

## On the Application of Phase Relationships to Complex Structures. XXI. An Extension to the *MAGEX* Procedure

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### Abstract

In the previously described *MAGEX* procedure [Hull, Viterbo, Woolfson & Zhang Shao-Hui (1981). *Acta Cryst.* A37, 566–572] trial phases found from a  $\psi$  map were refined by a parameter-shift process which maximized a function depending on the overall satisfaction of the triple-phase relationships. Advantages have been found in using a different function which has a somewhat stronger physical basis. Two algorithms are described which may be used either for centrosymmetric structures or for individual reflexions which can take only restricted phase values.

### Introduction

The direct-methods procedure *MAGEX*, which is currently part of the York/Louvain distributed structure-solving package, has recently undergone two minor developments which seem significantly to increase its effectiveness and, in particular, to make it applicable to centrosymmetric structures.

The first development relates to alternative procedures for dealing with special reflexions. These are:

(i) Ignore the special nature of these reflexions and refine them as general reflexions. At the end of the refinement they are then set to the nearest special value.

(ii) At all stages of refinement, including the initial parameter-shift refinement of trial phases, special reflexions are allowed to take only their restricted values.

The use of these procedures is not novel – they have been used by practitioners of direct methods for some time – and, in addition, it cannot be said that one procedure is better than the other. For some structures both refinement procedures will lead to a solution while occasionally only one or the other will do so. Our observation that this is so has led to both options being provided in *MAGEX* and if there is no success with one of them then the other may be tried.

The second development concerns the function used in the parameter-shift refinement of initial phases from the  $\psi$  map, prior to phase extension by the tangent formula. In the original description of *MAGEX* (Hull *et al.*, 1981) the function used was

$$F_1 = \sum_t \kappa_t \frac{I_1(\kappa_t)}{I_0(\kappa_t)} \cos \varphi_{3t}, \quad (1)$$

which is large when the triple-phase relationships cluster around zero (modulo  $2\pi$ ). A second function was described,

$$F_2 = \sum_r \left\{ \sum_s \kappa_{rs} \cos \varphi_{3rs} - \left| \sum_s \kappa_{rs} \sin \varphi_{3rs} \right| \right\}, \quad (2)$$

which was used only to select the most likely sets of starting-set phases after parameter-shift refinement. In the expression for  $F_2$  the inner summations (over  $s$ ) are for all relationships involving a particular reflexion (indicated by  $r$ ). This function is more restrictive than  $F_1$ ; it demands that not only should the phase relationships be well satisfied but also that the phases should be close to tangent-formula self-consistency. However, when used for parameter-shift refinement it does give a solution very different from that which is obtained by straightforward use of the tangent formula because of the restriction on phase shifts imposed by the parameter-shift process.

It is our experience that  $F_2$  is always at least as good as  $F_1$  in providing a starting set for phase extension by the tangent formula and is usually better, the quality criterion being based on the attainment of correct structure solutions. Sometimes the use of  $F_2$  provides a solution when using  $F_1$  is unsuccessful or, even if  $F_1$  is successful,  $F_2$  may give a multiplicity of correct solutions. There is, unfortunately, a cost for this increased benefit. The function  $F_2$  cannot be as efficiently programmed for parameter-shift refinement as can  $F_1$  and there is an increase of more than 50% in time for this part of the program. However, since much time is subsequently spent on tangent-formula phase extension and refinement the overall increase in computer time is only between 10 and 20%.

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To illustrate the application of these two modifications to *MAGEX* the solution of two structures will be described.

### The structure of guainolide

This structure had already been solved (Posner, Babiak, Loomis, Frazee, Mittal & Karle, 1981) but it was known to be a challenging one and so was subjected to the modified *MAGEX*. The space group is  $P2_1/n$  with formula  $C_{14}H_{20}O_3$  and  $Z = 8$ . The *MULTAN80* system selected 340 reflexions with large  $E$  values and allocated signs to three of them to fix the origin. The phases of eleven primary reflexions were represented in terms of the magic-integer sequence

144 199 233 254 267 275 280 283 285 286 287.

With *MAGEX* running on default parameters 53 secondary reflexions were found and the  $\psi_{\text{big}}$  map was based on 90 triple-phase relationships and 67 constraint terms. The 200 highest peaks in this map yielded 200 different sets of 67 phases which were set to their closest permissible values before refinement.

Parameter-shift refinement was based on maximizing  $F_1$  but the phases were allowed to take only their two permitted values and the refinement was stopped after 20 cycles if  $F_1$  had not been maximized. The 100 sets

of 67 reflexions with the largest values of  $F_1$  were extended by the tangent-formula routine in *MULTAN80* to give phases for the complete set of 340 reflexions. The set corresponding to the peak 73 in  $\psi_{\text{big}}$  gave the highest combined figure of merit (CFOM) and revealed all but one of the non-hydrogen atoms (Fig. 1).

Other variants of *MAGEX* procedures were tried. With  $F_2$  as the parameter-shift refinement function a solution could also be found. However, if the phases were treated as general, and then given special values only at the end of the process, no solution resulted.

### An unknown structure

Data for an unknown structure were provided by Watkin (1981). The formula was  $C_{22}H_{22}N_2O_9$  with space group  $Pc$  and  $Z = 2$ . Attempts to solve this structure over many years had been unsuccessful prior to the *MAGEX* solution.

