Besides the merits, Tables 4–10 also show some limits:

(*a*) The present approach postulates the mutual statistical independence of the various phase relationships which concur to define φ_u. This is not strictly true: the consequence is that the accuracy of the sign indication may often be overestimated.

(*b*) The procedure may fail on some occasions. For example, a wrong estimate of φ_u is possible when: (i) it is wrongly estimated *via* its second representation with a very high probability value; luckily that occurs rarely if $|E_u|$ is sufficiently large; (ii) a large percentage of two-phase seminvariants $\varphi_u + \varphi_v$ is wrongly estimated with high probability values. This case is not frequent either.

There are several ways for improving the present situation: *e.g.* (i) to improve the estimates of the one-phase seminvariants by application of the concept of generalized representations (Giacovazzo, 1980*b*,*c*); (ii) to obtain improved estimates of the two-phase seminvariants, *e.g. via* their second representations; (iii) by application of the three-phase seminvariants.

The work in these fields is in progress.

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DELCRI, an Enantiomorph-Specific Figure of Merit

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Abstract

A figure of merit DELCRI, with estimates Δ_3 for the absolute values of the triplet phase sums φ_3, is described for the selection of numerical values of symbols used in a symbolic addition procedure. From tests with a number of structures crystallizing in polar space groups this figure of merit was found to enable the selection of enantiomorph-specific phase sets.

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Introduction

In direct-method procedures the phase determination critically depends either on the $\sum_2$ relation

$$\varphi_H = \frac{\sum_K E_3(\varphi_K + \varphi_{H-K})}{\sum_K E_3}, \quad (1)$$

with

$$E_3 = N^{-1/2}|E_H E_K E_{H-K}|, \quad (2)$$

or on the related tangent formula

$$\tan(\varphi_H) = \frac{\sum_K E_3 \sin(\varphi_K + \varphi_{H-K})}{\sum_K E_3 \cos(\varphi_K + \varphi_{H-K})}. \quad (3)$$

For each term in (1) and (3) it is assumed that the value of the triplet phase sum

$$\varphi_3 = -\varphi_H + \varphi_K + \varphi_{H-K} \quad (4)$$

is most probably equal to 0. Hence the application of (1) or (3) tends to result in sets of centrosymmetric phases, in particular in polar space groups such as $P2_1$.

Such artefacts could be avoided if φ_3 could be determined, but this is not possible in general. Only if suitable heavy atoms are present can φ_3 values be obtained from Bijvoet differences (Kroon, Spek & Krabbendam, 1977). There exist, however, methods to estimate $|\varphi_3|$, the absolute value of φ_3. Knowledge of this quantity could facilitate direct-method procedures, because the phase of a reflection H can then be found from

$$\varphi_H = \varphi_K + \varphi_{H-K} - s|\varphi_3|, \quad (5)$$

where the sign s is the only unknown. When there are several triplets (5) with known values φ_K and φ_{H-K} for a given reflection H the quantity

$$\Phi(\varphi_H) = \sum_K E_3|-\varphi_H + \varphi_K + \varphi_{H-K} - s|\varphi_3|| \quad (6)$$

will have a minimum value for approximately correct phases, provided that the $|\varphi_3|$ values are known to a good approximation. Expression (6) is evaluated by varying φ_H in small steps and taking for each triplet that sign s which leads to the smallest sum (6). Then, when there is one minimum in Φ, this corresponds to the correct φ_H value. Based on (5), an enantiomorph-specific refinement procedure has been developed (Sint & Schenk, 1975; Busetta, 1976; Olthof, Sint & Schenk, 1979):

$$\tan(\varphi_H) = \frac{\sum_K E_3 \sin(\varphi_K + \varphi_{H-K} - s|\varphi_3|)}{\sum_K E_3 \cos(\varphi_K + \varphi_{H-K} - s|\varphi_3|)}. \quad (7)$$

