectively.

There are six sign relationships interrelating the members of group (*a*). These are

$$\begin{aligned} a_5a_8a_{10} &= -a_5 \approx + ,\\ a_1a_1a_7 &= a_7 \approx + ,\\ a_4a_5a_9 &= -a_4a_5 \approx + ,\\ a_2a_3a_{10} &= -a_2a_3 \approx + ,\\ a_1a_4a_5 &\approx + ,\\ a_1a_3a_6 &\approx + . \end{aligned}$$

Of the 128 possible sets of signs for the unknown members of group (*a*) 14 satisfied 5 or more of these six sign relationships. These 14 sets are

	a_1	a_2	a_3	a_4	a_5	a_6	a_7
1	+	−	+	+	−	+	+
2	−	−	+	+	−	−	+
3	−	−	+	+	−	+	+
4	−	+	+	+	−	−	+
5	−	−	+	+	−	−	−
6	−	−	+	−	+	−	+
7	+	−	+	−	−	+	+
8	+	+	−	+	−	−	+
9	−	+	−	+	−	+	+
10	−	+	−	+	−	−	−
11	−	−	−	+	−	+	+
12	−	+	−	+	−	+	−
13	−	+	−	−	+	+	+
14	+	+	−	−	−	−	+

Table 5

	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8
b_1		−		−	(− / a_5)	a_3		(− / a_5)
b_2	−	a_6	a_7 / a_2	+	a_4		a_3 / a_1	a_4
b_3		a_7 / a_2					a_1	
b_4	−	+						
b_5	− / a_5	a_4						+
b_6	a_3							a_2
b_7		a_3 / a_1	a_1					
b_8	− / a_5	a_4			+	a_2		a_5

Tables 5 and 6 show the sign relationships of the type $a_rb_sb_t$ and $a_rc_sc_t$.

Table 6

	c_1	c_2	c_3	c_4	c_5	c_6	c_7
c_1		$-a_6$ / $-a_4$		(+ / $-a_5$)	−	$-a_2$ / a_3	
c_2	$-a_6$ / $-a_4$				(+ / $-a_5$)	$-a_1$	
c_3				$-a_4$			a_6
c_4	+ / $-a_5$		$-a_4$		$-a_4$		$-a_7$
c_5	−	+ / $-a_5$		$-a_4$			
c_6	a_3 / $-a_2$	$-a_1$					−
c_7			a_6	$-a_7$		−	

The information in brackets in the tables, together with the sign relationship $a_5a_8a_{10} \approx +$, points unmistakably to the conclusion that a_5 is negative, and this eliminates sets 6 and 13 of possible signs for group (*a*).

For each of the remaining 12 sets of group (*a*), signs are developed for groups (*b*) and (*c*) by the method described in § 2. Then signs are found for group (*d*) from the sign relationships

$$\begin{aligned} d_1 &\approx -b_2c_5 & d_2 &\approx b_3c_6 & d_3 &\approx b_5c_4\\ d_1 &\approx -b_1c_4 & d_2 &\approx -b_1c_5 & d_3 &\approx b_5c_1\\ d_1 &\approx -b_1c_1 & d_2 &\approx -b_1c_2 & d_3 &\approx b_2c_5\\ d_1 &\approx b_4c_1 & d_2 &\approx -b_2c_1 & d_3 &\approx b_1c_4\\ d_1 &\approx b_8c_4 & d_2 &\approx -b_3c_7 & d_3 &\approx b_1c_1\\ d_1 &\approx b_8c_1 & d_2 &\approx b_8c_5 & d_3 &\approx b_4c_1\\ & & d_2 &\approx b_8c_2 & & \end{aligned}$$

Sets 1 and 9 of signs for group (*a*) gave well developed sets of signs for groups (*b*) and (*c*), and consistent indications of sign for the three members of group (*d*).