In the successful run of *MAGEX* the number of primary reflexions was user-designated as twelve rather than the default value of ten. This was done to increase the number of reflexions and relationships incorporated in the  $\psi$  map. The *MAGEX* system fixed the origin by assigning phases of  $0^\circ$  to two reflexions. The  $\psi_{\text{big}}$  map contained 65 reflexions, 926 independent triple-phase relationships and one constraint term. The map was centrosymmetric and finding the 200 highest peaks in one asymmetric unit was equivalent to selecting the enantiomorph.

Parameter-shift refinement used the function  $F_2$ , special reflexions were considered as general and only at the end of refinement were their phases set to the nearest permitted value. The fifty sets of 65 phases with the highest values of  $F_2$  were extended by the tangent formula to give a total of 282 phases. The set with the highest CFOM gave a twenty-atom fragment (Fig. 2) and by conventional weighted Fourier refinement all the non-hydrogen atoms were readily found.

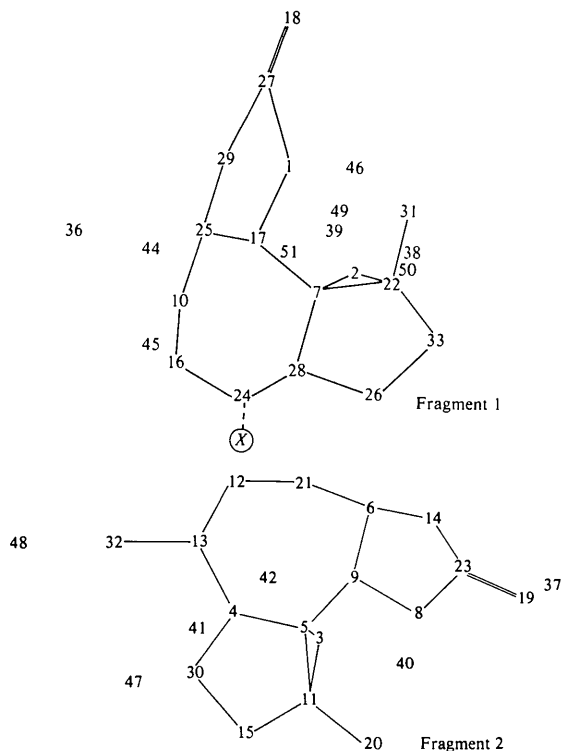


Fig. 1. The *MAGEX* output for the structure guainolide. The missing atom is filled in with a cross.

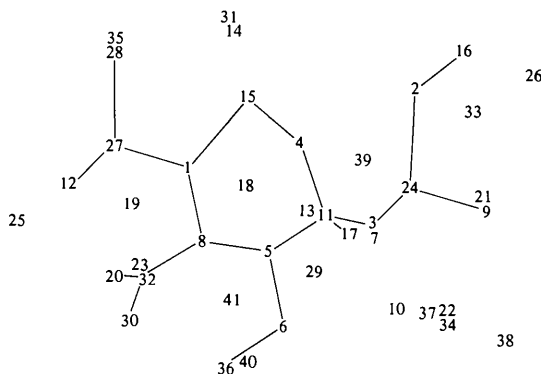


Fig. 2. The fragment found by *MAGEX* for the  $C_{22}H_{22}N_2O_9$  compound.

### Discussion

During the past few years several developments have shown that there is a great deal of unpredictability, even randomness, in the application of direct methods. *MULTAN* was devised in the first place to provide an objective and therefore programmable procedure for solving crystal structures. Much time and effort have been expended in designing systematic procedures for obtaining good starting points (convergence) and good phase extension (weighted tangent formulae). In the event, for complex structures, *MULTAN* is sometimes made to give a solution by imposing some quite arbitrary and irrational change in the systematic procedure – by artificially halving or doubling the temperature factor, for example.

The message that emerges is this – that the greater the number of different processes or pathways that can be provided in the phase-determining procedure the greater is the chance of success. Here, in the development of *MAGEX*, there are alternative functions for parameter-shift refinement, one of them seemingly more effective but also more expensive, and also alternative ways of handling special reflexions. A clear preference for the latter process cannot be given. In fact there is little point in trying to provide quantitative comparisons between one procedure and another – at any rate for the ones described here. There is far too great a variation in their performance from one structure to another to make the exercise worthwhile.

These alternatives are included as standard components of *MAGEX* 80 which is run with *MULTAN* 80, the current version of that program. Our experience shows that *MAGEX* 80 is certainly more effective than both the original *MAGIC* program and also the first version of *MAGEX*. Indeed we have an impression from numbers of tests that it may be somewhat more effective than any other procedure devised and distributed by the York/Louvain group.

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## High-Resolution Electron Microscopy of McGillite. I. One-Layer Monoclinic Structure

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### Abstract

The crystal structure of McGillite from Sullivan mine, Kimberley, Canada, which has been described as the fifth member of the pyrosmalite family, has been studied using electron diffraction and high-resolution electron microscopy. A new monoclinic structure for this mineral is proposed with  $a = \sqrt{3}a_0 = 23.279$ ,  $b =$

$a_0 = 13.498$ ,  $c = c_0/\sin \beta = 7.390$  Å,  $\beta = \tan^{-1}(\sqrt{3}a_0/12c_0) = 105.3^\circ$ , where  $a_0 = 13.498$ ,  $c_0 = 85.657/12 = 7.138$  Å for the trigonal cell proposed by Donnay, Betournay & Hamill [*Can. Mineral.* (1980), **18**, 31–36]. The space group is  $C2/m$ . The crystal is considerably disordered, which results from frequent occurrences of the  $120^\circ$  rotation twinning about  $\{100\}$ . Some of these twins have a thickness of only one unit cell. It is proposed that crystal structures of other members of manganpyrosmalites whose structures are reported as rhombohedral or hexagonal should be

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