If the $|\varphi_3|$ estimates and the starting phases are reasonable approximations the phases refine to the true values and the quantity

$$\sum_H \sum_K E_3 \sin^2 \tfrac{1}{2}(-\varphi_H + \varphi_K + \varphi_{H-K} - s|\varphi_3|) \quad (8)$$

is minimized. It is commonly observed that $|\varphi_3|$ estimates obtained by expressions such as $B_{3,0}$ (Karle & Hauptman, 1958) and MDKS (Fisher, Hancock & Hauptman, 1970) are not very reliable. This is the limiting factor for the success of methods based on (5), such as those described by Hauptman, Fisher, Hancock & Norton (1969) and Olthof, Sint & Schenk (1979). Studies by Schenk (1973) and Krieger & Schenk (1973) have shown that in centrosymmetric structures the hyperbolic tangent formula is likewise not reliable and they suggest that the reliability of a triplet may be estimated on the basis of the value of $E_3/(E_3)_{max}$. These ideas were worked out in the extension and refinement method described by Olthof, Sint & Schenk (1979), in which an empirical procedure was described to determine reliable $|\varphi_3|$ estimates from a relatively large starting set of phases.

In direct-method procedures success depends critically on the selection of the correct set of phases. This selection is commonly achieved by calculating a figure of merit (FOM) for each possible solution. Such FOM's are, generally speaking, functions which are expected to yield extreme values for the correct set of phases.

In polar space groups such as $P2_1$, FOM's based on phase relations with probability maxima at 0 and π tend to favour sets of centrosymmetric phases. To cover these cases three enantiomorph-specific FOM's were recently described (van der Putten & Schenk, 1979; van der Putten, Schenk & Hauptman, 1980) based on estimates of quartet, quintet and seminvariant phase sums. Although the results are encouraging when applied to small structures, problems are to be expected in applications to larger structures, since the reliability of the quartets, quintets and seminvariants involved will then be small, and their number large.

From the above it should now be possible to test another enantiomorph-specific FOM based on empirical $\langle|\varphi_3|\rangle_{E_3}$ values. In the present paper such a FOM, DELCRI is described. DELCRI, which is related to the Q **criterion**, is applied to a number of structures, both **known** and unknown, to illustrate its applicability.

Symbolic phases and relations

In an automated symbolic addition procedure phase extension starts from a small set of reflections, the phases of which are either known by definition of the origin or represented by symbols x_i. New phases are calculated from (4):

$$\varphi_H = \sum_{i=1}^{M} (a_i x_i) + c - \varphi_3. \tag{9}$$

M is the number of symbols and $a_i = 0$ or 1. The numerical value c originates both from origin-defined phases and from space-group-imposed phase shifts.

Next comes the stage of symbolic phase extension, where now phases are found by combination of several phases (9). Again the result is of type (9), but now the a_i are small integers and φ_3 is a sum of φ_3 values. As mentioned in the introduction the common assumption is that $\varphi_3 = 0$. Hence the final phases are

$$\varphi_H = \sum_{i=1}^{M} (a_i x_i) + c. \tag{10}$$

At the end of the symbolic addition there will be a number of reflections which are uniquely determined and given by (10). For quite a few reflections, however, the phase indications are not unique, and if these multiple phase indications are assumed to be equal in pairs then a number of relations is obtained of the form

$$\sum_{i=1}^{M} (A_i x_i) + C = 0 \tag{11}$$

with $A_i = a_i' - a_i''$ and $C = c - c''$. These can be combined to give the Q FOM (Schenk, 1971):

$$Q = \sum_j W_j \left| \sum_{i=1}^{M} (A_i x_i) + C \right|_j. \tag{12}$$

W_j is the sum of the individual weights of relations (11) with the same symbolic phase sums $\sum A_i x_i$. The lowest value of Q is considered to approximate the correct set of phases.

The DELCRI figure of merit

Whereas the assumption $\varphi_3 = 0$ in (9) led to the FOM Q, the FOM DELCRI is obtained by substitution of $|\varphi_3|$ by its empirical estimate Δ_3. These estimates are obtained from a correlation between $|\varphi_3|$ and E_3, deduced from a large number of structures in a way similar to that described by Olthof, Sint & Schenk (1979). Substitution of Δ_3 for $|\varphi_3|$ in (5) results in

$$\varphi_H = \varphi_K + \varphi_{H-K} - s\Delta_3. \tag{13}$$

Hence the symbolic phases (9) take the form

$$\varphi_H = \sum_{i=1}^{M} (a_i x_i) + c - s\Delta_3, \tag{14}$$

in which s is unknown.