Thus set 1 gave

b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8
−	+	−	+	+	−	+	+

c_1	c_2	c_3	c_4	c_5	c_6	c_7
−	+	+	−	+	−	+

and the indications of sign for the members of group (*d*) are

d_1	−	−	−	−	−	−	
d_2	+	+	+	+	+	+	+
d_3	+	+	+	+	+	+	

Set 9 gave

b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8
−	+	+	+	+	+	−	+

c_1	c_2	c_3	c_4	c_5	c_6	c_7
−	+	+	−	+	+	+

with indications for group (*d*)

d_1	−	−	−	−	−	−	
d_2	+	+	+	+	−	+	+
d_3	+	+	+	+	+	+	

Electron-density maps for these two plausible solutions are shown in Fig. 1. It was found possible to

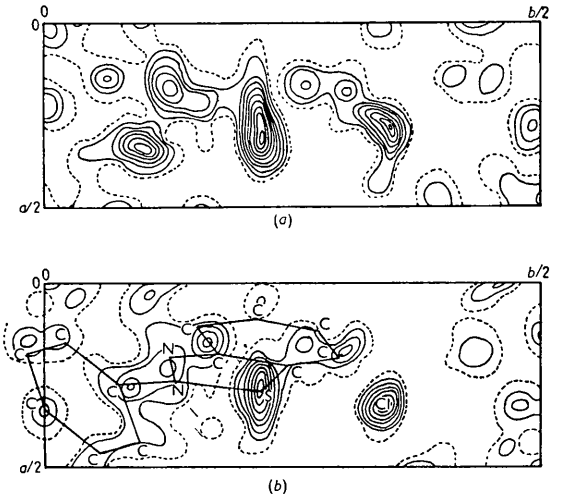

Fig. 1. Electron-density maps corresponding to (*a*) solution 1, (*b*) solution 9. The contours are at arbitrary equal intervals, with the lowest contour dashed.

interpret the map from set 9 in the way shown. This structure is being successfully refined by Dr G. W. R. Bartindale and Mr G. Farrow, who will report on the completed structure in due course. At the present stage of refinement the value of the reliability index is 0·26. These workers had previously obtained a similar electron-density map by finding the sulphur and chlorine atomic positions from the Patterson function and taking the sign of their contribution as the sign of the corresponding structure factor. However, it was not until the direct method had shown that the solution *must* be one of those given in Fig. 1 that the not very obvious interpretation of Fig. 1 was found. The special advantage of the direct method in this case is that, in finding the correct solution, it excluded any other possibility.

5. The efficiency of the method

The method of this paper enables problems for which there are up to 7 indeterminate members of group (*a*), and about 25–30 unknown signs in all, to be tackled by hand calculation. Other conditions must also be satisfied: sign relationships must interrelate group (*a*) with groups (*b*), (*c*) and (*d*) well enough for signs to be developed from the tables, and about 85% or more of these sign relationships must be satisfied.

To show fully the advantages of this method it will be compared with the electronic-computer method of Cochran & Douglas (1955). Let us take an example where there are 25 structure factors of unknown sign and where 3 of the 25 strongest sign relationships are expected to fail. Then the computer method makes a preliminary examination of

$$1+\frac{25!}{24!\,1!}+\frac{25!}{23!\,2!}+\frac{25!}{22!\,3!}$$

possible sets of signs for the 25 structure factors although, by other tests, most of these are subsequently rejected. This number of sets, 2626, would be impossible to examine by hand. How is it that so many fewer possibilities (say 128) can be examined by the method of this paper without missing the correct solution? The answer to this is found in § 3. For a particular set of signs for group (*a*) it is often found that signs cannot be deduced for some members of the other groups with any degree of certainty. For these reflexions, signs may be chosen in a number of ways all equally efficient as far as the satisfaction of sign relationships is concerned. Thus, for each solution found by this method, the Cochran–Douglas method would tend to give a family of similar solutions. The single solution found would be the best representative of the family from the point of view of satisfying sign relationships with perhaps some signs indeterminate.

An electronic computer can be used to extend the range of the method. A programme has been designed for the Cambridge computer, the EDSAC, such that up to 11 members of group (*a*) may be accepted. It is hoped to reprogramme this for the Manchester computer in such a way that the information fed into the machine is the sign relationships and some numerical data, with the output as Fourier syntheses in a suitable form to be contoured directly.

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References

Cochran, W. & Douglas, A. S. (1954). *Proc. Roy. Soc.* A, **227**, 486.

Cochran, W. & Woolfson, M. M. (1955). *Acta Cryst.* **8**, 1.

Woolfson, M. M. (1954). *Acta Cryst.* **7**, 721.