As usual, reflections are obtained with multiple phase indications, and in close analogy to (11) we obtain

$$\sum_{i=1}^{M} (A_i x_i) + C - s'\Delta_3' + s''\Delta_3'' = 0. \tag{15}$$

These expressions are combined to yield the analogue of (12):

$$\text{DELCRI} = \sum_j w_j \left| \sum_{i=1}^{M} (A_i x_i) + C - s'\Delta_3 + s''\Delta_3'' \right|_j. \tag{16}$$

DELCRI is evaluated by substituting trial values for the symbolic phases x_i. For each term of (16) $\sum_{i=1}^{M} (A_1 x_i)$ is calculated and that one of the four possible values $C - s'\Delta_3' + s''\Delta_3''$ (see Fig. 1*a*) is taken which minimizes

$$\left| \sum_{i=1}^{M} (A_i x_i) + C - s'\Delta_3' + s''\Delta_3'' \right|_j. \tag{17}$$

When the Δ_3 values represent a good approximation to the $|\varphi_3|$ values, DELCRI may be expected to attain a minimum for the proper set of phases.

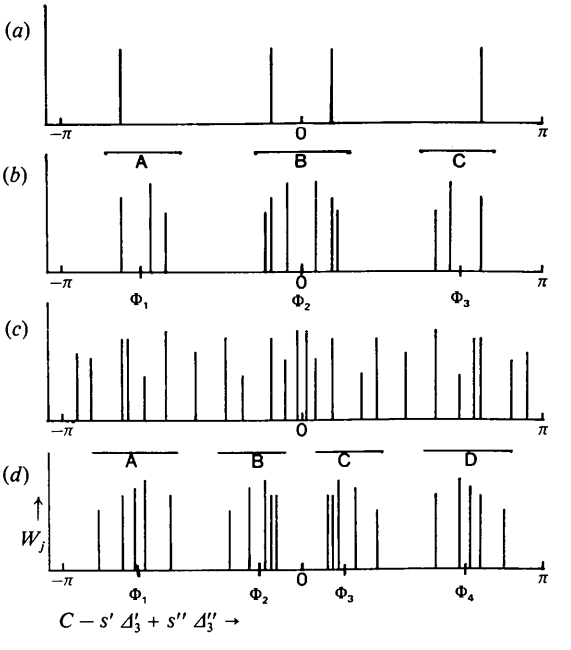

Fig. 1. Some distributions of values for $C - s'\Delta_3' + s''\Delta_3''$ in the interval from $-\pi$ to π. (*a*), (*b*), (*c*) and (*d*) one, three, six and five values of $C - s'\Delta_3' + s''\Delta_3''$ respectively.

Use of the DELCRI criterion

Evaluation of (16) as such is quite laborious. Its summation involves many more terms than is the case for the Q criterion (12), because terms with the same value of $\sum (A_i x_i)$ cannot be added in a straightforward way owing to the presence of the Δ_3 terms. Our approach has been to use a weighted arithmetic mean value when concentrations of $(C - s'\Delta_3' + s''\Delta_3'')_j$ values are found. This procedure is best outlined by the examples sketched in Figs. 1(*b*),(*c*),(*d*). In Fig. 1(*d*) the values of $(C - s'\Delta_3' + s''\Delta_3'')$ fall into distinct sets, indicated by *A*, *B*, *C* and *D*. The weighted arithmetic mean values of these sets are indicated by Φ_1, Φ_2, Φ_3 and Φ_4. From the figure it is obvious that the Φ values contribute to the FOM in much the same way as the original $(C - s'\Delta_3' + s''\Delta_3'')$ values. Likewise the situation in Fig. 1(*b*) can be reduced to three mean values. In the case of Fig. 1(*c*) the values of $(C - s'\Delta_3' + s''\Delta_3'')$ do not form identifiable concentrations, and hence the corresponding relations will not contribute to the selectivity of DELCRI. They can therefore be ignored without loss of generality.

In this way the information contained in (16) can be approximated by an expression with a greatly reduced number of terms:

$$\text{DELCRI} = \sum_j W_j \left| \sum_{i=1}^{M} (A_i x_i) + (\Phi_1, \Phi_k, \ldots, \Phi_n) \right|_j. \quad (18)$$

That Φ_k value is selected which gives the minimum value for

$$W_j \left| \sum_{i=1}^{M} (A_i x_i) + \Phi_k \right|_j. \quad (19)$$

A few comments are in order with respect to the use of (18).

$n = 1$ represents centrosymmetric information, the corresponding terms are neglected.

$n = 4$ represents too many possible values to contribute to the selectivity of the FOM, the corresponding terms are rejected.

The weights W_j are obtained from the quality of the Φ_k values; they vary between 1 and 3.

For a reliable result it suffices to use in (18) only the $2M$–$3M$ relations (19) with highest weights W_j.

$\Phi_k = 0$ (such as Φ_2 in Fig. 1*b*) imparts to the FOM a tendency towards centrosymmetric solutions. Such Φ values are ignored unless the corresponding $(C - s'\Delta_3' + s''\Delta_3'')$ distribution is exceptionally good.

It is to be expected that the lowest value of the DELCRI FOM obtained in this way corresponds to the correct phase set.

Finally, the phase sets corresponding to minima in DELCRI are refined by an iterative least-squares technique which minimizes

$$\text{DELREF} = \sum_j W_j \left\{ \sum_{i=1} (A_i x_i) + \Phi_k \right\}_j^2. \quad (20)$$

Φ_k is chosen such that (19) is closest to 0 at the start of each refinement cycle. One of the low values of DELREF obtained in this way is expected to correspond to the proper set of phases.

Test results of DELCRI

The DELCRI FOM has been applied to three known structures:

(1) Diethylmalonic acid (DIEMAL) (van der Putten, unpublished) $C_7H_{12}O_4$, $Z = 4$, $N = 44$, $P2_1$.

(2) *N*-cyanomethylangustifoline (ANGUST) (Rychlewska, Bratek & Wiewiórowski, 1978), $C_{16}H_{23}N_3O$, $Z = 2$, $N = 40$, $P2_1$.

(3) 3-Chloro-1,3,4-triphenyl-2-azetidinone (AZET) (Colens, Declercq, Germain, Putzeys & Van Meerssche, 1974), $C_{21}H_{16}ClNO$, $Z = 8$, $N = 192$, $Pca2_1$.

(4) A naphthoquinone (INDIAN) (Agarwal, Rastogi, van Koningsveld, Goubitz & Olthof, 1980), $C_{24}H_{26}O_4$, $Z = 2$, $N = 56$, $P2_1$.

(5) Andrographolide (ANDRO) (Maulik, Venkatasubramanian, Olthof & Schenk, 1981), $C_{20}H_{30}O_5$, $Z = 2$, $N = 50$, $P2_1$.

In all cases the interactive program system *SIMPEL* (Overbeek & Schenk, 1978) was applied for the symbolic addition. On the basis of triplets and quartets *SIMPEL* selects a starting set, which is extended on the basis of triplets alone subject to strict acceptance criteria. Then DELCRI and the $\sum_2$ consistency FOM Q were calculated for all trial values of the symbols. Table 1 contains the most important results of all five structure determinations, which hereafter will be discussed in more detail.

For DIEMAL, 200 reflections with $E \geq 1{\cdot}5$, interrelated by 1782 triplets with $E_3 \geq 0{\cdot}55$, were used in the symbolic addition procedure. 84 reflections could be phased uniquely, and approximately 70 reflections had multiple phase indications. Q and DELCRI were calculated and the two best FOM values of each kind are given in Table 1 in the columns headed $Q1$, $Q2$, $D1$ and $D2$, respectively. It is striking that the phases corresponding to the Q minima are obviously centrosymmetric, while those corresponding to the DELCRI minima differ by 0 or 500 millicycles.

The solution $D1$ corresponds to the true phases and subsequent numerical phase extension and refinement solved the structure. Also, the phase set $D2$ led to the solution of the structure, although a few phases were incorrect and an origin shift of 0·5 along the *b* axis is present.

With 250 reflections of ANGUST 2290 triplets with $E_3 \geq 1{\cdot}17$ were generated. The final set of symbolically

Table 1. *Starting sets with their symbolic phases, their true phases, their phases according to the two lowest $\sum_2$ consistency FOM values ($Q1$, $Q2$) and those according to the two lowest DELCRI values ($D1$, $D2$)*

The phase deviations of the sets $Q1$, $Q2$, $D1$ and $D2$, calculated for the noncentrosymmetric reflections with respect to the structure (PS) and the other enantiomorph (PE), are given. The phases and the phase deviations are given in units of $2\pi/1000$.

Structure		h k l	E	Symbolic phase	True phase	$Q1$	$Q2$	$D1$	$D2$
DIEMAL		1 0 10	4·25	0	0	0	0	0	0
		0 1 10	4·11	0	0	0	0	0	0
		2 0 13	3·54	0	0	0	0	0	0
		5 3 5	2·67	*A*	243	500	0	162	662
		−5 3 5	2·71	*B*	561	500	500	605	105
		−3 5 6	2·79	*C*	996	0	0	929	429
	PS				0	100	76	36	116
	PE				154	100	76	121	111
ANGUST		4 0 5	2·73	0	0	0	0	0	0
		5 1 1	2·20	852	852	852	852	852	852
		−3 0 6	2·85	0	0	0	0	0	0
		1 5 0	2·76	*A*	612	310	210	680	185
		−3 4 6	2·50	*B*	508	440	370	348	854
		1 6 4	3·15	*C*	153	190	40	164	669
		5 0 4	2·65	*D*	500	500	500	500	500
		0 8 3	2·65	*E*	427	400	230	497	2
	PS				0	91	87	57	71
	PE				133	86	88	103	104
AZET		2 7 0	3·12	0	0	0	0	0	0
		15 3 1	2·57	984	984	984	984	984	984
		7 2 0	2·04	500	500	500	500	500	500
		8 2 0	2·85	*A*	500	500	500	500	500
		2 5 4	2·81	*B*	874	340	490	597	743
		0 5 6	2·48	*C*	939	260	480	378	879
		9 8 2	2·48	*D*	155	920	990	601	70
		17 3 3	2·60	*E*	69	910	960	347	11
	PS				0	85	60	124	36
	PE				133	57	81	83	136
INDIAN		9 0 4	2·79	0	500	0	0	0	0
		−1 1 2	2·43	0	929	0	0	0	0
		10 0 1	2·31	0	0	0	0	0	0
		2 6 3	3·15	*A*	733	50	650	874	398
		12 2 0	2·65	*B*	286	10	50	292	800
		−9 4 4	3·23	*C*	305	0	670	392	408
		8 2 4	3·23	*D*	224	30	30	382	890
		3 7 3	2·79	*E*	324	0	40	510	34
	PS				0	97	115	39	102
	PE				181	107	135	166	131
ANDRO		3 0 11	4·74	0	0	0	0	0	0
		4 0 9	3·65	0	0	0	0	0	0
		2 1 13	3·07	0	25	0	0	0	0
		6 0 0	3·31	*A*	500	500	500	0	500
		4 4 11	3·23	*B*	78	940	900	16	997
		0 2 15	2·35	*C*	463	940	960	837	337
		2 0 19	2·95	*D*	500	500	500	500	500
		−6 4 2	2·51	*E*	606	430	400	167	650
	PS				0	83	88	148	61
	PE				58	101	86	162	109

phased reflections, consisting of 70 phases expressed in five symbols, was used in the Q and DELCRI calculations. The two solutions of lowest Q and DELCRI are given in Table 1. Again, the phases found from the Q FOM are centrosymmetric, while those indicated by $D1$ correspond to the structure. The structure AZET behaved similarly. The procedure was carried out with 500 reflections interrelated by 3022 triplets with $E_3 \geq 0{\cdot}40$. In this case the Q solutions possess some non-centrosymmetry although the phases are not correct. Phases of the DELCRI solution $D2$ led to the approximately correct values for the symbols.

Table 2. *Average absolute values of the errors of the relationships used in the Q and DELCRI FOM's of Table* 1

Structure	Q FOM	DELCRI FOM
DIEMAL	145	147
ANGUST	248	84
AZET	127	58
INDIAN	214	118
ANDRO	108	103

The DELCRI FOM was also successful when applied to the unknown structure INDIAN. Attempts to solve this structure with *MULTAN* (Germain & Woolfson, 1968) and *SIMPEL* failed. In the symbolic addition 300 reflections with $E \geq 1{\cdot}31$ and 2690 triplets with $E_2 \geq 0{\cdot}60$ were used, leading to a set of 45 uniquely phased reflections. From Table 1 it is clear that the sets labelled $Q1$ and $Q2$ are again approximately centrosymmetric. The DELCRI FOM yielded six phase sets with equally low DELREF values; after phase extension and refinement applying the tangent formula (3) the set labelled $D1$ corresponded to an interpretable Fourier map. It can be noted that the reflection 904 was wrongly phased in all Q and DELCRI solutions; this origin-defining reflection apparently did not fix the origin. From a *post mortem* examination of the symbolic addition process it appeared that this reflection was hardly used to phase other reflections.

Another success of the DELCRI FOM was the determination of the structure ANDRO. In this case 300 reflections with $E \geq 1{\cdot}28$ were used in the symbolic addition procedure. The reflections were linked by 2061 triplets with $E_3 \geq 0{\cdot}70$. At the end of the symbolic addition a unique phase was assigned to 72 reflections. With DELCRI two phase sets with almost equal probability were obtained (see Table 1). After phase extension of solution $D2$ a large and easily recognizable fragment of the structure was found in the subsequent Fourier map. As can be concluded from Table 1 the $\sum_2$ FOM phase sets labelled $Q1$ and $Q2$ had again a highly centrosymmetric character.

In Table 2 the errors of the relationships used in the Q and DELCRI criteria for the five discussed structures are given. In three cases the DELCRI relations have appreciably smaller errors than the Q relations. In the two remaining cases the errors are equally large: here the success of DELCRI can be ascribed completely to the fact that whereas the errors in the Q relations are based on (5) with $\varphi_3 = 0$ (systematic errors), those in the DELCRI relations are based on (6) (random errors). In the three other structures DELCRI is clearly even more effective.

From the above experiments it is concluded that the enantiomorph-specific FOM DELCRI can be of great value for structure determinations in polar space groups such as $P2_1$.

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Phase Extension and Refinement for Small Structures

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Abstract

A procedure is described to extend and refine phases starting from small starting sets. Tests with a number of real crystal structures show that the enantiomorph-maintaining refinement procedure [Olthof, Sint & Schenk (1979). *Acta Cryst.* A**35**, 941–946] can be successful in these cases as well, provided that a few modifications are introduced.

Introduction

For quite a few structures, particularly in polar space groups and space groups without translational symmetry, it is difficult or even impossible to define and maintain the enantiomorph in the course of a direct phase determination (*e.g.* Schenk, 1972; Lessinger, 1976; Busetta, 1976; Woolfson, 1977). In these cases the definition of the enantiomorph can be achieved with enantiomorph-specific figures of merit, such as those based on quartets and quintets (van der Putten & Schenk, 1979) or three-phase seminvariants (van der Putten, Schenk & Hauptman, 1980). We have shown (Olthof & Schenk, 1981) that in a symbolic addition procedure this problem can also be solved by means of the figure of merit DELCRI, which selects a small set of approximately correct phases. DELCRI is based on the relationship

$$\varphi_3 = -\varphi_H + \varphi_K + \varphi_{H-K}, \tag{1}$$

in which φ_3 is approximated by $s\Delta_3$:

$$\varphi_H = \varphi_K + \varphi_{H-K} - s\Delta_3. \tag{2}$$

The Δ_3 values are empirical estimates, and the signs s are determined in the procedure.

If, however, the subsequent numerical phase extension and refinement is carried out by means of the tangent formula

$$\tan(\varphi_H) = \frac{\sum_K E_3 \sin(\varphi_K + \varphi_{H-K})}{\sum_K E_3 \cos(\varphi_K + \varphi_{H-K})} \tag{3}$$

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